

THE MICROSTRUCTURE OF PURE AND DOPED IONIC CRYSTALS

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by

Anowarur Rahman Khan,
M.Sc. (Dacca).

Department of Physical Metallurgy,
Imperial College,
University of London.

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A B S T R A C T

An experimental technique has been developed to study the precipitate structure in doped NaCl at electron-microscopic scale. After depositing 2 - 3 atom layer of gold on the vacuum cleaved surface of doped NaCl and examining the distribution of gold nuclei in an electron microscope it has been found that the density of nuclei on the precipitates is appreciably higher than the density on the matrix.

A semi-quantitative relation for this differential nucleation has been worked out. The difference in the density of nuclei has been exploited to study the precipitation in NaCl doped with CdCl_2 , MgCl_2 , CaCl_2 and BaCl_2 .

As this process enables accurate measurement of the precipitate size on an atomically smooth cleavage plane, it is found specially suited for the determination of precipitate shape, size and volume.

In CdCl_2 , MnCl_2 and MgCl_2 doped NaCl crystals, the precipitates have been found to be cubic in shape. The volume ratio of the precipitate and the matrix has been found to be nearly 8 times the molar concentration of the divalent chlorides. This is consistent with Suzuki's (1961) x-ray determination of the precipitate of $\text{CdCl}_2 \cdot 6\text{NaCl}$

phase in CdCl_2 doped NaCl . A phenomenological explanation for the formation of $\text{CdCl}_2 \cdot 6\text{NaCl}$ type phase in CdCl_2 , MnCl_2 and MgCl_2 doped crystals has been offered. The precipitates in CaCl_2 doped crystals have been found to be platelets in the $\{111\}$ matrix plane and in BaCl_2 doped crystals, platelets in the $\{522\}$ matrix plane.

The observed numbers of precipitates per unit volume in CdCl_2 and MnCl_2 doped crystals for different concentration and cooling rate, have been found to be in qualitative agreement with the theory developed by Kahlweit (1965)

The solution temperatures for the precipitates have been found by subsequent heat treatments. The solution temperatures coincided closely with the temperatures at which quench hardening was observed in divalent doped NaCl , by Harrison, Newey and Pratt (1964) and Harrison (1965).

Transmission electron microscopy of pure NaCl has been tried. The specimens have been found to be damaged by the beam. The damage process has been investigated. The early stages of the damage have been studied by using high speed x-ray films. The defects have been found to cluster along the $\{100\}$ plane of the NaCl , at a very early stage. The diffraction spots at this stage show spiking

in the $\langle 100 \rangle_r$ directions , with the increase of irradiation the clusters enlarge and the spikes in the diffraction spots reduce. It has been found possible to locally polygonize the NaCl specimens by increasing the beam intensity. From the amount of damage and the density change produced in the NaCl specimens by the beam electrons, it has been concluded that the damage is primarily due to point defects being generated through the ionization and excitation processes and the subsequent clustering of these point defects.

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CHAPTER IINTRODUCTION

Sodium Chloride has long been studied as a model solid because its ionic bonding is easier to understand and better suited for theoretical treatments. The effects of impurities on the physical properties of NaCl has also been a subject of extensive investigation.

The Changes in physical properties of NaCl due to divalent cationic impurities.

1.1. Electrical properties :-

1.1.1. Conductivity :-

Tubandt (1932) with a series of experiments showed that the electrical charges in alkali halides are predominantly carried by the cations. In presence of vacancies in the lattice the ions move under an applied field by jumping into vacancies in the general direction of the field. So the drift of the ions in one direction is equivalent to an equal drift of their vacancies in the opposite direction. If n is the number of effective charge carriers in the crystal, in this case cation vacancies, μ is their mobility and e is the charge they carry, then the conductivity σ of the crystal is given by

$$\sigma = n \mu e \dots\dots\dots 1.1.$$

A typical Arrhenius plot of the ionic conducti-

vity of NaCl is shown in Fig 1.1. In the region I or intrinsic region the number of vacancies are in thermal equilibrium with the lattice.

In ionic solids equal numbers of cation and anion vacancies have to be present to maintain charge neutrality. If 'W' is the energy required to create a vacancy pair then the equilibrium number of cation-vacancies at any temperature is given by the relation

$$n = A_1 \exp (-W/2kT) \dots\dots\dots 1.2$$

where A_1 is a constant and k & T have their usual meaning.

The mobility μ of the Cation vacancies at any temperature is given by the relation

$$\mu = \frac{A_2}{T} \exp (-G_m/kT) \dots\dots\dots 1.3$$

where A_2 is another constant and G_m is the activation energy required by a cation to jump into a vacancy.

Substituting eq 1.2 & 1.3 in eq 1.1 we have

$$\sigma = \frac{A}{T} \exp -(W/2 + G_m)/kT \dots\dots 1.4$$

where $A = A_1 A_2 c$.

so that the slope of region I in the conductivity plot is $= -(W/2 + G_m)$.

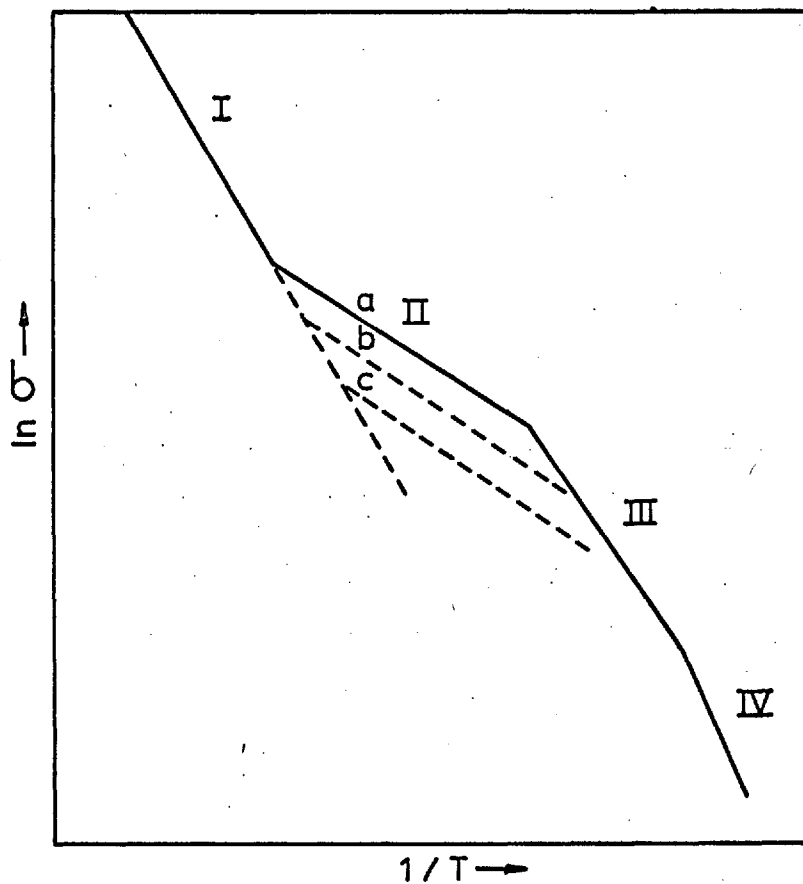


Fig.1.1. Schematic Arrhenius plot of ionic conductivity in alkali halides.

I Intrinsic region, II Extrinsic region, III Association region
IV Precipitation region.

Curves a, b and c correspond to crystals containing decreasing amounts of divalent impurities.

The divalent cations in solid solution occupy substitutional sites in ^{the} alkali halides (Pick & Weber, 1950). To maintain charge neutrality of the lattice, one cation-vacancy is created for each divalent cation. At lower temperature, region II, the number of vacancies in the lattice is determined by the number of divalent cations in solution and it remains essentially unchanged with the variation of temperature above the solution temperature. The conductivity in this extrinsic region follows the equation

$$= A_3 \exp (-G_m/kT) \dots\dots\dots 1.5$$

where $A_3 T = N A_2 c$, N = number of cation in solution.

The slope of the curve in region II = $-G_m$

Lelfeldt (1933) and Kelting & Witt (1949) found that the transition between region I and region II, better known as the 'knee' of the conductivity curve, occurs at increasingly higher temperatures with higher level of doping with divalent cations (Ca^{2+} , Cd^{2+} , Sr^{2+} , Ba^{2+}).

With the lowering of temperature the divalent cations and the cation vacancies start to associate and form dipoles. The number of free vacancies available for conduction then goes down and the slope of the conductivity

curve again changes. This is known as region III or Association region. The slope of this region is $= -(C_m + E_a/2)$ where E_a is the energy of association.

From the temperature of transition for region II to region III as a function of the concentration of divalent cations, Haven (1954) determined the solubility of CaCl_2 , CdCl_2 and MnCl_2 in NaCl .

Dreyfus and Nowick (1962) found that the slope of the region III again changes at a lower temperature (about 200°C). This they named as region IV and identified as the precipitation region.

1.1.2. Dielectric Loss :-

A substitutional divalent cation and an associated cation vacancy in one of the near neighbour sites, forms a electrical dipole in alkali halides. In an alternating electric field the dipoles contribute to the current by aligning themselves along the field. But the current due to the orientation of the dipoles lags behind the applied field. This leads to energy dissipation and dielectric loss. The lag angle δ is given by

$$\tan \delta = \frac{16\pi N p^2}{3 \epsilon kT} \cdot \frac{W}{1 + W^2 \tau^2}$$

where N is the number of dipoles, p is the dipole moment, ω the frequency of the alternating field, τ the relaxation time or the average time needed for the dipole to change orientation, ϵ' is the real part of the dielectric constant. (This loss angle is in addition to the loss angle due to unassociated vacancies). Maximum in $\tan \delta$ occurs when $\omega = 1/\tau$, $\tan \delta$ (max) is then proportional to the number of associated dipole pair present in the crystal. Haven (1954) made measurements of dielectric loss in NaCl containing Ca^{2+} , Cd^{2+} , and Mn^{2+} , as a function of concentration and temperature from which he deduced the jump frequency of the associated and free vacancies. He also deduced the ratio of the associated and free vacancies. He found that for the same concentration of Ca^{2+} and Cd^{2+} , the number of associated vacancies in the Cadmium doped crystals were much less than that in the Calcium doped crystals. He concluded that this must be due to smaller solubility of CdCl_2 in NaCl which might be due to the formation of a compound $2\text{NaCl} \cdot \text{CdCl}_2$. Dryden and Meakins (1957) studied dielectric loss in Lithium, Sodium and Potassium halides. With increasing concentration of divalent metals they observed a second absorption peak in some of their crystals. Up to a calcium concentration of

0.075 mole % in NaCl there was only one peak but as the calcium concentration was increased to 0.95 mole % the second peak became comparable in intensity to the primary peak. The authors attributed this second peak to the dipoles that are formed across the boundary of the precipitates of CaCl_2 and the matrix.

Cook and Dryden (1960) studied the decay of the primary dielectric absorption peak and the rise of the secondary peak as a function of ageing time and temperature, in calcium doped NaCl quenched from 130°C . From their decay curve these authors concluded that the aggregation proceeds in two stages. In the second stage the number of vacancies are less than the number of divalent ions in the aggregates. The same authors (Cook & Dryden, 1962; Dryden, 1963) also studied dielectric absorption in Mn^{2+} doped NaCl, Sr^{2+} and Ba^{2+} doped KCl. They did not observe any secondary peak in these crystals. From the decay curve which was similar in all three crystals they concluded that a third order kinetics is involved and proposed formation of 'trimer' where three dipoles associate in the form of a triangle in the $\{111\}$ planes. Higher complexes are then formed from the 'trimers'.

Fig 5.15.

1.2. Optical properties :-

Enhanced F-center production in NaCl containing Ca^{2+} , during the initial stage of irradiation with x-rays has been reported by Rabin & Click (1960). This is supposed to be due to the increased number of cation vacancies that are present in the crystal to maintain charge neutrality. These vacancies are converted to F-centers during irradiation. Grigoruk and Melik-Gaikazyan (1963) investigated the effect of Mn^{2+} , Cd^{2+} and Pb^{2+} doping on the formation of colorcenters in NaCl by x-irradiation. They observed that enhancement in F-center production reaches a maximum with increasing concentration of divalent ion and then decreases.

1.3. Mechanical properties :-

The Mechanical properties of crystals, in the main depend on the movement of dislocations and different obstacles to this movement. Divalent cations may create such obstacles by forming large precipitates and aggregates which ^{the} dislocations have to cut through or go round. Divalent ions may also form a dipole in association with a cation vacancy in ^{the} nearest or next nearest neighbour site.

If the dipole lies across the slip-plane, the dislocation has to cut through it and separate the divalent ion from the vacancy. If the dipole lies near the slip plane, the dislocation has to pass through the tetragonal strain field of the dipole (Fleischer, 1962), or orient the dipole ahead of the dislocations (Schoeck, 1959). Finally the divalent ion can impede the movement of dislocations by Cottrell type pinning of the dislocations (Cottrell and Bilby, 1949).

Edner (1932), Schonfeld (1932) and Metag (1932) observed that considerable strengthening is caused in NaCl due to the presence of divalent metal ions.

Brown and Pratt (1963) examined the effect of strain ageing on the yield stress of NaCl doped with

50 ppm cadmium. In contrast to pure crystals which showed softening due to ageing at 100°C , the doped crystals showed a marked increase in ^{the} yield stress and an effective yield point phenomena, with Luder's band propagation.

This behaviour which is similar to segregation hardening in metals has been explained in terms of complexes of Cd^{2+} and cation vacancies moving to the dislocations and locking them during ageing.

The effect of calcium doping on the strength of

NaCl crystals have been reported by Pratt, Chang and Newey (1963); Newey (1963); Harrison and Newey (1964). The increase in the 0.1% proof stress of crystals, air cooled from about 170°C, increased linearly with ^{the} increasing concentration of calcium, whereas in the slowly cooled crystals the increase in strength was proportional to the square root of the calcium concentration. The reason for such a difference in ^{the} hardening behaviour in air cooled and slowly cooled crystals was supposed to be that, in air cooled crystals most of the dipoles formed by Ca^{2+} and cation vacancies are in a dispersed form. At room temperature and above, during dislocation motion these dipoles near the slip planes can be oriented by the interaction of the tetragonal strain field of the dipole and the long range stress field of the dislocation (Snoek Ordering) so as to minimise the elastic energy. The resistance to dislocation motion offered by such long range ordering is proportional to the number of dipoles that have to be ordered and the strength and calcium concentration of the crystal are therefore linearly related. In the slowly cooled crystals on the other hand the dipoles are in some form of aggregates and are not free to orient. Dislocations have to pass through them or their stress field which gives rise to

essentially, precipitation type hardening and depends on the size, structure and distribution of the aggregates. Pratt, Harrison and Newey (1966) have examined the effect of Cadmium and Manganese on the flow stress of NaCl. They noticed a considerable increase in room temperature flow stress in crystals containing 450 ppm Cd and 675 ppm Mn when air cooled from above 300°C . The crystals tested below -30°C showed a temperature dependence of ^{the} flow stress and the magnitude of the temperature dependent part of the flow stress was considerably larger in ^{the} quenched crystals than that in ^{the} slowly cooled crystals. Cd doped crystals tested above room temperature, showed a small peak in ^{the} flow stress, in ^{the} quenched crystals, at about 215°C and yield drop in that region. A larger peak was observed in slowly cooled crystals ^{at} about 245°C accompanied with a small yield drop. Mn doped crystals also behaved similarly and showed peaks around 270°C and 300°C respectively.

Harrison (1965) studied the room temperature flow stress of slowly cooled crystals of NaCl doped with Ca, Cd, Mn, Mg, Ba, and Zn as a function of subsequent quenching temperature. In all but calcium doped crystals appreciable quench hardening was observed when crystals were quenched from above certain temperatures. In Cd and Mn

doped crystals those temperatures were quite well defined, about 250°C & 280°C respectively. In Mg, Ba and Zn doped crystals the quenching temperature range in which rapid hardening was observed were $300^{\circ} - 400^{\circ}\text{C}$ for Mg, $500^{\circ} - 600^{\circ}\text{C}$ for Ba and $300^{\circ} - 425^{\circ}\text{C}$ for Zn doping.

It is seen that a knowledge of the state of distribution of the divalent cations in the NaCl lattice is required in most cases to interpret the changes in the physical properties. An endeavour was therefore made to study the distributions of divalent cations in doped NaCl crystals, on an electron microscopic scale.

CHAPTER IIPREVIOUS WORKS

2.1. X-Ray Work :-

Miyake and Suzuki (1954) and Suzuki (1955) published a series of three papers on the x-ray analysis of NaCl single crystals containing few mole % CaCl_2 . They took stationary crystal x-ray diffractions. With either $\langle 100 \rangle$ or $\langle 110 \rangle$ directions of the specimen vertical and varying successively the azimuth angle around the vertical axis. They observed spikes in the reciprocal lattice space. These spikes were along $\langle 111 \rangle_r$ and $\langle 310 \rangle_r$ directions and centered on the reciprocal lattice spots. From the study of the intensity distribution of those spikes they deduced that thin platelets, coherent with NaCl lattice (similar to Guinier Preston Zones) are formed on the $\{111\}$ and $\{310\}$ planes of the crystals. The platelets are between 10 - 20 Å thick and consist of subunits of domains in antiphase orientation. The structures of these domains are also closely related to CaCl_2 structure and the orientation between $\{111\}$ plates and the Matrix are $(111)_m, \parallel (101)_p$ and $[110]_m \parallel [001]_p$. To maintain coherency with the matrix and also charge neutrality the platelets consist of equal numbers of Ca^{2+} ion and Cation vacancy.

With various heat treatments of the crystals they found that $\{310\}$ plates were only stable at low temperature. When crystals, quenched from 400°C , were kept at room

temperature, diffuse reflections due to the $\{310\}$ platelets appeared after about 3 days and slowly grew in intensity, whereas the reflections due to the $\{111\}$ platelets could just be detected after about a month. Ageing at 50°C did not show any qualitative difference from that of the room temperature ageing, such that the reflection due to $\{310\}$ platelets first appeared and were stronger than that due to $\{111\}$ platelets. Annealing at 100°C however produced stronger reflections due to $\{111\}$ platelets than $\{310\}$ platelets. Ageing at 150°C caused $\{310\}$ platelets to disappear, strengthen the reflections due to $\{111\}$ platelets and also some sharp spots to appear. On annealing at 300°C diffuse spots completely disappeared and a sharp spot pattern was observed. Analysis of these spots showed that they were due to precipitates of CaCl_2 with orientation relations

$$\begin{aligned} (100)_p \text{ or } (010)_p & \parallel \{111\}_M, \\ [001]_p & \parallel \langle 110 \rangle_M. \end{aligned}$$

Suzuki (1961) also made x-ray studies of CdCl_2 doped NaCl. In Debye-Scherrer photographs of slowly cooled crystals of NaCl containing between 1 to 33.3 mol % CdCl_2 and he observed two kinds of extra lines. First kind of extra lines appeared from 1 Mol % of CdCl_2 and became most

distinct in the region between 2 - 10 Mole % and disappeared near 20 mol % of CdCl_2 . These lines could be indexed as having half integer indices of the matrix which showed that the structure responsible for these lines has a unit cell which is twice the linear dimension of the NaCl unit cell and possesses the same cubic symmetry.

The second kind of lines appeared at about 2 mol % of CdCl_2 and became stronger with increasing concentration till at 33.3 mol % of CdCl_2 , which corresponds to the composition of $\text{CdCl}_2 \cdot 2\text{NaCl}$, the pattern became exclusively composed of the lines of the second kind. It was therefore presumed that the second kind of lines were due to the $\text{CdCl}_2 \cdot 2\text{NaCl}$ compound and the lines could be indexed as due to a rhombohedral structure with $a = 9.92\text{\AA}$ & $\alpha = 118^\circ 18'$. Small crystalites, that were established by x-ray to have the same structure as the first kind, were collected and chemically analysed. These were found to have the composition $\text{CdCl}_2 \cdot 6\text{NaCl}$.

Considering relative intensities of the diffraction spots and the parameter and the symmetry of the lattice, Suzuki proposed a structure of this $\text{CdCl}_2 \cdot 6\text{NaCl}$ phase. The structure belongs to the holohedral cubic space group O_h^5 . 1/8th of the unit cell of this structure is shown in Fig (5.9).

The heat treatment of crystals containing 1 mol % CdCl_2 showed that this phase is absent in crystals quenched from 500°C . After the crystals were kept at room temperature for several months, weak super-lattice reflections appeared which were identified as thin platelet zones in the $\{100\}$ plane having the same structure as the $\text{CdCl}_2 \cdot 6\text{NaCl}$ phase. Similar reflections were also observed when quenched crystals were reheated at 200°C for one hour. Sharp spot patterns of the $\text{CdCl}_2 \cdot 6\text{NaCl}$ phase could be regained by prolonged ageing at 200°C or slow cooling from 500°C . From these observations, Suzuki proposed a modification to the $\text{NaCl} - \text{CdCl}_2$ phase diagram given by Brand (1911). In the light of present work it will be seen (section 5.3.5) that this phase diagram may bear a further modification.

Following Suzuki's works, Toman (1962), (1963) examined Cadmium and Calcium doped single crystals of NaCl grown by Czochralski technique. He basically confirmed Suzuki's findings with some modifications. The ratio of the unit cell dimensions of $\text{CdCl}_2 \cdot 6\text{NaCl}$ phase^{to} that of NaCl was found to be 2.02 and , the displacement of the Chlorine ions towards the Calcium ions, was determined as 0.014 a as against Suzuki's proposed value of 0.028 a (a is the unit cell dimension of NaCl). In crystals containing 0.3 mol % CdCl_2 the super lattice reflections disappeared

between 250°C - 300°C and in ~~the~~ crystals containing 0.06 mol % CdCl_2 this phase disappeared at temperatures 30° - 40° lower than the previous case. Toman also studied the effect of cooling rate on the precipitate size in the crystals containing 0.3 mol % CdCl_2 . The size of the precipitates in the crystals cooled at the rate of $200^{\circ}\text{C}/\text{sec}$ was around $200\text{\AA}$, in those cooled at $1^{\circ}\text{C}/\text{sec}$ the size was around $500\text{\AA}$ and in very slowly cooled crystals (rate not mentioned) the size was over $1000\text{\AA}$. In slowly cooled crystals containing 0.06 mol % CdCl_2 the precipitate size was around $450\text{\AA}$. The precipitates below $1000\text{\AA}$ in size were coherent with the matrix and those above $1000\text{\AA}$ were partially coherent.

Toman examined Calcium doped NaCl containing 0.7 mol % CaCl_2 as opposed to 10 mol % CaCl_2 reported by Suzuki. In this lighter doped crystal Toman did not find any reflection due to ^(K2) stable phase of CaCl_2 . Instead a metastable orthorhombic structure of CaCl_2 was observed with $a = 6.10\text{\AA}$, $b = 6.93\text{\AA}$ and $c = 4.00\text{\AA}$. The orientation relations of this phase with the NaCl matrix are $[100]_p \parallel [111]_m$, $[010]_p \parallel [112]_m$ and $[001]_p \parallel [110]_m$. The lattice constants b and c of this metastable modification correspond exactly to $(\sqrt{6}/2)a_{\text{NaCl}}$ and $a/\sqrt{2}$ NaCl so that $(100)_{\text{CaCl}_2}$ and the $(111)_{\text{NaCl}}$ are coherent planes probably having the atoms arranged in a similar manner.

Ageing the crystals at 170°C after quenching from 500°C produced the reflections due to the metastable structure which finally resolved into spot patterns which show that they were not just plate zones but a three dimensional structure with a thickness of about $70\text{\AA}$. When crystals were kept at 300°C the reflection due to the precipitates disappeared leaving only the matrix spots. As the reflections due to the stable phase of CaCl_2 did not appear at any stage of ^{the} heat treatment, Toman concluded that in ~~these~~ lower Calcium doped crystals only the metastable modification of CaCl_2 precipitates out as coherent platelets in the $\{111\}$ matrix plane and they go into solution below 300°C . (No mention of $\{310\}$ plate zones were made, presumably they are also absent in the lower doped crystals).

2.2. Rayleigh Scattering and Ultramicroscopy :-

Bansigir and Schneider (1962) examined various alkali halides including high purity, nominally pure and Mn doped NaCl, by Rayleigh scattering and Ultramicroscopy. They observed a maxima in the light scattered at right angles to the directions of the beam in the wave length region of $350 - 400 \text{ m}\mu$ in all their crystals. With increase in ~~the~~ temperature the intensity of the scattered light went

down as a whole without shifting the peak position. Ultramicroscopy showed that the centers of scattering disappeared and reappeared at the same position after temperature cycling. They concluded that the scattering was due to π decorated networks of dislocations.

Girard (1963) examined NaCl single crystal by Rayleigh scattering and Ultramicroscopy. He studied the amplitude of 90° scattering as a function of crystal orientation and came to the conclusion that some of the scattering centers were small compared to the wave length of light others were about 900 Å in dimension. Their shape could be plate like or spherical. As spectroscopic analysis showed various impurities, 50, the nature of the scattering centers could not be specified. Ultramicroscopic examination in conjunction with surface etching revealed that the precipitates were decorating dislocations and grain boundaries.

On heating and cooling the specimen and observing it under Ultramicroscope Girard-Nottin and Tanrel (1965) found that precipitation occurred at preferential sites.

From the Rayleigh scattering of MnCl_2 doped crystals of NaCl grown by Bridgeman technique Girard-Nottin and Benoit (1965) concluded that there are cylindrical precipitates of radius about 600 Å mostly on grain

boundaries.

Abaev and Kornfel'd (1966) studied the Rayleigh scattering as a function of crystal orientation in NaCl doped with BaCl_2 , SrCl_2 , CaCl_2 , CoCl_2 , NiCl_2 , MnCl_2 , CdCl_2 , ZnCl_2 and PbCl_2 . From the angular distribution of the intensity of the scattered light they found that the scattering centers in the BaCl_2 , CaCl_2 and SrCl_2 doped crystals were in $\langle 110 \rangle$ direction; some made a small angle with $\langle 110 \rangle$ directions. Addition of CoCl_2 or NiCl_2 induced ^{the} formation of centers only in $\langle 110 \rangle$ directions. The scattering centers in CdCl_2 and MnCl_2 doped crystals were in $\langle 100 \rangle$ directions and those in PbCl_2 and ZnCl_2 doped crystals were very small and of unknown shape. Curiously enough, these authors concluded that the scattering centers ~~were~~ 'pores' in NaCl lattice formed by the aggregation of cation and anion vacancies released by the divalent chlorides when they come out of solid solution.

2.3. Electron Microscopy :-

Yagi and Honjo (1964) examined in transmission electromicroscopy, NaCl containing 0.05 mol %, 0.1 mol %, 0.3 mol % and 2.3 mol % CaCl_2 . They prepared their specimens by beam flashing technique. Specimen about 2 - 10 μ thick was introduced in the microscope and subjected to an

intense beam of electron for one to two seconds. Surface of the specimen flaked off leaving thin transparent areas. They used a Prototype JEM 150 operated at 150KV. In crystals containing 0.05 and 0.1 mol % CaCl_2 they did not observe any precipitate but noted a reduced rate of speckles formation in the specimen compared to pure crystals. In crystals containing 0.3 mol % CaCl_2 they observed thin platelet precipitates in $\{111\}$ plane of the matrix which gave fringe contrast along their length i.e. $\langle 110 \rangle$ directions in $\{100\}$ matrix plane, which were identified as ~~the~~ coherent precipitates or incipient precipitates as they call it, of CaCl_2 . In crystals containing 2.3 mol % CaCl_2 they observed precipitates in the same orientation as the earlier ones. But the diffraction contrast in them was irregular and these precipitates were identified as the stable precipitates of CaCl_2 .

2.4. Paramagnetic Resonance :-

Schneider & Caffyn (1955), Schneider (1961) and Bansigir & Schneider (1962) reported investigation of MnCl_2 doped NaCl by Paramagnetic resonance method. In well aged crystals they observed a Lorentzian resonance peak of half width of about 200 gauss. As the line width of MnCl_2

in native crystalline form is 1250 gauss, Schneider concluded that the crystal structure in which Mn^{2+} finds itself in the precipitate is different from ^{that in the} bulk anhydrous MnCl_2 crystals. When the doped (50 - 500 ppm) were heated to high temperature this single absorption peak disappeared and a well resolved complex spectra and six prominent hyperfine lines were found. The complex spectra was identified as that due to the dipoles of Mn^{2+} and an associated cation vacancy. The intensity of this complex spectra reached a maximum at about 300°C , which incidentally also coincide with the maxima in flow stress found by Pratt Harrison & Newey (1964). This temperature was taken ~~as~~ ^{as} the eutectic temperature by Schneider.

Watkins (1959) also found this single peak absorption in his vacuum grown Mn doped NaCl crystals which gave way to multiple peaked complex spectra on heating. Single peak absorption could be regained after keeping the specimen for several days at room temperature.

Symmons and Kemp (1966) studied the change in the different spectra of Mn doped NaCl, quenched from 350°C - 400°C as a function of time and ageing temperature. They found that the initial decay of the spectra corresponding to dipoles could be fitted to a third order reaction and

proposed that 'trimers' are formed from the dipoles. A second stage of ageing was observed which ~~was~~ believed to be due to ^{the} formation of higher complexes from the 'trimers'. The single peak resonance due to large aggregates or precipitates could be found after ageing at room temperature.

CHAPTER III

EXPERIMENTAL DETAILS

3.1. Growing single crystals of pure and doped NaCl :-

Single crystals of pure and doped NaCl were grown by a modified Czochralski method. The apparatus is shown schematically in Fig 3.1. 'Analar reagent grade NaCl was molten in the silica beaker in the furnace and the temperature was adjusted to just above the melting temperature of NaCl, i.e. 800°C , when the furnace reached equilibrium, the seed was lowered on to the melt. The seed crystal was clamped in the water cooled chuck. A screw was fixed to the water cooling jacket, which went through a block fixed to the supporting pillars. The seed could be raised by rotating the jacket. The rotation was supplied by a motor drive system. It could also be done by hand when necessary by disengaging the drive system. After lowering the seed, the drive was kept switched off till a growth of about one inch in diameter took place round the seed. Then the motor was switched on. The seed rotated about twice an hour and raised about $\frac{1}{4}$ ". The level of the melt also went down as the crystal grew and the final rate of growth of the crystal was about $\frac{1}{2}$ " an hour. Visual check was kept through a mica window at the top of the furnace and necessary adjustments in temperature of the furnace were made. Crystals between 1"- $1\frac{1}{4}$ " in diameter and 3"- 4" in length

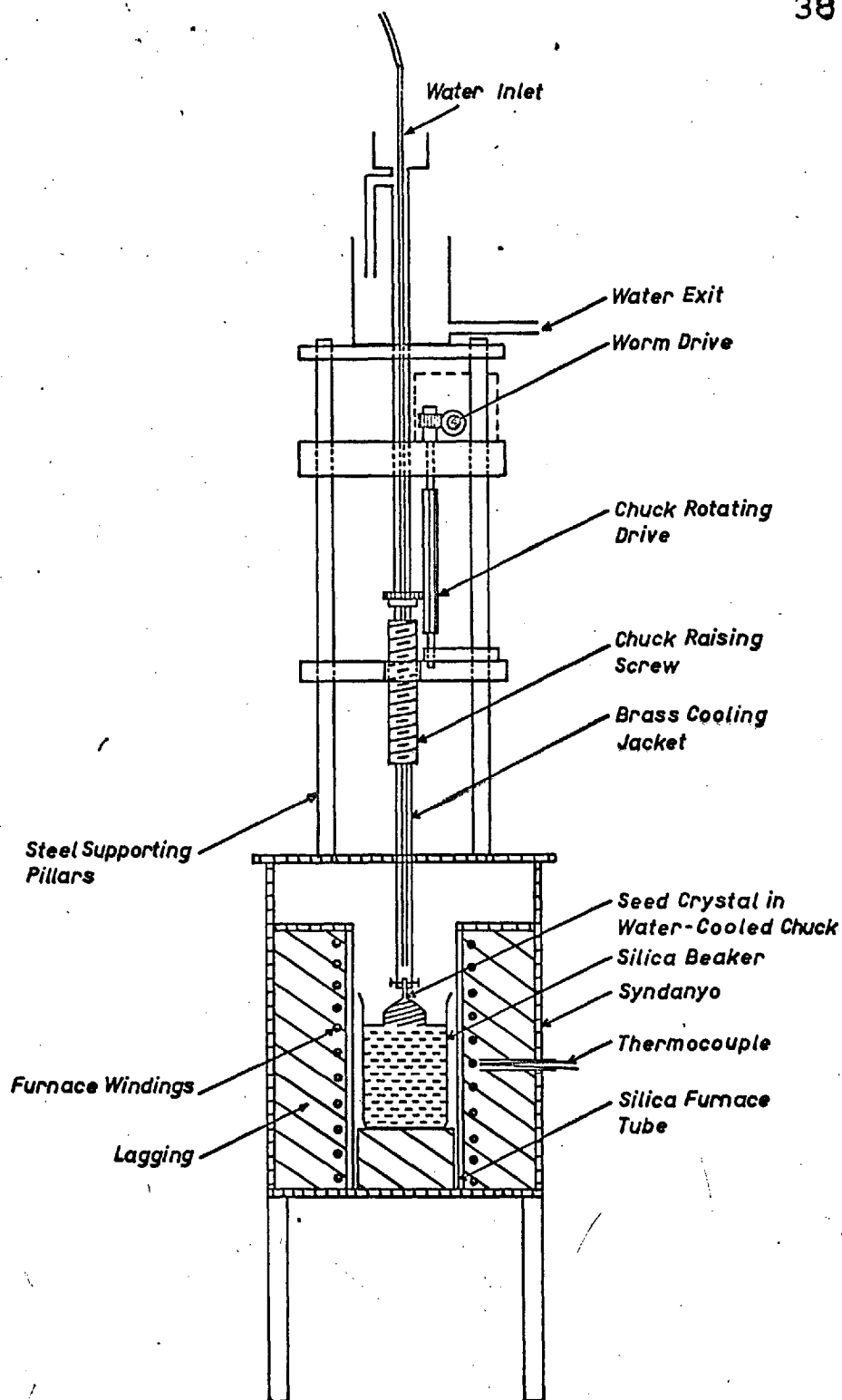


FIG.3.1. The Crystal Growing Apparatus.

were grown in this way. A typical boule is shown in Fig 3.2.

To dope the crystals with divalent metal chlorides, a measured amount of dried reagent grade metal chlorides were added to the melt before growing the crystals. After growing, the crystals were kept in an annealing furnace at 650°C for several hours and then cooled down to room temperature at the rate of $0.25^{\circ}\text{C}/\text{min}$.

3.2. Analysis of the Crystals :-

3.2.1. Cadmium Analysis :-

Cadmium content of the crystals were analysed by polarographic method. A differential cathode ray polarograph type A.1660 made by Southern Analytical Limited was used in the Double Cell mode. (The apparatus has been described by Davis & Seaborn in 'Advances in Polarography' Ed.I. Longmuir P239, Pergamon Press. 1960). The cell voltage i.e. the voltage across the freshly prepared mercury droplet-cathode and the mercury pool-anode, is increased through 0.5 volts in two seconds. The rate of increase in current with voltage, dc/dv , is displayed on the long persistence screen of the cathode ray tube. The process is repeated every seven seconds. When the cell voltage reaches the reduction potential of the metal ion



Fig.3.2 Photograph of a typical boule of NaCl single crystal.



Fig.3.4 Photograph of the cleaving apparatus.

present in the solution there is a rapid increase in the cell current. This gives rise to a peak in the dc/dv curve and the height of the peak with respect to the initial level is proportional to the concentration of the metal ions in the solution. In the differential polarograph any interference due to the supporting solution can be subtracted out by putting a blank supporting solution in the compensating cell. The sample and the standard solutions were made in a supporting solution containing 0.2 M sodium acetate and 10 ml per litre HCl (cons). The solutions were degassed by passing nitrogen bubbles through them before taking the readings. Readings were taken at 35°C with the blank supporting solution in the compensating cell. The cell voltage was increased from 0.4 volts to 0.9 volts in each sweep, the peak appeared at about 0.65 volts. Sample peak-heights were compared against the calibration curve made from the peak-heights due to the standard solutions containing known amount of Cadmium. A small correction was found necessary for the difference in the NaCl content of the different sample solutions. A separate run of selected standard solutions containing different amount of NaCl, was made to find this correction. The expected accuracy of the cadmium analysis was about $\pm 5\%$.

3.2.2. Manganese Analysis :-

The manganese content of the crystals were determined by converting the Manganese in the samples to KMnO_4 by heating the samples with excess of KIO_4 in a solution containing sulphuric acid. The absorption peak of KMnO_4 , at 525 m μ , was then measured with a Parkin-Elmer Model 450 Spectrophotometer. The spectrophotometer was used in the double beam mode with blank solutions containing ^{the} same amount of NaCl , KIO_4 and H_2SO_4 as in the sample solutions, in the compensating cell. The absorption peaks were compared against the calibration curve made from the absorptions in standard solutions.

3.2.3. Calcium and Magnesium Analysis :-

Calcium and Magnesium were analysed by ^{the} atomic absorption method. Hilger and Watts Spectrophotometer type H 700 was used in conjunction with their Atomic Absorption attachment. A Calcium-Magnesium alloy holo-cathode light source was used. Sample and standard solutions were made in distilled water with few drops of HCl . The solutions were passed through an atomizer and fine droplets were pumped into an air-propane flame situated between the light source and the entrance slit of the spectrophotometer.

Atomic Calcium or Magnesium present in the flame acted as absorber for the Calcium and Magnesium lines emitted by the light source. Absorption of the 4226 Å line of Calcium was used to determine the Calcium content. It was found that presence of Sodium suppressed this absorption to some extent. So the standards had to be prepared with same amount of NaCl in them as in the sample solution. Even then the overall accuracy of the Calcium analysis is probably not much better than 15%. The situation was much better in the case of Magnesium analysis. 2852 Å line of Magnesium was used. The sensitivity was high and the interference was low. Sample and standard solution were prepared with same amount of NaCl in each and the accuracy of the analysis was about $\pm 5\%$.

3.2.4. Barium Analysis :-

Barium was analysed by ^{the} spectrographic method by Mr. D. Hinds at the Analytical Services Laboratory of this Department.

3.3. Heat Treatments :-

All heat treatments were carried out in air. Specimens 5 x 5 x 8 mm were put into a silica tube, about 8 mm in internal diameter and 30 cm in length. This tube was put into the furnace with a chromel/alumel recording thermo-couple, the junction of which rested on the specimen. The recording thermocouple was checked with an N.P.L. standardised Platinum/Platinum + Rhodium thermocouple and was found to agree within two degrees upto 600°C. The furnace temperature was controlled by an 'Ether Transistrol' anticipatory controller. The temperature variation was within one degree of the controlled temperature at the specimen. The temperatures were recorded on a Honeywell chart-recorder. At 200°C annealing time was 24 hours and at other temperatures the product of the annealing temperature in °C and annealing time in hours were kept approximately constant.

Quenching of the specimen was done by taking the specimen tube out of the furnace and turning it over on a block of metal at room temperature.

3.4. Ageing :-

Ageing was carried out on CdCl_2 and MnCl_2 doped

crystals quenched from 400°C , at temperatures between $50^{\circ} - 200^{\circ}\text{C}$ at 50° intervals and in MnCl_2 doped crystals at 225° , 235° , 250°C . Ageing times were 6 hours, 12 hours, 24 hours and doubled each time upto 192 hours.

3.5. Vacuum cleaving and decorating :-

3.5.1. Description of the vacuum cleaving apparatus :-

The vacuum cleaving apparatus was designed to work with ~~our~~ existing 'Balzers' evaporating unit type Mikro BA 3. A sectional diagram of the apparatus and a photograph of it ~~are~~ shown in Fig.3.3. and Fig.3.4.

The apparatus consisted of a 1.2 cm diameter shaft passing through a Wilson seal at the base. At the end of this shaft a bracket was screwed on, to take the crystal holder block. The block was 0.8 cm in diameter and 1.2 cm in height and it was in three parts. The top part had a 0.5 cm square and 0.3 cm deep recess to take the crystal. The crystal was held into position by two screws and between the screws and the crystal was placed an 'L' shaped piece of copper to distribute the pressure evenly and to make a good thermal contact. There was a hole on one side of the recess to introduce a thermocouple. The junction of the thermocouple rested on the crystal. The middle part

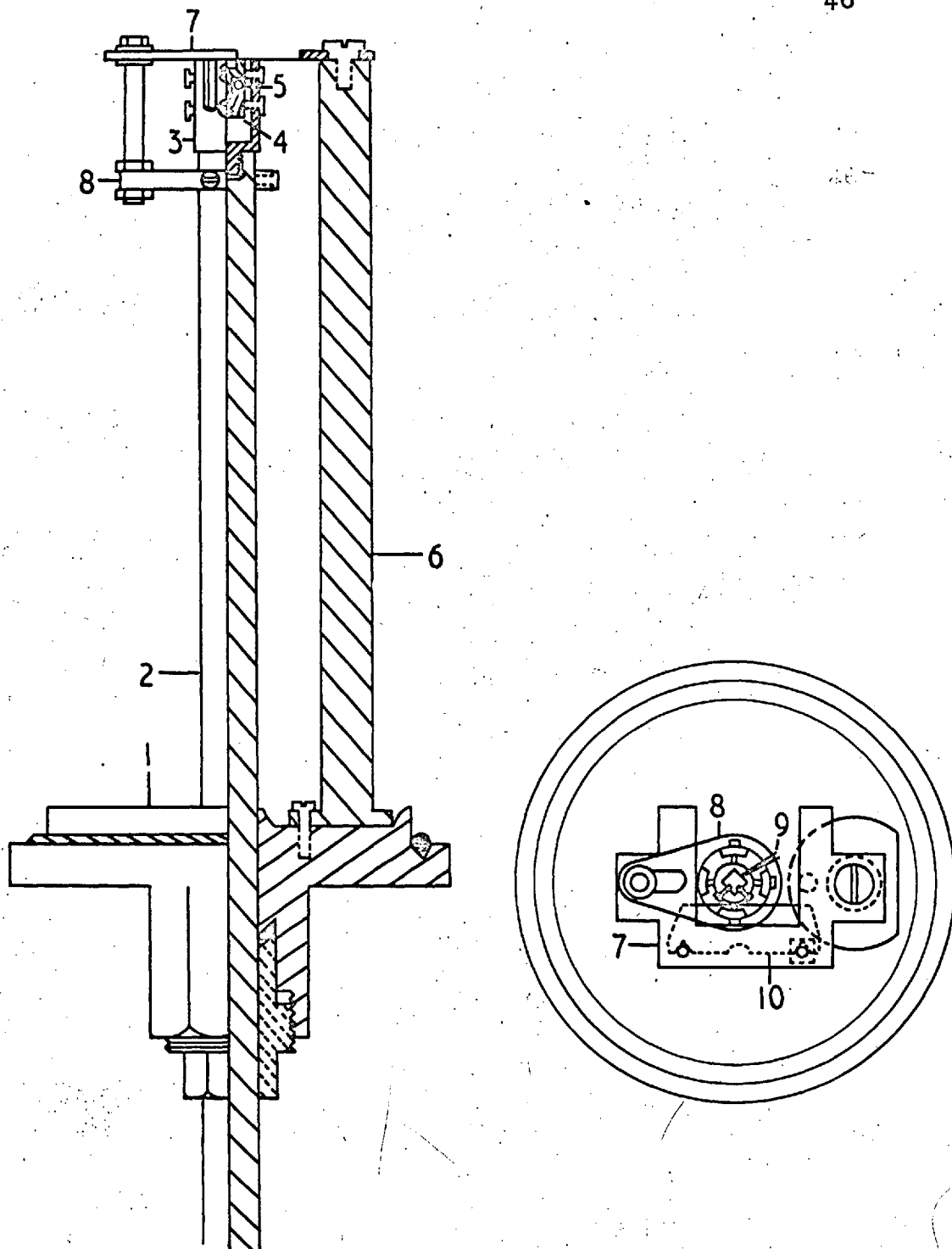


Fig.3.3 Diagram of the cleaving apparatus. 1-Base, 2-Shaft, 3-Bracket, 4-Block, 5-Heater, 6-Pillar, 7-Frame, 8-Cam, 9-Thermocouple, 10-Cleaving blade.

of the block was a heater. The heating element consisted of a 0.1 cm diameter spiral of 40 gauge Tungsten wire. A 0.3 cm high annular piece cut from 0.4 cm diameter silica tube was grooved round the middle and the tungsten wire spiral was put round this piece of silica. The bottom part of the crystal holder block screwed on to the top part and the heating element was sandwiched between the two. It was completely enclosed in the block and the leads were taken out through a fine twin bore silica tubing. The crystal could be raised upto 300°C by the heater. The block was held and positioned in the bracket with eight screws. Pieces of asbestos sheet were placed between the screws and the block to thermally insulate it from the bracket.

A pillar was fixed to the base, parallel to the shaft and at a distance of 1.4 cm from it. At the end of the pillar was pivoted one end of a frame. On to this frame was fitted a piece of stainless steel razor blade, which was used as the cleaving edge. At the other end of the frame, there was a slot. A cam was fitted to the shaft just below the point where the bracket was screwed on. The cam was held in position by three grub screws. A rod from the cam was guided through the slot in the frame.

Now, when the shaft was rotated, the rod pushed the frame over the block. The height of the cam and the shaft was so adjusted, that the blade, fixed to the frame just glanced over the face of the block and cleaved off the part of the crystal that was protruding out of it. A mask with a 4 mm square window was fitted over the frame and the window could be positioned over the cleaved face by rotating the shaft back after cleaving. The mask was used to stop other parts of the apparatus being covered with carbon when replicating the cleaved face of the crystal. It also reduces the rate of contamination of the cleaved face by restricting the directions at which the residual gas molecules could hit the cleaved face.

3.5.2. Evaporating Gold and Depositing Carbon :-

To evaporate gold and deposit carbon without breaking vacuum, a specially shaped filament was used in conjunction with the carbon deposition attachment of the 'Balzers' evaporating unit. It was made of 36 gauge tungsten wire and shaped as a bow with edges turned up, shown in Fig 3.5. There was a small 'V' shaped depression in the middle. The two turned up edges were put round the two screws used for fixing the carbon electrodes to the terminals.

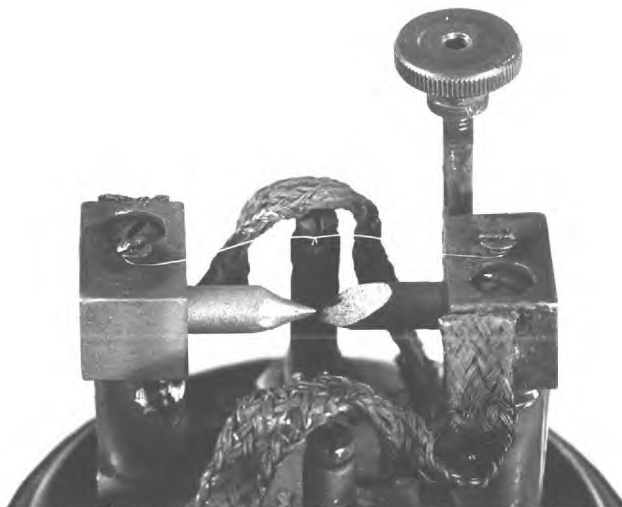


Fig.3.5 Photograph of the carbon deposition unit with the filament for gold evaporation.

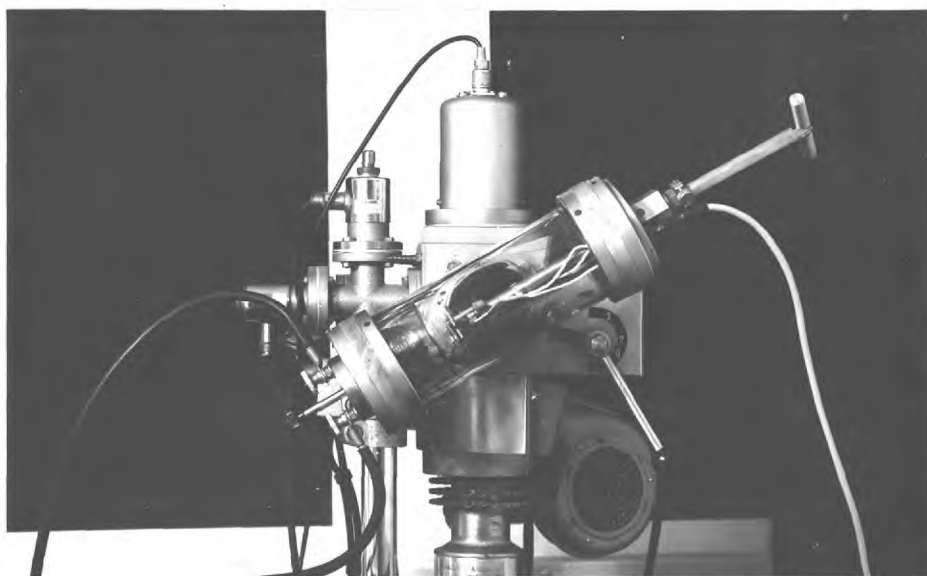


Fig.3.6 Photograph of the vacuum-cleaving and decorating set up.

The terminals could be moved closer and apart from outside by a mechanism fitted at its base. When the filament was in position and the terminals were moved apart the filament was straightened, the ends went further round the screws to make a good fit, at the same time carbon electrodes moved apart and could not strike an arc. When the terminals were moved closer the filament bent back and the ends came loose from the screws and the filament fell off from the terminals. (The set up was used at an angle as shown in Fig 3.6, to enable the filament to fall off from the terminals when it came loose). The carbon electrodes then came in contact and could strike an arc.

3.5.3. Decorating procedure :-

The specimen after the required heat treatment was cleaved to a size 3mm x 3mm x 5mm and set into the recess of the crystal holder block of the cleaving apparatus with about 2 mm of the longer edge sticking out of the face of the block.

Required amount of gold was placed on the 'V' groove of the filament. The mass of gold needed was calculated assuming evaporation is equal in all directions. The required mass of gold is given by the relation

$$m = 4\pi l^2 t \rho$$

where l is the distance between the source and the substrate, t the required thickness and ρ the density of gold.

In the set up used, l was about 3.3 cm and the optimum equivalent thickness ' t ' for good decoration is 5 - 10 Å. The amount of gold required was about 2×10^{-4} gm. To avoid the difficulty of weighing out such a small quantity each time, gold was rolled down to a thickness of about 0.02 mm and thin ribbons of about 0.5 mm wide were cut from it and their weight per unit length was found. Pieces of required length (about 2 mm) were cut off and pressed on to the filament.

After a vacuum of better than 10^{-5} torr was reached, the current through the filament was increased slowly till the filament was dull red-hot. Filament was kept at this temperature for about 10 minutes to get rid of the volatile contaminants. Temperature was then increased till the gold melted, current was then turned slightly down. The crystal was cleaved by turning the shaft of the cleaving apparatus. The temperature of the filament was then brought just above the melting temperature of gold and kept there, to allow the gold to evaporate slowly. After gold has evaporated off, which took about 10 minutes, the

current was turned down and the terminals were brought closer, the filament fell off and the carbon electrodes came in contact. The voltage across the terminals was increased from 4 volts to 16 volts. Carbon was then deposited in short bursts till required thickness ($\sim 100 \text{ \AA}$) was reached which was indicated by the just perceptible brownish colour on the glass tube surrounding the deposition attachment.

The crystal was then taken out and the replica floated on to distilled water. Replica was then collected on a 200 mesh specimen grid with $\langle 100 \rangle$ nearly along the grid bars.

3.6. Platinum shadowed Carbon replica :-

Platinum shadowed carbon replica were made of air cleaved surface after various etching treatments ranging from 10 seconds in Ethanol to 1 second in anhydrous ether and some of just as cleaved surface. The cleaved crystal after suitable etching, was stuck to the under surface of the metal cover plate of the carbon deposition attachment with a drop of 'Lacomit'. A small piece of platinum $0.03 \text{ mm} \times 1 \text{ m} \times 2 \text{ m}$ was placed between the carbon electrodes. When vacuum had reached about 10^{-5} torr an arc was struck.

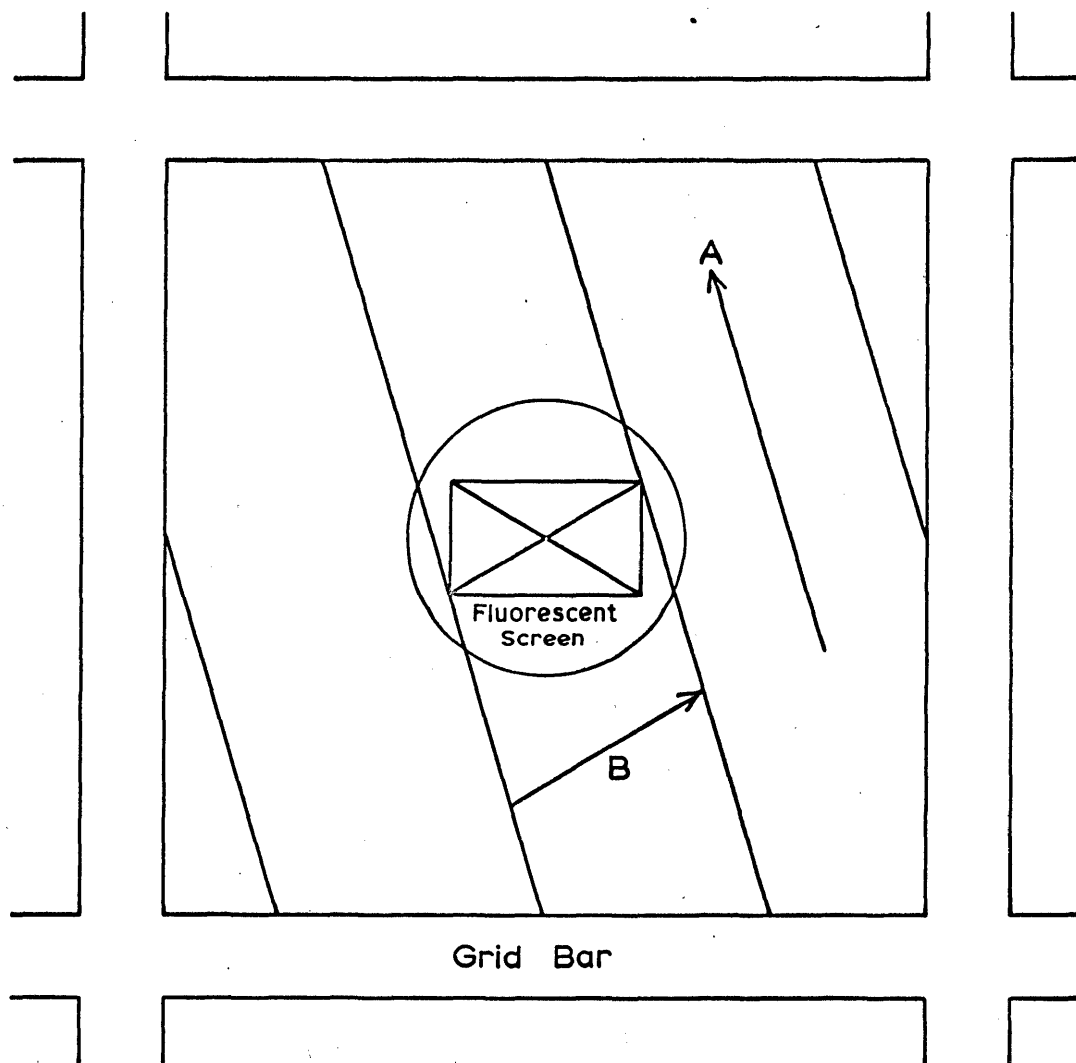
Platinum evaporated and shadowed the crystal surface, shadowing angle was about 34° . At the same time carbon was also deposited. The replica was floated and collected as in the case of the decoration replica.

3.7. Electron Microscopy :-

A Hitachi Model HU 11 electron microscope was used. The microscope was operated at 75 KV. The magnification of the microscope was calibrated with a replica of a 9000 lines per centimeter grating and the magnification was checked from time to time, specially after each servicing and recalibrated if necessary.

3.8. Counting of the precipitates and the determination of the precipitate size :-

The precipitates were counted by scanning the area in each grid square. The method is shown graphically in Fig 3.7. There is a rectangle scribed on the fluorescent screen of the electron microscope to show the area that is recorded on the photographic plate. One of the diagonals of this rectangle that lies approximately bottom-left and top right direction was used for scanning. During scanning only the right hand specimen traverse, which moves



Arrow 'A' showing the direction of motion of the image during the sweep
Arrow 'B' showing the displacement of the image after each sweep

Fig.3.7. The method used for scanning a grid area.

the specimen from top left to bottom right, was used for sweeping and both left hand and the right hand traverses were used for shifting the image through the length of the diagonal line, at the end of each sweep. To eliminate black-lash error sweeping was always done in one direction namely from top to bottom and started from the right hand side. The image of the precipitate was counted as it crossed the line. Lowest magnification that allowed comfortable viewing, was used to minimise any overlap error. The number of precipitates per grid-square was noted. Several grid squares were thus scanned and a total of 2,000 to 4,000 precipitates were counted, from which the average number of precipitates per grid square was calculated. The individual numbers of precipitates in each grid square were found to lie typically within 10% of the average value for about 100 ppt./gr.sq. to within 5% of the average value for 500 ppt/gr.sq. The area of the grid squares were found by measuring their internal dimensions with a Reichart Type Mc F optical microscope.

To determine the size and the size distribution of the precipitates, about a hundred precipitates were photographed at random and their dimensions were measured on the photographic plates with a fine glass-ruler fitted

with a micrometer dial-gauge. A visual check was also kept on the size distribution during precipitate counting.

3.9. Determination of the Precipitate Volume Ratio :-

A simple analysis shows that the volume ratio of the precipitate to the matrix

$$\frac{V_p}{V_m} \text{ is equal to } \frac{A_p}{A_m}$$

where A_p is the total cross sectional area of the precipitates in a random section through the matrix and A_m is the area of the matrix. The analysis is as follows :-

In a cube of dimension L , of the matrix containing precipitates, if sections are made say normal to x axis, then the total volume of the precipitates in the cube is given by

$$V_p = \int_0^L A_{px} \, dx \dots\dots\dots(1)$$

where A_{px} is the total area of the precipitates sectioned at a distance x from the origin.

Now if the distribution of the precipitates is homogeneous compared to the size of the cube, that is, if the number of the precipitates is large and their spatial distribution is random, then A_{px} can be treated as a constant, A_p , and taken out of the integration sign of

eq. (1). And on integration we then have

$$V_p = A_p \cdot L \dots\dots\dots(2)$$

Dividing both sides of eq (2) by the volume of the cube we have

$$\frac{V_p}{V_m} = \frac{A_p}{A_m}$$

From the measurement on the photographic plates the average sectional area per precipitate was found, which was then multiplied by the number of precipitates per grid-square, to obtain A_p the total area of precipitate sectioned in a grid square. This was then divided by the area of the grid-square A_m , found by the optical measurements, to get the volume ratio of the precipitates.

3.10. Limits of errors and detectability :-

3.10.1. Limits of errors :-

Sources of errors :-

(1). Variation in the concentration of divalent ions at different parts of the crystals.

Doping levels are known to vary along the length of the boule and sometimes along the radius as well. The amount of variation depends on many factors such as the average doping level, the rejection ratio of the doping

species, boule and melt size ratio, rate of growth etc. In general variation is smaller for lighter doped crystals and depends with lower rejection ratio. In Czochralski or Kyropoulos grown crystals the doping level and its rate of variation increases towards the bottom of the boule. In the case of radial variation, the concentration is high towards the center. To avoid the error due to such variations, boules were cleaved into plates about 0.8 cm thick normal to the growth axis, and numbered 1, 2, 3, etc. starting from the top (near the seed). For one set of experiments specimens were taken from one of these top plates and preferably from areas **about** the same distance from the centre. The specimens were saved after experiments and used for analysis. Except in the case of MgCl_2 doped crystals no variation within the same batch of specimens could be detected.

(2). Error due to the variation in magnification of the Electron microscope.

As magnetic lenses are of variable focal length it is possible that the magnification of the electron microscope may sometimes vary. As any error in magnification will introduce more than twice that error in the measurement of area and therefore in the volume ratio of

the precipitates, the magnification of the microscope was carefully calibrated and checked from time to time. It is felt that the error in volume ratio, introduced through the error in magnification was not more than $\pm 10\%$.

(3). Error due to sampling of the precipitates:

For practical reasons sample size had to be limited to about 100 for determining the average area of the precipitates. However in view of the narrow range of precipitate size distribution, specially in the lower doped crystals, the expected error in the mean of 100 samples is about $\pm 5\%$. Over all error in the estimation of the volume fraction of the precipitates is therefore within $\pm 15\%$. The error in the chemical analysis of Cd and Mn was about $\pm 5\%$. These error limits have been shown on the data for the Concentration Vs. Volume fraction of precipitates plots of CdCl_2 and MnCl_2 doped crystals.

3.10.2. Limits of Detectibility :-

Precipitate size-

As the precipitates are detected by the difference in the density of nucleation of gold on them compared to that on the NaCl matrix there has to be a certain number of nuclei on the precipitates for this difference to be detectable.

Minimum size of a square section of a precipitate that is detectable is about 100 A across. For a linear section it is about 300 A. Error due to this limit in detectability is probably very small as the number of precipitates approaching this size in slow cooled crystals were negligible.

3.9.3. Limit of the detection of volume ratio;-

If the precipitate size is above the detection level, there is however, no theoretical limit to the minimum volume ratio that can be detected. In practice, for homogeneously distributed cubic precipitates, a volume ratio of 1×10^{-7} with an accuracy of $\pm 10\%$ can be detected in a 0.25 c.c. specimen without much difficulty.

C H A P T E R I V

EXPERIMENTAL RESULTS

4.1. Observation of precipitates in CdCl_2 doped NaCl :-

CdCl_2 doped crystals were examined in five different concentrations. Namely, crystals containing 35 mol ppm, 200 mol ppm, 350 mol ppm, 500 mol ppm and 950 mol ppm CdCl_2 .

4.1.1. Slowly cooled crystals :-

In the crystals containing 35 mol ppm CdCl_2 no precipitate could be found. In other crystals, precipitates with square sections and edges along the $\langle 100 \rangle$ matrix directions were found on the $\{100\}$ cleavage plane of NaCl as shown in Fig 4.1.

The precipitates were highly soluble in water, alcohol and even ether, compared to NaCl. Specimens thinned with solutions of alcohol and water for transmission electron microscopy showed only square holes in the place the precipitates, as shown in Fig 4.2. Shadowed replica of air-cleaved surfaces showed that the precipitates are affected by the few minutes exposure to air, Fig 4.3.

The size distribution of the precipitates for different CdCl_2 content is shown in Fig 4.4.. The size of the precipitates increased and also the size distribution widened with increasing doping level. Low angle boundaries were found in higher doped crystals. The precipitates decorating these boundaries were larger in size and in

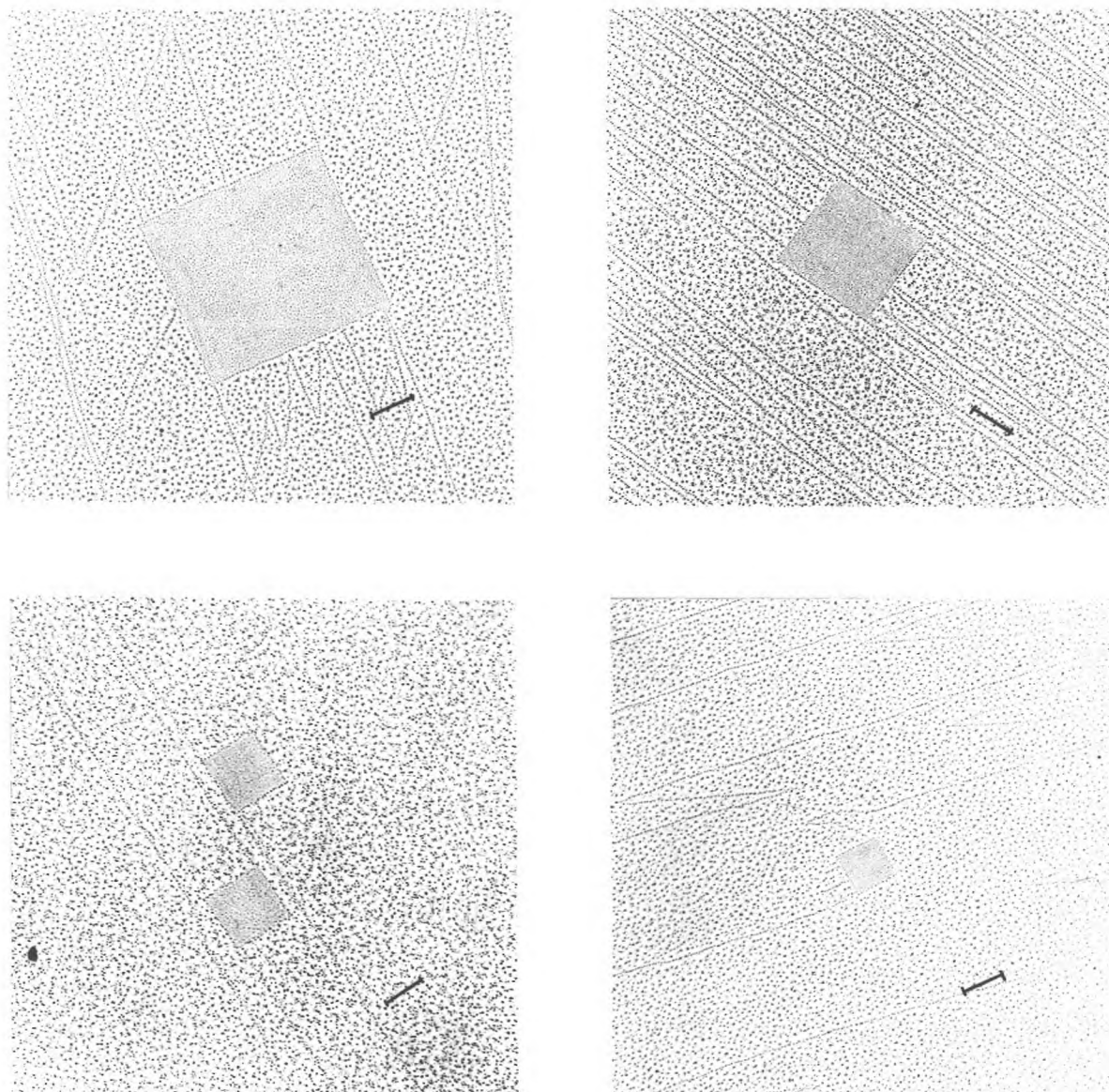


Fig. 4.1. Gold decoration replica showing precipitates with square sections in the (100) plane of CdCl_2 doped (200 - 950 mol.ppm.) NaCl . (Markers, 1000 $\text{\AA}$ along $\langle 100 \rangle$.)



Fig. 4.2. Thinned specimen of CdCl_2 doped (950 ppm) NaCl , showing holes in place of the precipitates.

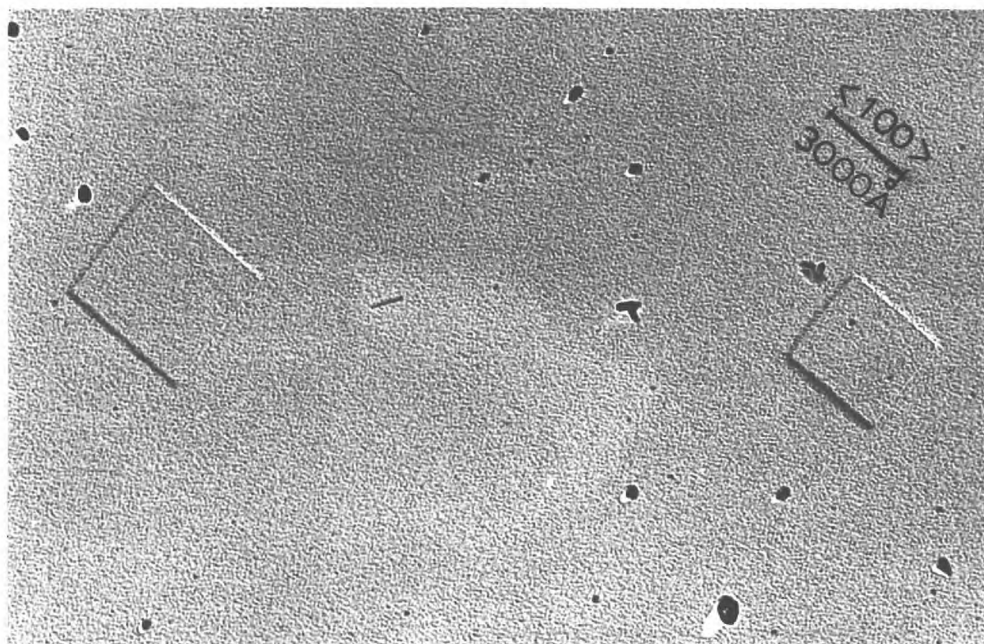


Fig. 4.3. Shadowed replica of the air-cleaved surface of CdCl_2 doped (950 ppm) NaCl , showing that the precipitates are readily attacked by the atmosphere.

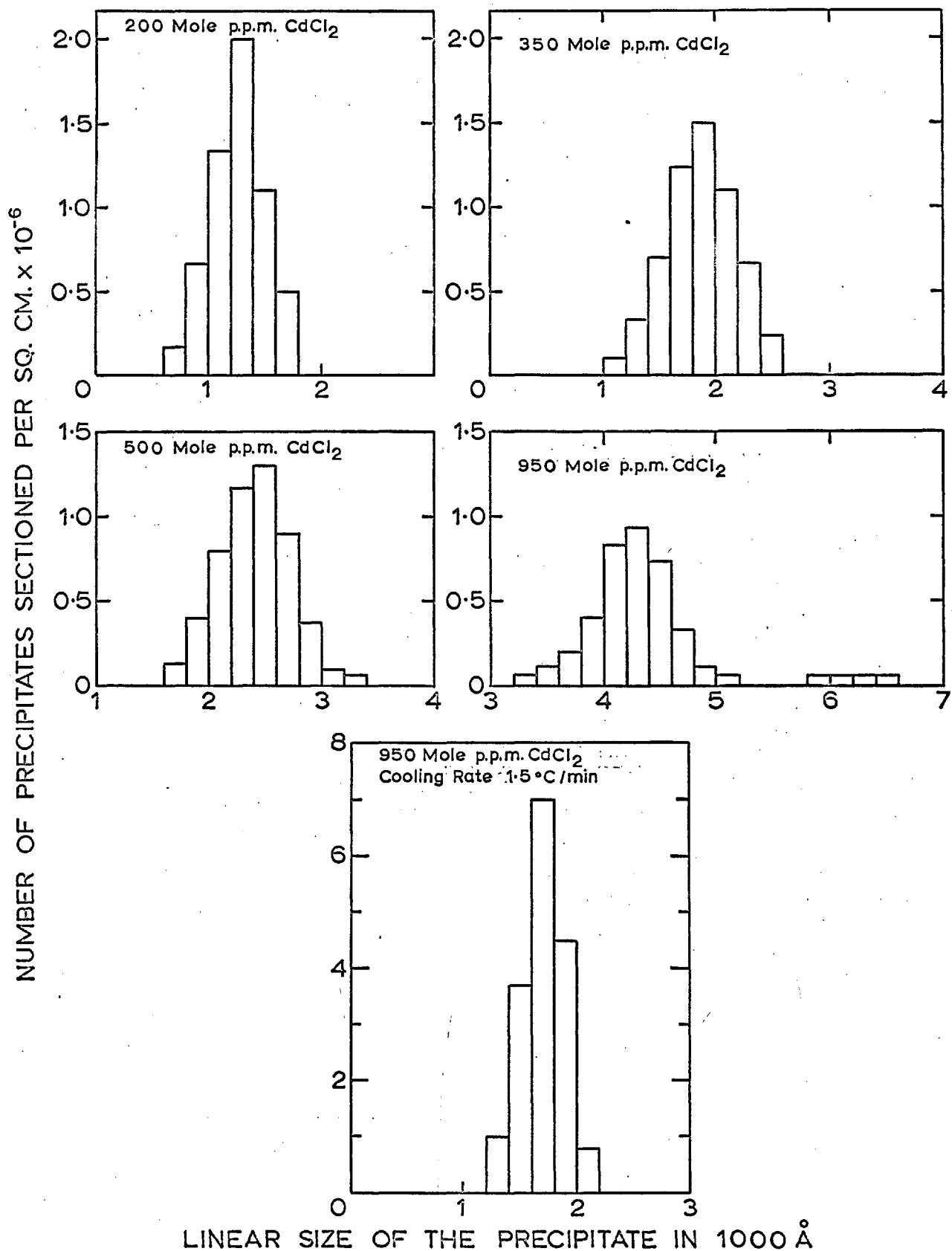


Fig.4.4. Size distribution of the precipitates in CdCl_2 doped NaCl crystals. (Cooling rate where not mentioned is 0.25°C/min)

general oblong in shape, Fig 4.5. The volume ratio of the precipitates as a function of the molar concentration of CdCl_2 has been plotted in Fig 4.6. A straight line fitted to the experimental points has a slope of 8.4 volume fraction/molar concentration. This straight line cut the concentration axis at 85 mol ppm. The significance of this apparent room temperature solubility of 85 mol ppm of CdCl_2 in NaCl has been discussed in section 5.3.2.

The number of precipitates per cubic cm of the matrix were calculated from the size and the number of precipitates sectioned per sq.cm. This is done by dividing the number of precipitates per sq.cm. with the linear size of the precipitates (in cm.). The numbers of precipitates per cubic cm. in crystals containing different amount of CdCl_2 and also for two different cooling rates for crystals containing 950 mol ppm CdCl_2 , have been shown in Table 4.1.

4.1.2. Determination of the solution temperature :-

The slowly cooled crystals were raised to 100°C , 150°C , 200°C , 225°C , 250°C , 275°C , 300°C and 350°C . The crystals were then air quenched to room temperature and examined. No change in the precipitate volume was observed in crystals quenched from temperatures upto 200°C . A decrease in the volume of the precipitates could be

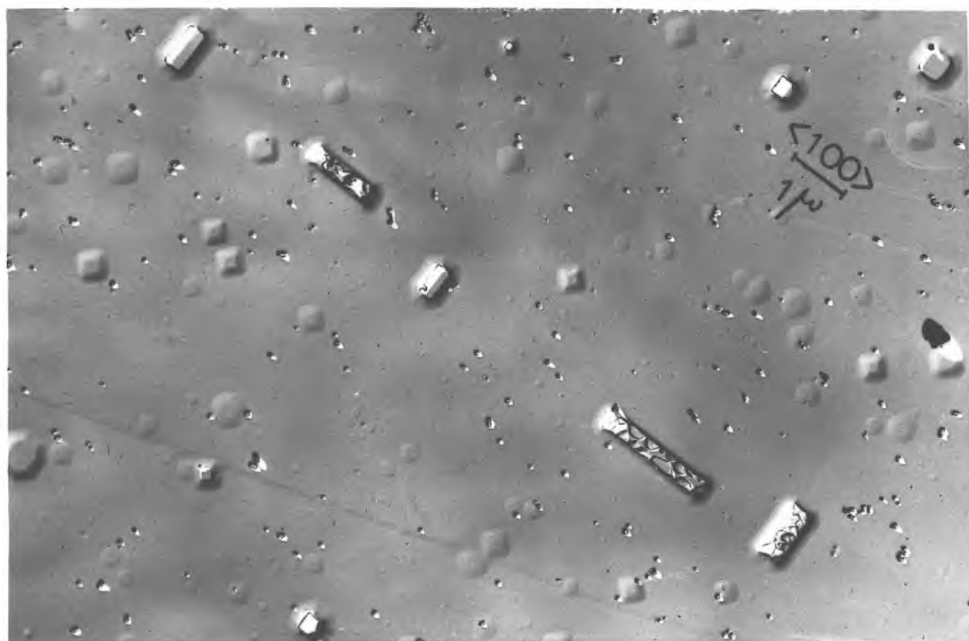
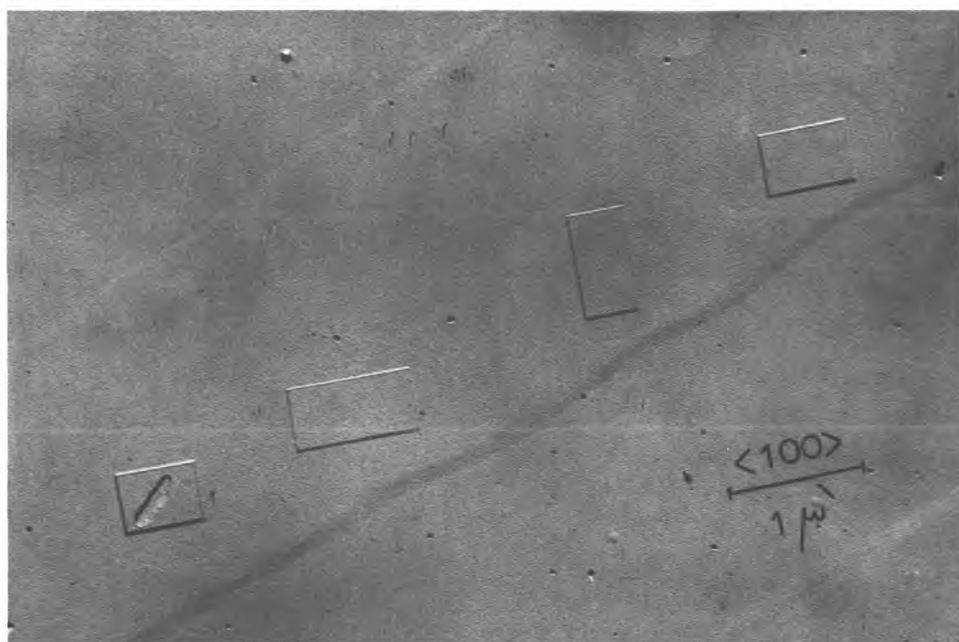


Fig. 4.5. Showing precipitates with oblong sections on the sub-boundaries of CdCl_2 doped (950 ppm.) NaCl .

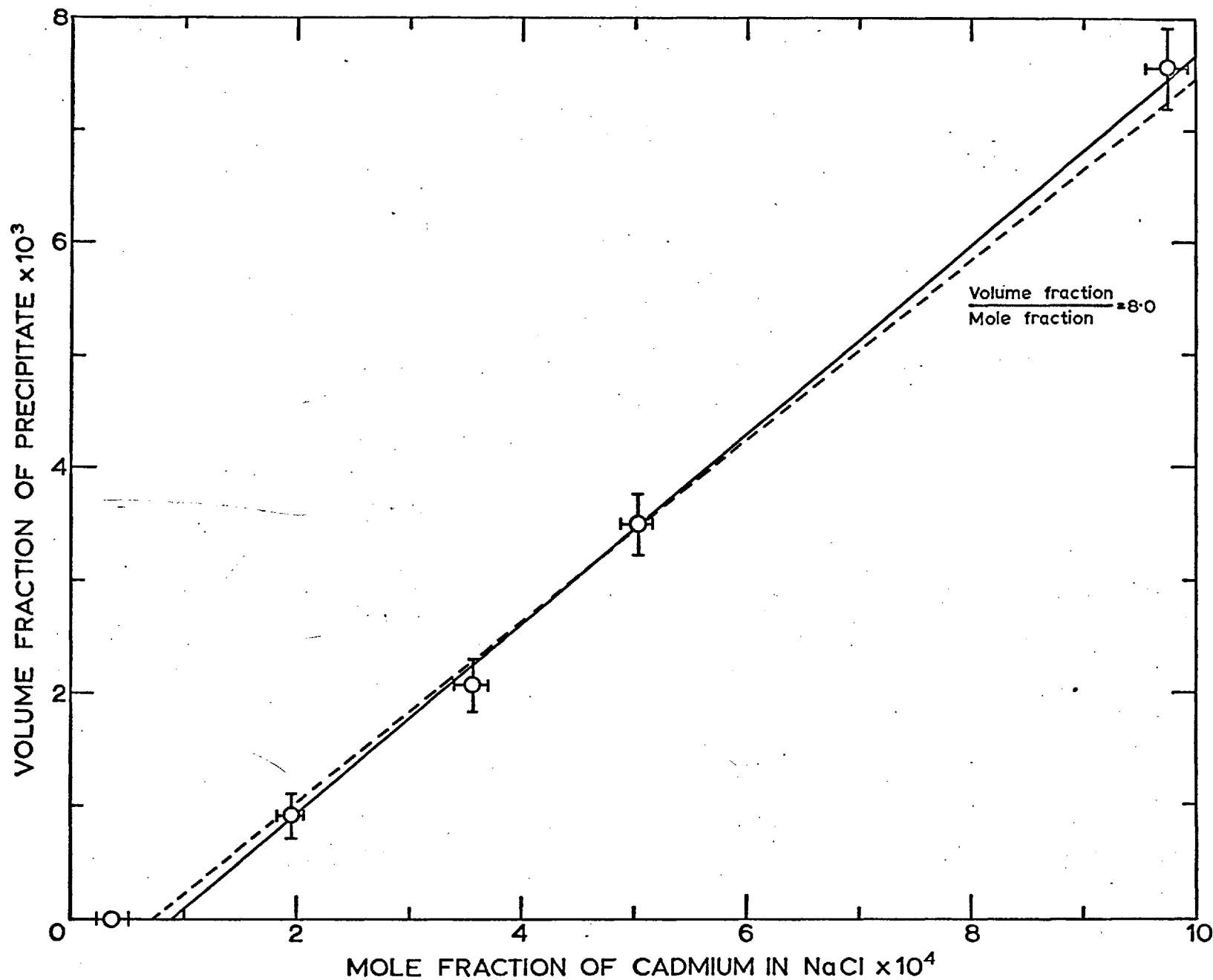


Fig.4.6. The volume fraction of precipitates as a function of CdCl_2 concentration.

Table 4.1

Precipitates in CdCl_2 doped NaCl .

Concentration of CdCl_2	Cooling rate	No. of ppt. per cm^3 .	Average linear size of ppt.	Vol. of ppt. per cm^3 .
35 mol.ppm.	$0.25^\circ\text{C}/\text{min.}$	No ppt.	—	—
200 mol.ppm.	"	4.4×10^{11}	$1.3 \times 10^3 \text{ A}$	$9.5 \times 10^{-4} \text{ cc.}$
350 mol.ppm.	"	2.9×10^{11}	$1.9 \times 10^3 \text{ A}$	$2.1 \times 10^{-3} \text{ cc.}$
500 mol.ppm.	"	2.2×10^{11}	$2.5 \times 10^3 \text{ A}$	$3.5 \times 10^{-3} \text{ cc.}$
950 mol.ppm.	"	9.3×10^{10}	$4.3 \times 10^3 \text{ A}$	$7.6 \times 10^{-3} \text{ cc.}$
950 mol.ppm.	$1.5^\circ\text{C}/\text{min.}$	1.1×10^{12}	$1.7 \times 10^3 \text{ A}$	$5.3 \times 10^{-3} \text{ cc.}$

noticed in crystals quenched from 225°C . The precipitates in the crystal containing 200 mol ppm CdCl_2 went into solution between 225°C and 250°C . The precipitates in crystals containing higher amount of CdCl_2 went into solution at progressively higher temperatures. Finally no precipitate was found in crystals containing 950 mol ppm CdCl_2 when quenched from 300°C . The precipitate Volume as a function of quenching temperature for different crystals has been presented in Fig 4.7. Some of the precipitates in crystals quenched from the region of solution temperature showed octagonal cross section as in Fig 4.8. The significance of this octagonal section has been discussed in section 5.3.1.

4.1.3. Ageing experiment :-

Crystal containing 950 mol ppm CdCl_2 was solution treated at 400°C for 12 hours and air quenched to room temperature. The crystal was then aged at 100°C , 150°C and 200°C for 6 hours, 12 hours, 24 hours, 48 hours and 96 hours. No precipitate was found in crystals aged upto 96 hours at 150°C . At 200°C precipitates were detectable after 6 hours of ageing and after 24 hours there were about 1.3×10^7 precipitates per square cm. The precipitates in the quenched and aged crystals were oblong in shape, with a wide variation in size and they tend to appear in groups with the

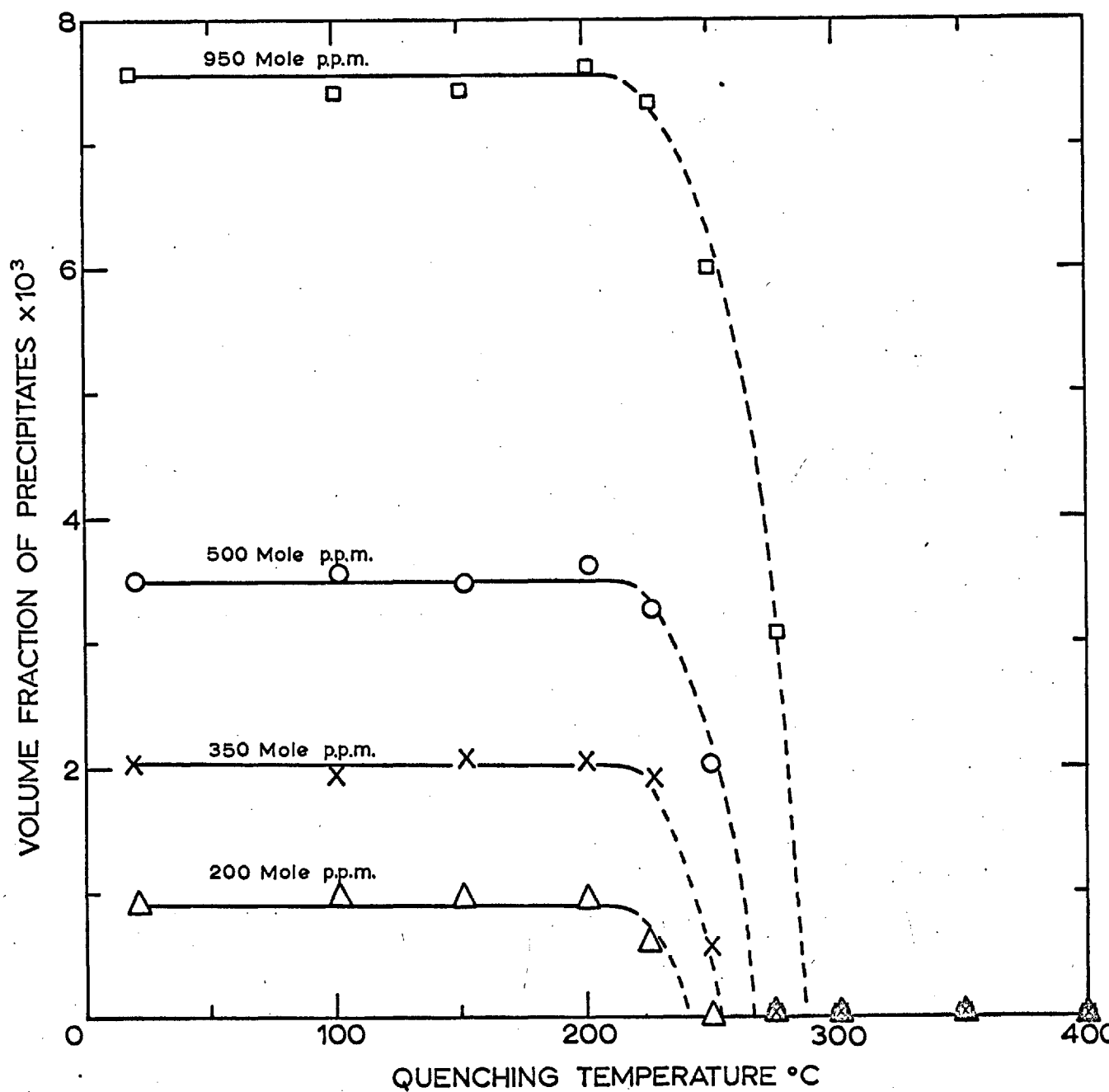


Fig.4.7. The volume fraction of precipitates in slow cooled CdCl₂ doped NaCl as a function of subsequent quenching temperature.

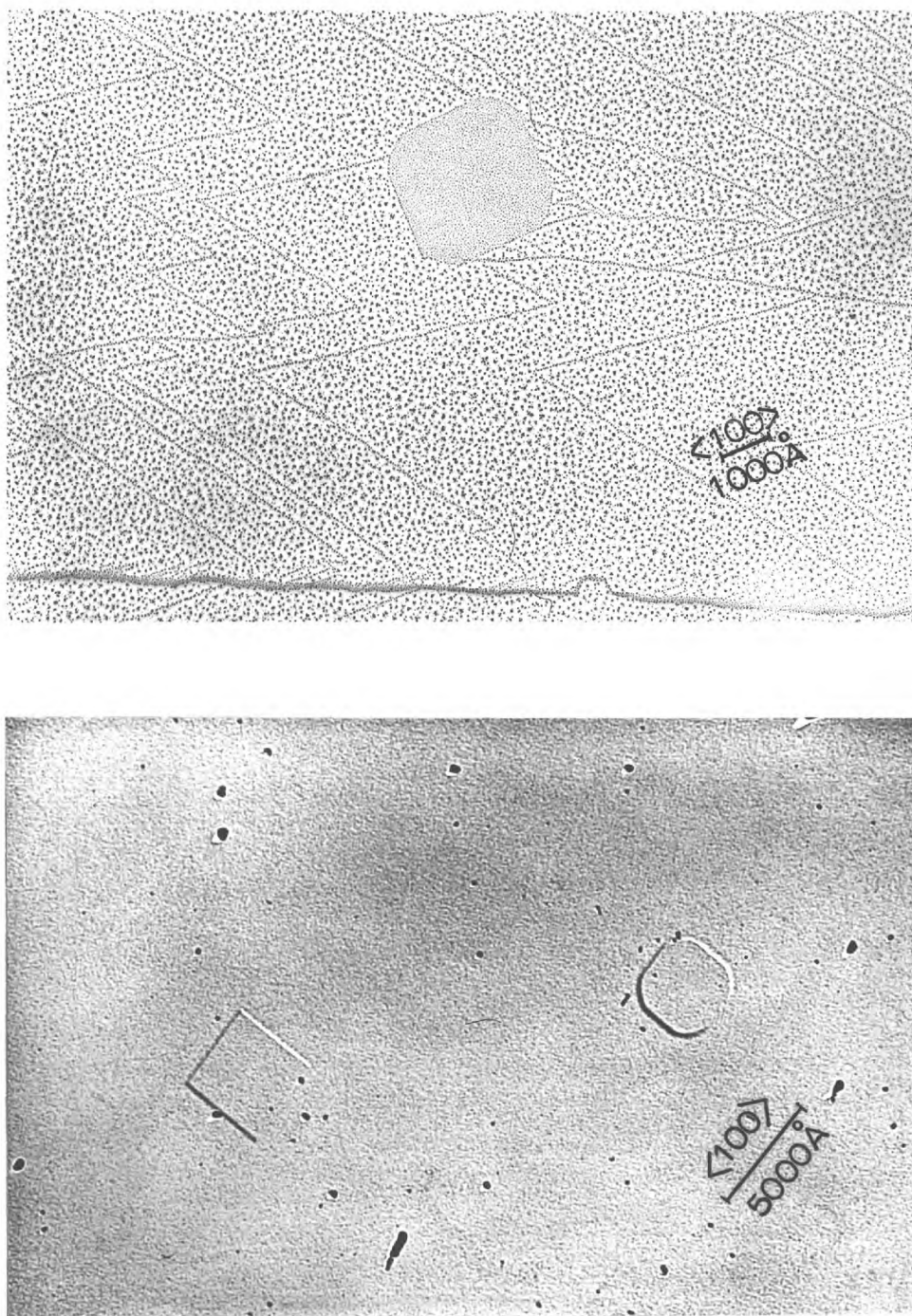


Fig 4.8. Showing precipitates with octagonal sections in CdCl_2 doped (950 ppm.) NaCl , quenched from 225°C .

precipitates arranged along general direction of $\langle 110 \rangle$ as in Fig 4.9. This is in contrast to the precipitates in the slowly cooled crystals which had a square cross-section, narrow size range and were randomly distributed.

4.2. Precipitates in MnCl_2 doped NaCl :-

MnCl_2 doped crystals were examined in six concentrations, namely crystals containing 35 mol ppm, 225 mol ppm, 375 mol ppm, 600 mol ppm, 750 mol ppm and 900 mol ppm of MnCl_2 .

4.2.1. Slowly cooled crystals :-

In the slowly cooled crystals containing 35 mol ppm MnCl_2 no precipitate was found. In higher doped crystals, precipitates with square cross sections similar to those in the CdCl_2 doped crystals were observed as shown in Fig 4.10. In addition to the normal precipitates a distribution of small precipitates was found in the MnCl_2 doped crystals as shown in Fig 4.11.

The precipitate volume as a function of MnCl_2 concentration has been plotted in Fig 4.12. A straight line fitted to the experimental points has a slope of 8.3 volume fraction/mol fraction, and this straight line cut the concentration axis at 70 mol ppm indicating that 70 mol ppm MnCl_2 did not precipitate out. The significance

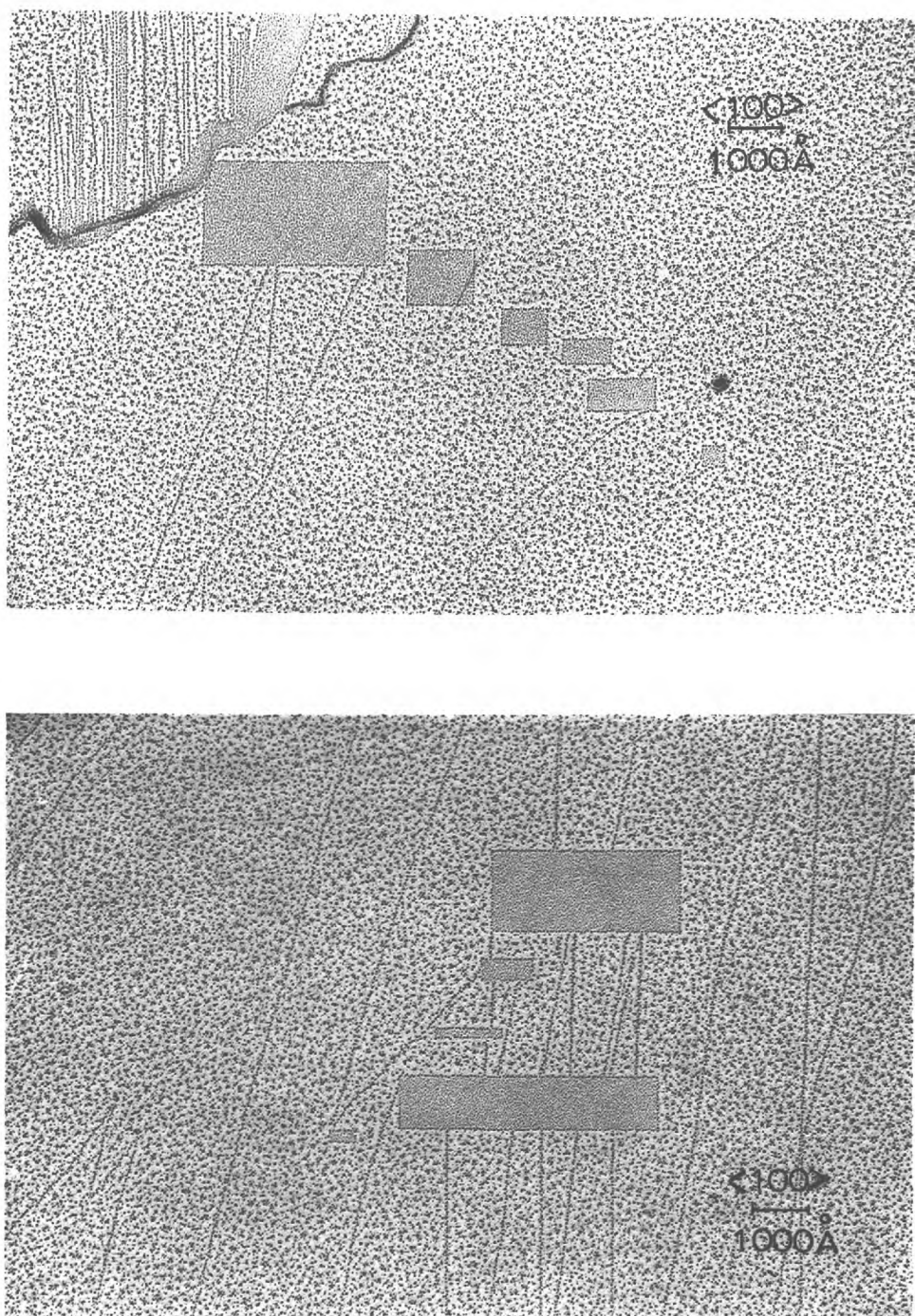


Fig. 4.9. Showing groups of oblong precipitates along the general direction of $\langle 110 \rangle$ in CdCl_2 doped (950 ppm.) NaCl , quenched from 400°C and aged at 200°C for 24 hours.

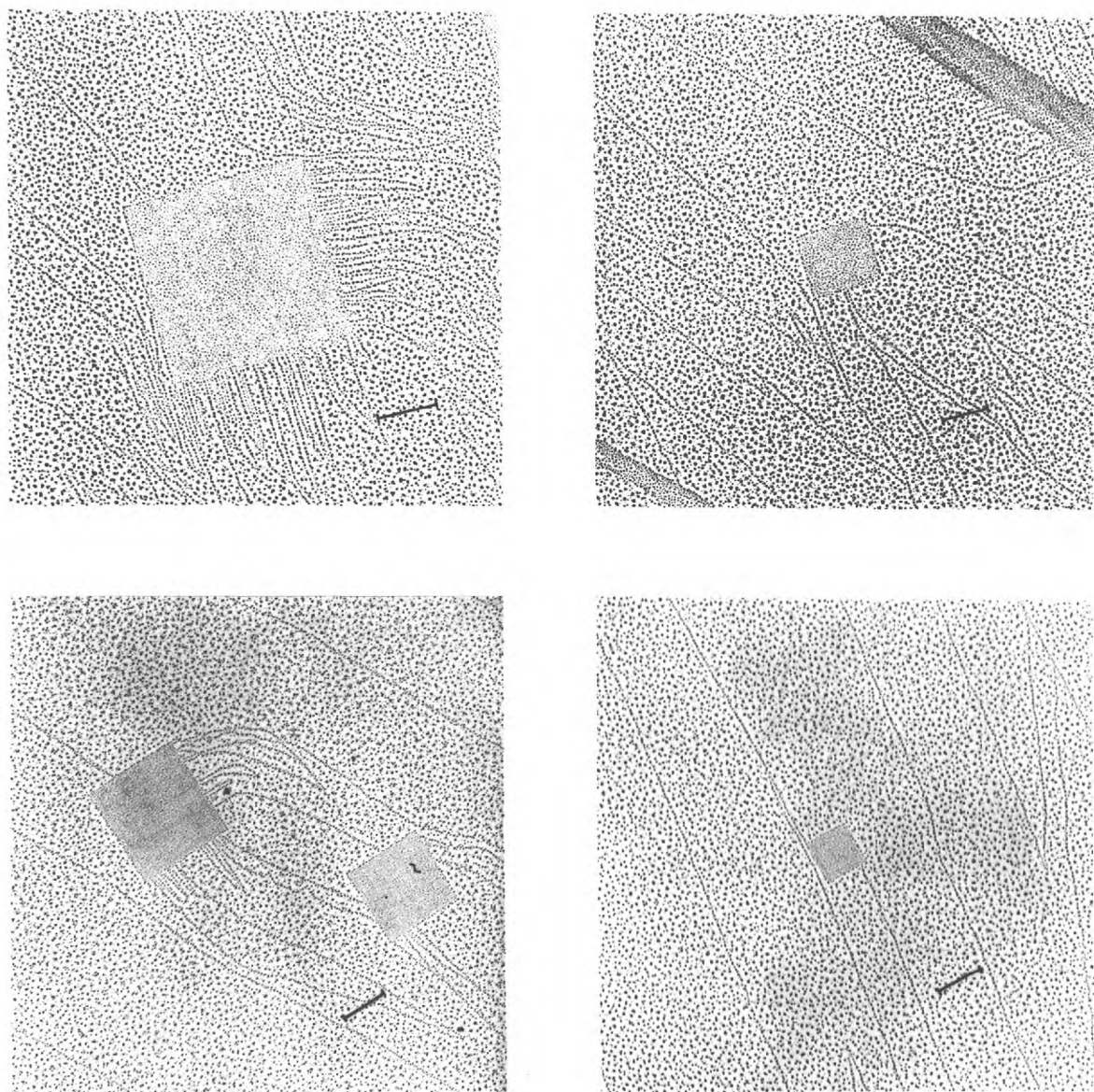


Fig. 4.10. Showing precipitates with square sections in the (100) plane of MnCl_2 doped (225 - 900 mol.ppm.) NaCl. (Markers, 1000 Å along $\langle 100 \rangle$.)

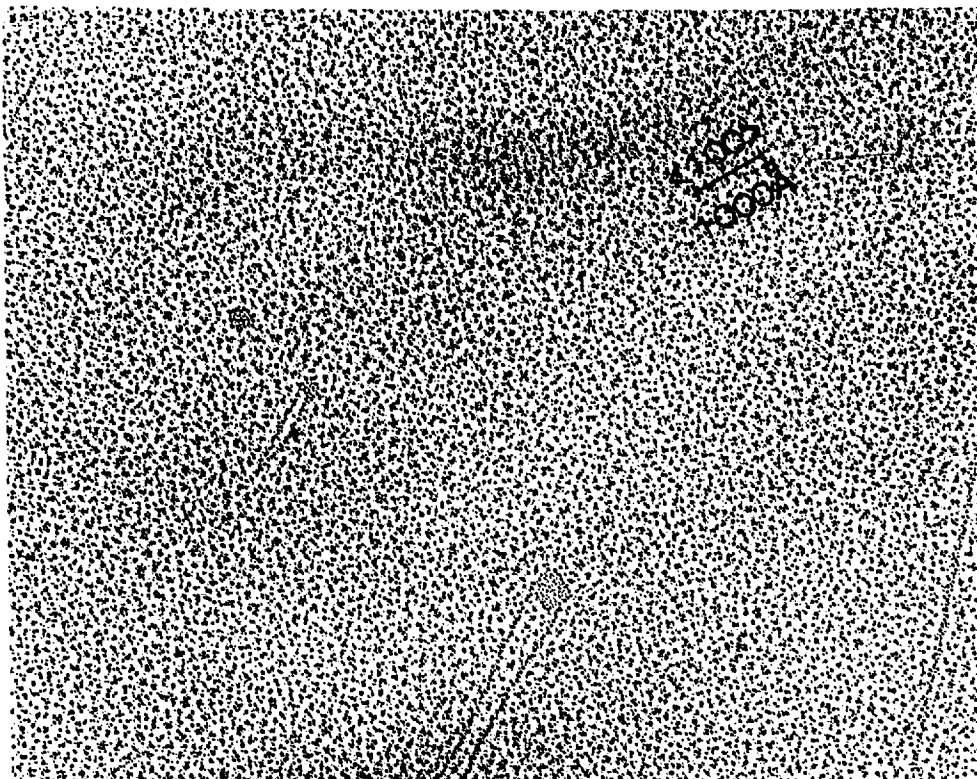


Fig. 4.11. Gold decoration replica, showing some very small precipitates in MnCl_2 doped (750 ppm.) NaCl .

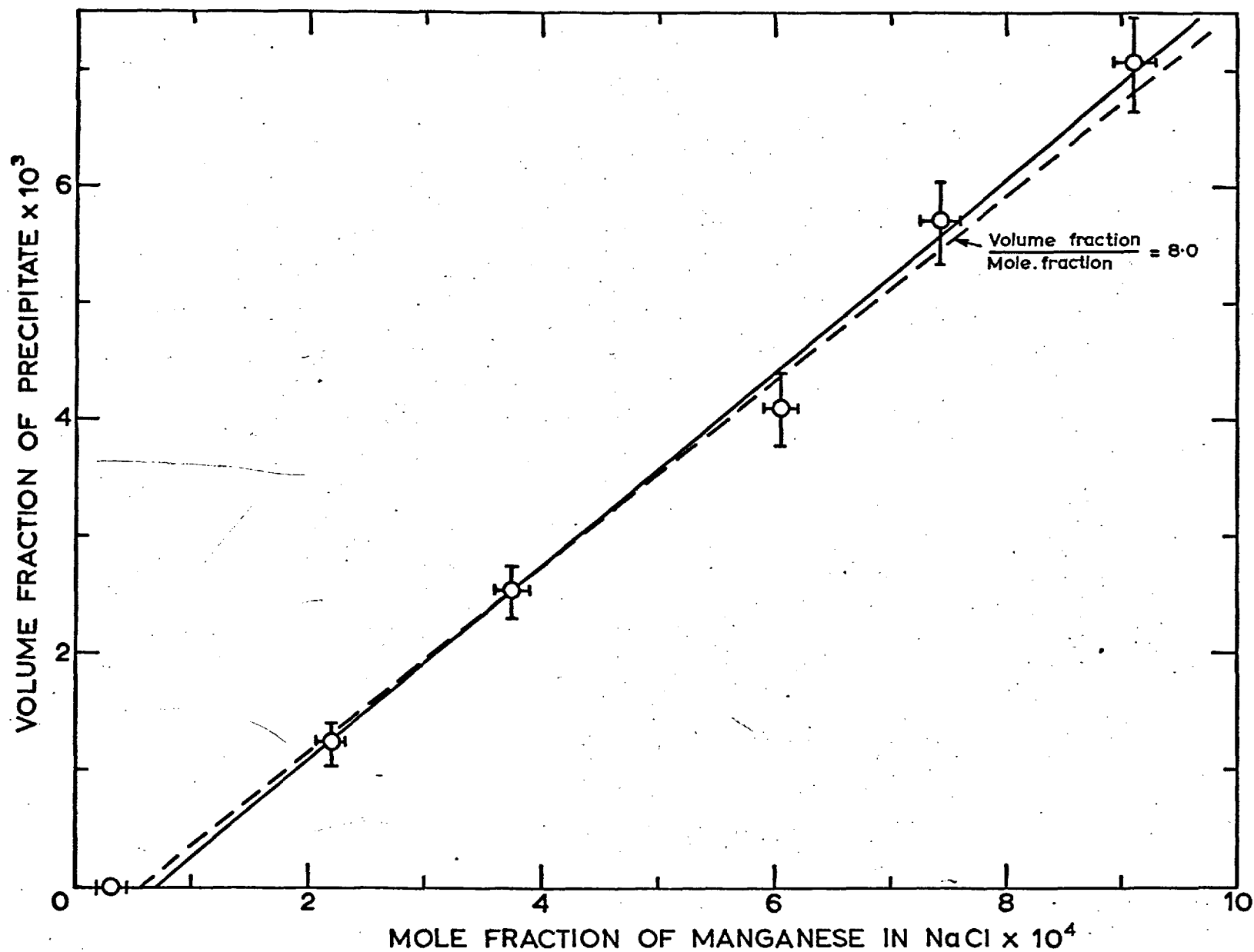


Fig.4.12. The volume fraction of precipitates as a function of MnCl_2 concentration.

of this apparent solubility has been discussed in section 5.4.2.

The precipitate size distributions are shown in Fig 4.13. The size of the precipitates increased and the size distribution became broader with increasing MnCl_2 concentration. At higher concentrations few large precipitates compared to the main population of precipitates were observed.

The calculated number of precipitates per cubic cm. in the crystals containing different amounts of MnCl_2 are shown in Table 4.2.

4.2.2. Determination of the solution temperature for the precipitates in MnCl_2 doped crystals :-

The slowly cooled crystals were raised to 100°C , 150°C , 200°C , 250°C , 275°C , 300°C , 350°C and 400°C . The crystals were then quenched to room temperature and examined. No significant change in π_{p} precipitate volume was found upto ~~the~~ quenching temperature of 250°C . The precipitates in crystals containing 225 mol ppm MnCl_2 went into solution between 250°C and 275°C . Precipitates in crystals containing higher concentration of MnCl_2 went into solution at a progressively higher temperatures. Finally no precipitate was found in crystals containing 900 mol ppm MnCl_2 when quenched from 350°C and above. The precipitate volume

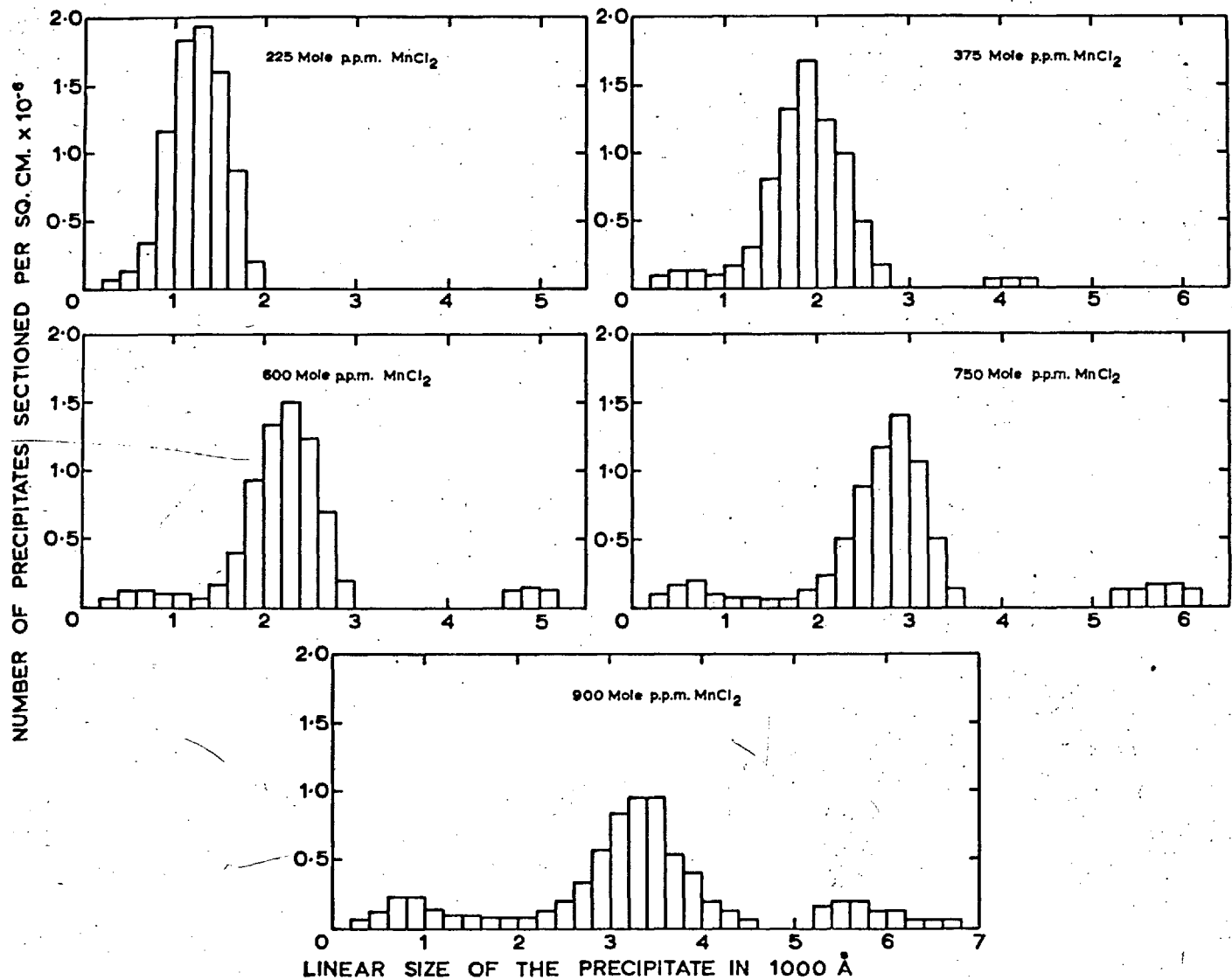


Fig.4.13. Size distribution of the precipitates in MnCl₂ doped NaCl crystals. (Cooling rate 0.25 °C/min).

Table 4.2
Precipitates in MnCl_2 doped NaCl .
(Rate of cooling $0.25^\circ\text{C}/\text{min.}$)

Concentration of MnCl_2	Number of ppt. per cubic cm.	Average linear size of ppt.	Vol. of ppt. per cubic cm.
35 mol.ppm.	No ppt. has been found.	_____	_____
225 mol.ppm.	6.4×10^{11}	$1.25 \times 10^3 \text{ A}$	$1.2 \times 10^{-3} \text{ cc.}$
375 mol.ppm.	3.7×10^{11}	$1.9 \times 10^3 \text{ A}$	$2.5 \times 10^{-3} \text{ cc.}$
600 mol.ppm.	2.8×10^{11}	$2.3 \times 10^3 \text{ A}$	$4.1 \times 10^{-3} \text{ cc.}$
750 mol.ppm.	2.2×10^{11}	$2.9 \times 10^3 \text{ A}$	$5.7 \times 10^{-3} \text{ cc.}$
900 mol.ppm.	$1.6 \times 10^{11},$	$3.4 \times 10^3 \text{ A}$	$7.0 \times 10^{-3} \text{ cc.}$

as a function of quenching temperature for different crystals has been shown in Fig 4.14.

Some precipitates with octagonal sections were also found in MnCl_2 doped crystals quenched from the temperature of the solution region as in Fig 4.15.

4.2.3. Ageing experiment :-

The crystal containing 600 mol ppm MnCl_2 was quenched from 450°C and aged at 100°C , 150°C , 200°C , 235°C for 6 hours, 12 hours, 24 hours and thus upto 192 hours. No precipitates could be found in crystals aged upto 200°C for 192 hours. Precipitates appeared after aging at 235°C for 24 hours. The precipitates were again oblong in section and tend to occur in groups as shown in Fig 4.16.

4.3. MgCl_2 doped NaCl :-

Magnesium was found to have a large rejection ratio. Crystals grown from melt containing 1 mol% MgCl_2 was found to contain less than 20 mol ppm Mg^{2+} . Crystal was grown from melt containing about 8 mol% MgCl_2 . The top part of the crystal contained about 200 mol ppm MgCl_2 while the bottom part, which was milky white, contained about 1500 mol ppm MgCl_2 . Samples were taken from the different parts of this crystal. Precipitates with square cross section, similar to those in CdCl_2 and MnCl_2 doped crystals were

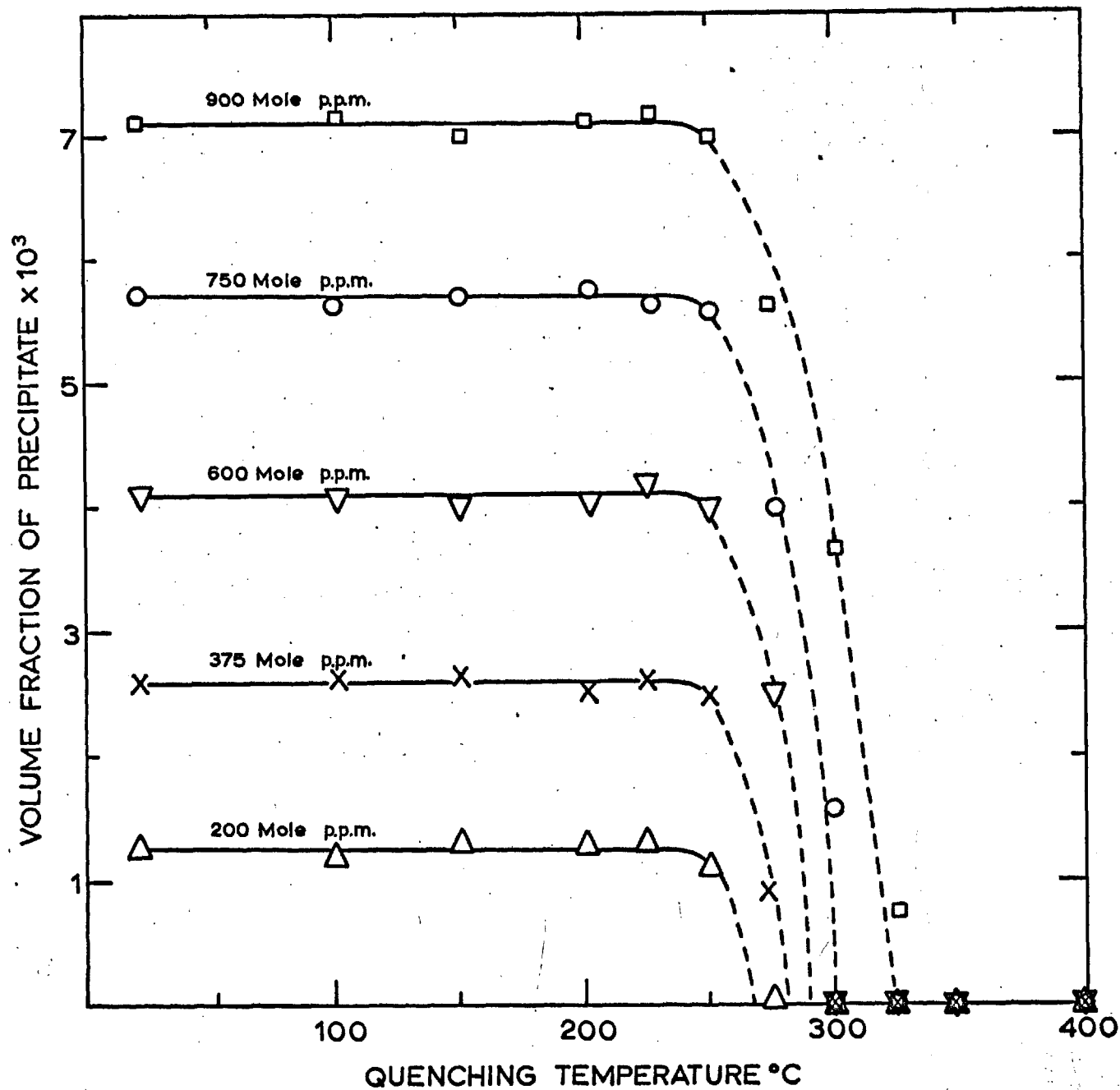


Fig.4.14. The volume fraction of precipitate in slow cooled MnCl_2 doped NaCl as a function of subsequent quenching temperature.

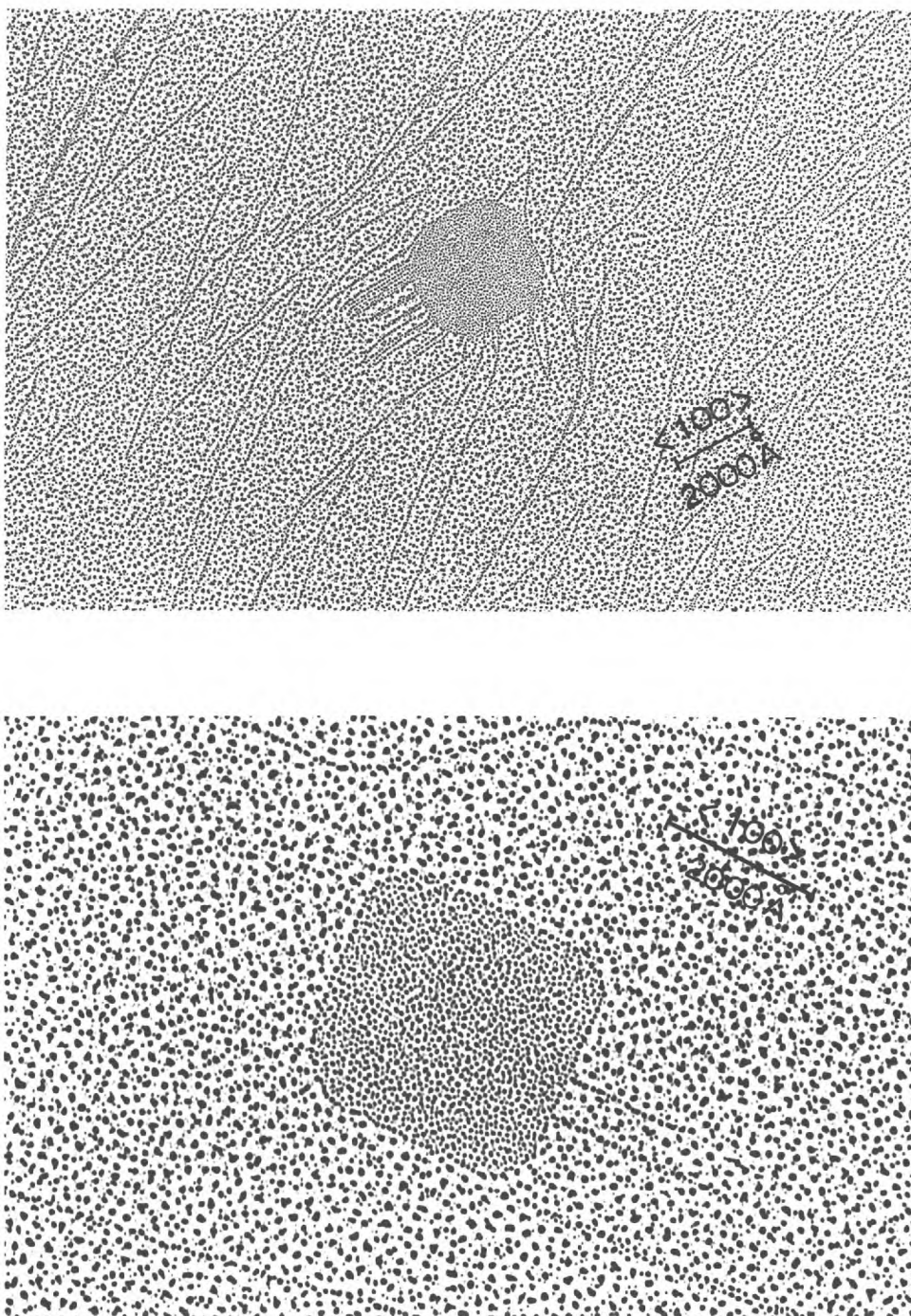


Fig. 4.15. Showing some precipitates with octagonal sections in MnCl_2 doped (750 ppm.) NaCl , quenched from 275°C .

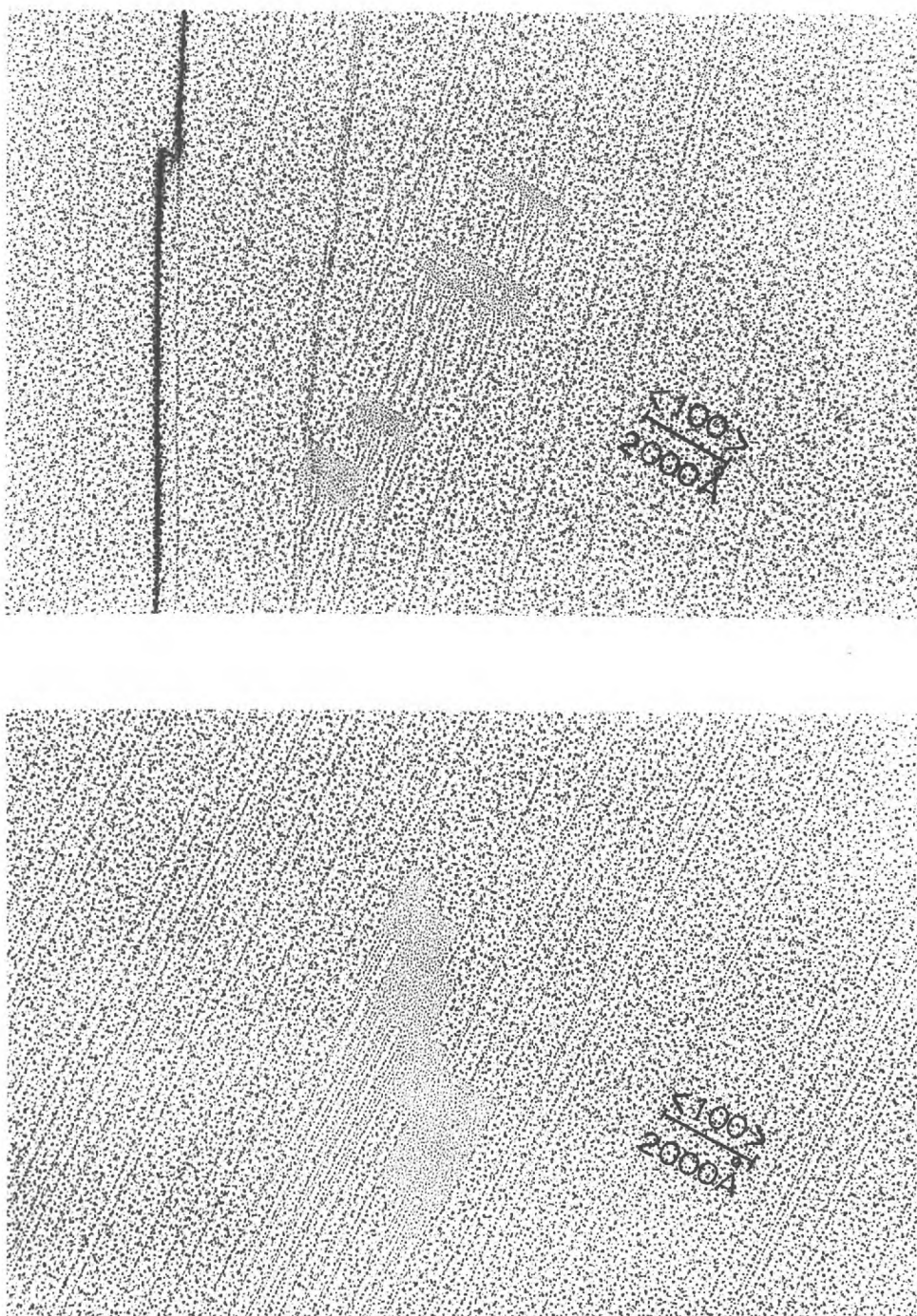


Fig. 4.16. Showing groups of oblong precipitates in MnCl_2 doped (600 ppm.) NaCl, quenched from 450°C and aged at 235°C for 96 hours.

found as shown in Fig 4.17. Their volume fractions were determined. But due to ^{the} large concentration gradient there was appreciable spread in the precipitate volume and also uncertainty in the Magnesium content. However this data with its probable error is presented in Fig 4.18.

Sample containing about 300 mol ppm MgCl_2 was quenched from 150°C , 200°C , 250°C , 275°C , 300°C , 325°C , 350°C and 400°C . The precipitates were found to go in solution between 325°C and 350°C .

4.4. CaCl_2 doped NaCl :-

CaCl_2 doped crystals were examined at concentrations of 450 mol ppm, 1000 mol ppm, 2000 mol ppm, 3000 mol ppm and 10,000 mol ppm. Precipitates were not found in crystals containing upto 2000 mol ppm CaCl_2 . In the crystals containing about 3000 mol ppm CaCl_2 , precipitates were found on the sub-boundaries as shown in Fig 4.19. These precipitates presented a linear section in the $\langle 110 \rangle$ directions on the $\{100\}$ cleavage plane of the NaCl matrix.

In the crystal containing 10,000 mol ppm CaCl_2 (which was milky white in appearance) precipitates were found to be distributed over the whole area of the cleaved

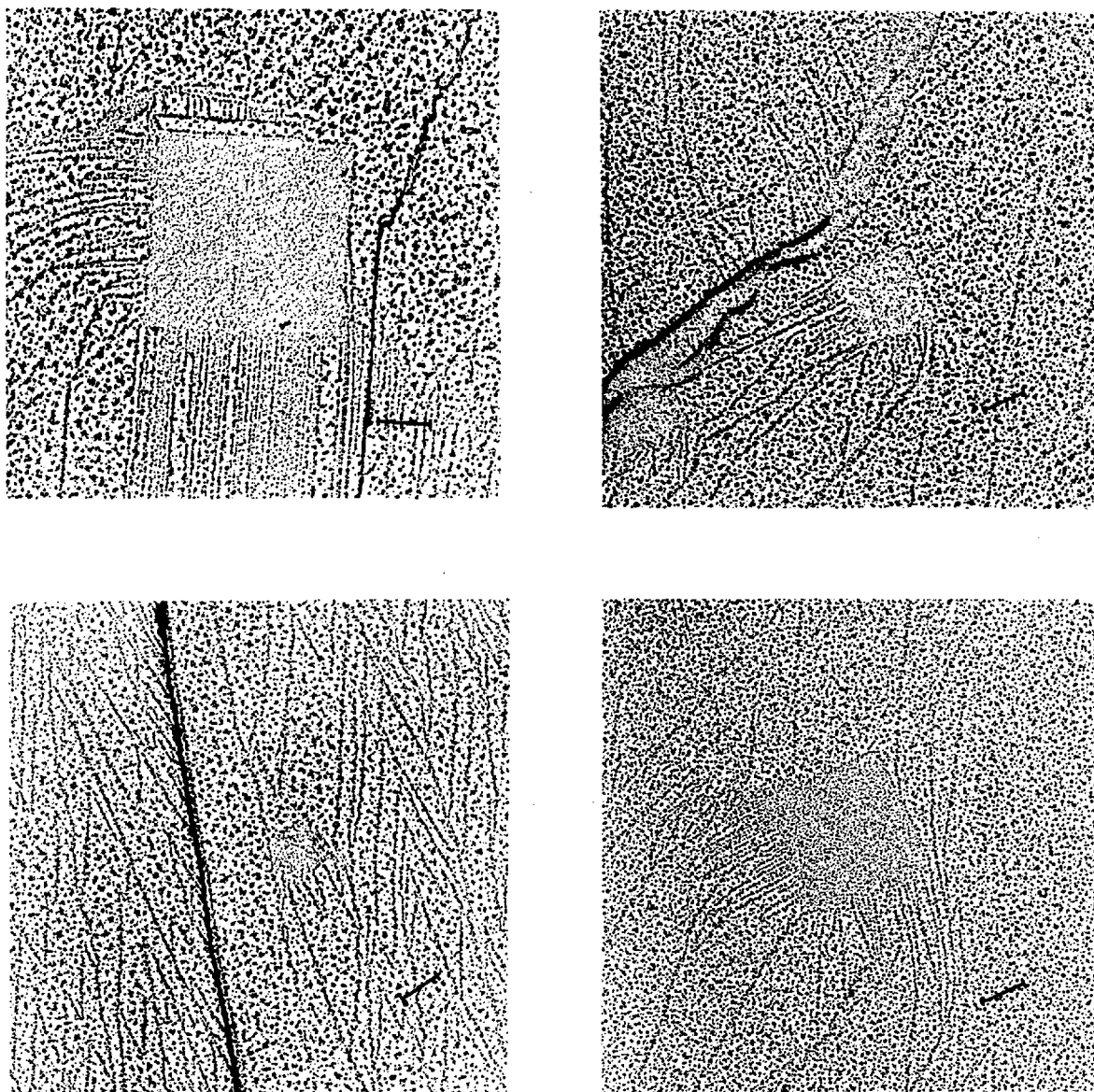


Fig. 4.17. Showing precipitates with square sections in the (100) plane of MgCl_2 doped (200 - 1000 mol. pp NaCl. (Markers, 1000 Å along $\langle 100 \rangle$.)

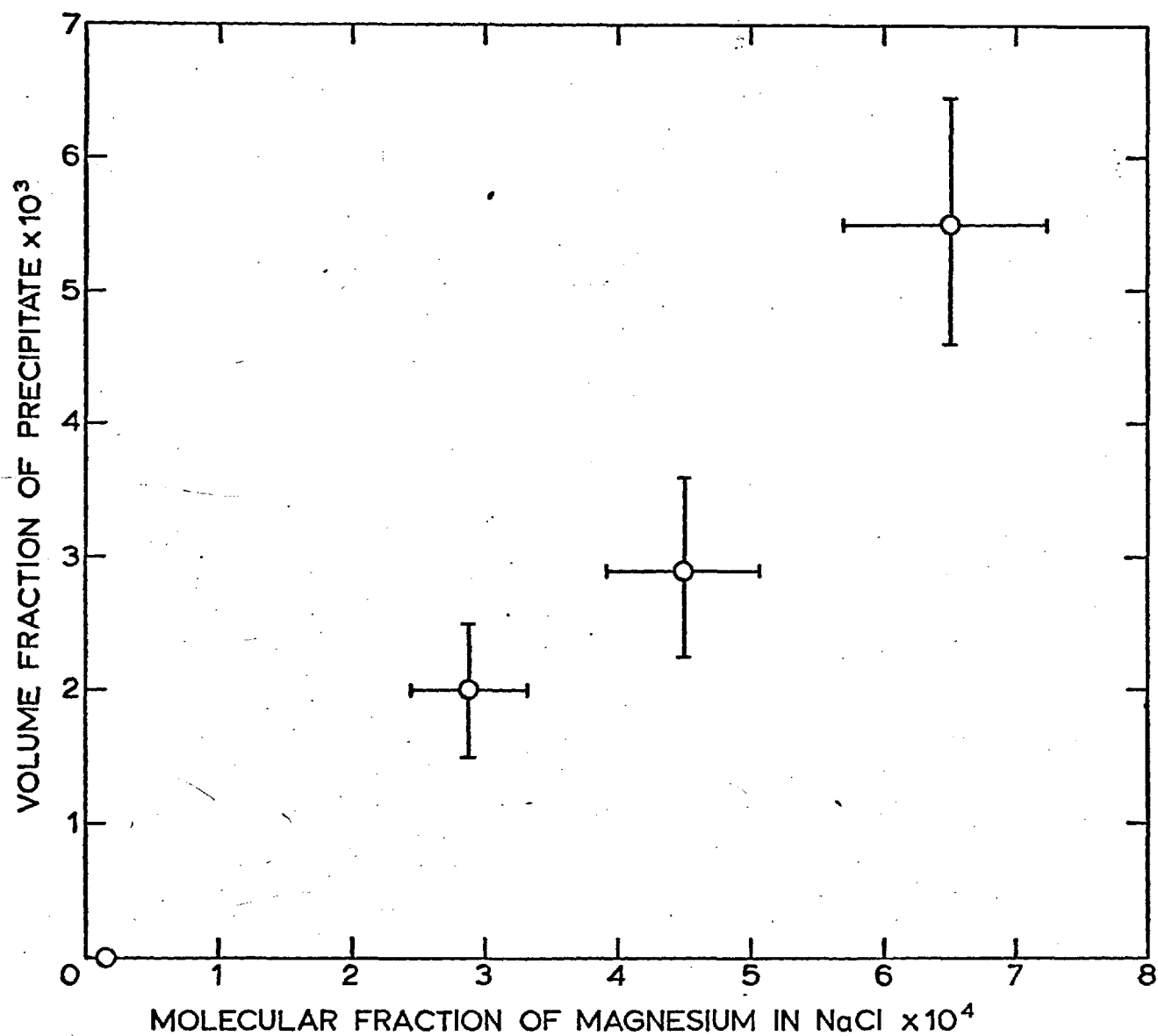


Fig.4.18 The volume fraction of precipitates as a function of MgCl_2 concentration.



Fig. 4.19. Etched and shadowed replica of the (100) face of CaCl_2 doped (~ 3000 mol. ppm.) NaCl , showing platelet precipitates along a sub-boundary.

surface. Number of precipitates per sq.cm. was about 5×10^5 . The precipitates were of two sizes. One thin and short and ^{the} other thicker and larger as shown in Fig 4.20.

The crystal was raised to different temperatures and quenched to room temperature. The number of precipitates as a function of quenching temperature is shown in Fig 4.21. The thinner precipitates disappeared in the temperature between 175°C to 200°C . The larger precipitates went into solution slowly and disappeared around 450°C .

4.5. BaCl_2 doped NaCl :-

BaCl_2 doped crystals were examined in two concentrations, containing about 10 mol ppm and 50 mol ppm BaCl_2 . Precipitates were found in both crystals. The precipitates cut the (100) plane of the matrix in the $\langle 110 \rangle$ and $\langle 520 \rangle$ directions shown in Fig 4.22. The sections in the $\langle 110 \rangle$ directions were fewer than those in the $\langle 520 \rangle$ directions. But the sections in the $\langle 110 \rangle$ directions when they occurred were about 5 to 10 times longer than the sections in the $\langle 520 \rangle$ directions.

The (110) plane of the NaCl matrix was also

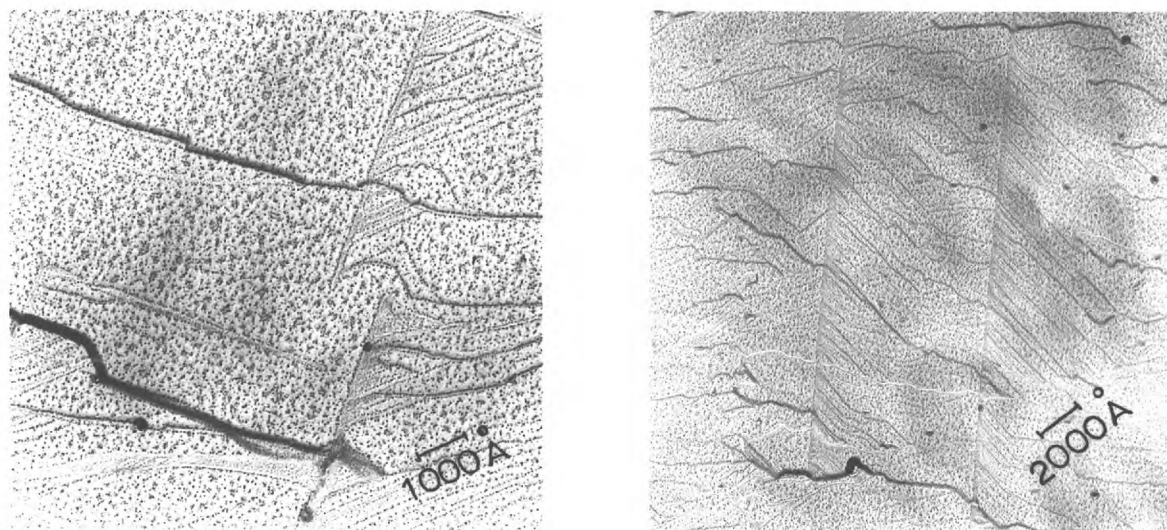


Fig. 4.20 (a). Gold decoration replica of CaCl_2 doped (1 mol.%) NaCl , showing precipitate sections along $\langle 110 \rangle$ directions in the (100) plane.

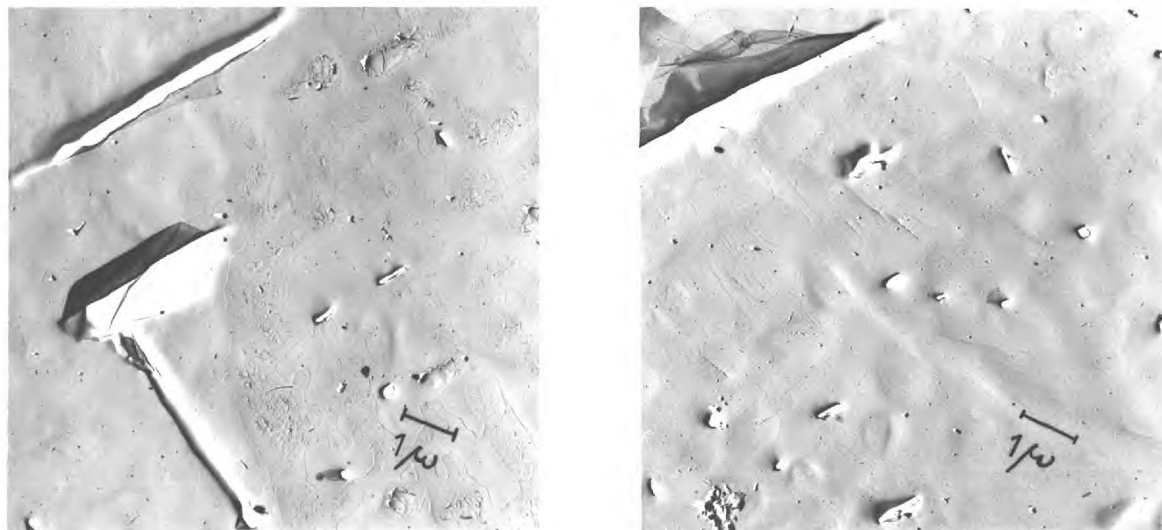


Fig. 4.20 (b). Etched and shadowed replica of CaCl_2 doped (1 mol.%) NaCl , showing two sizes of precipitates.

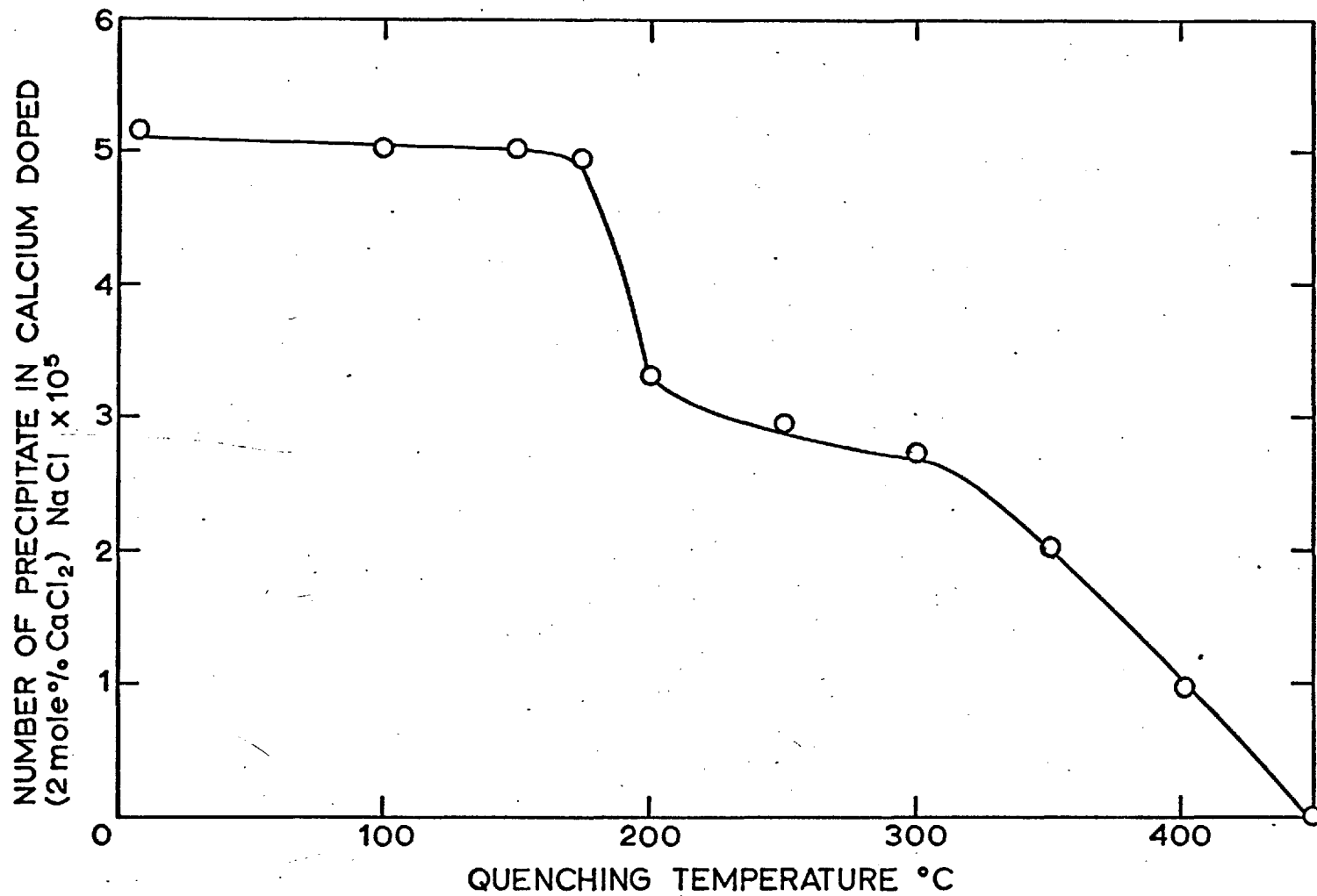


Fig.4.21. The number of precipitates in CaCl_2 doped (1 mole%) NaCl as a function of quenching temperature.

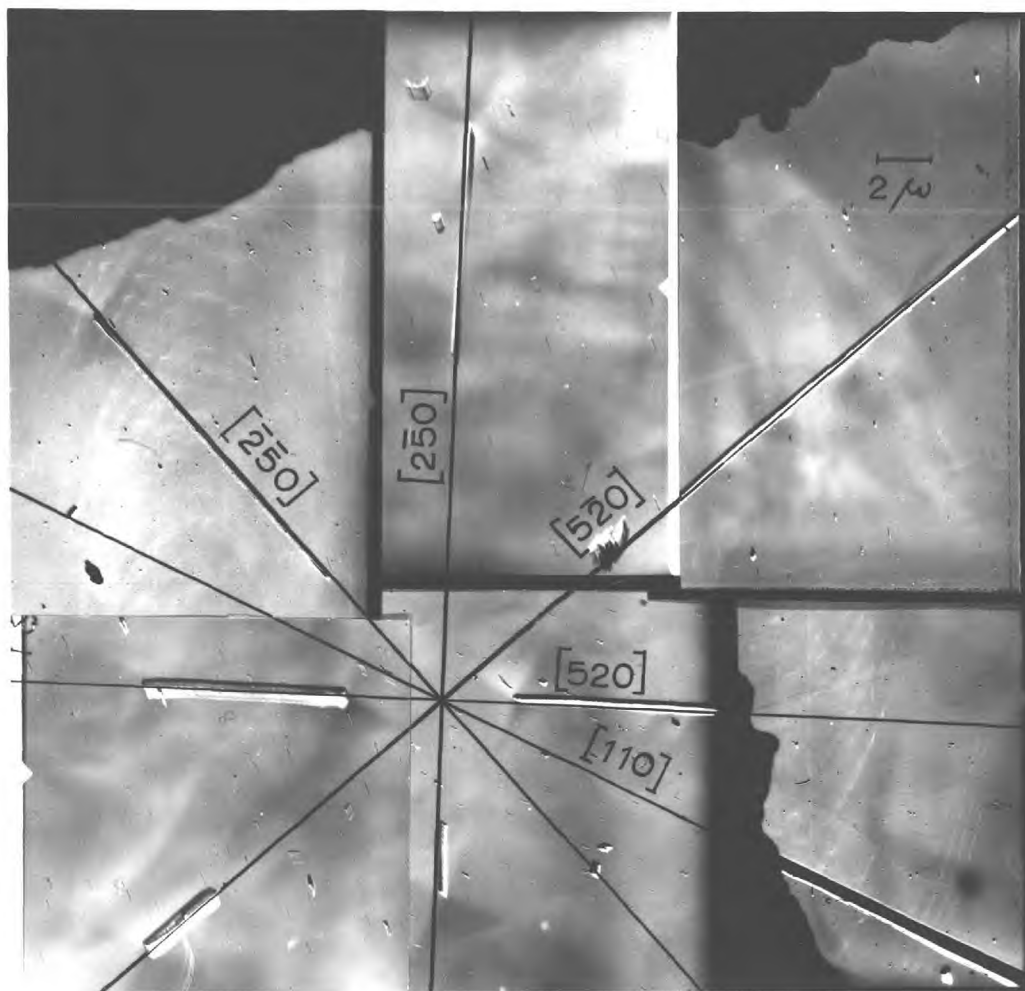


Fig. 4.22(a). Etched and shadowed replica of the (001) face of BaCl_2 doped NaCl , showing precipitate sections along $\langle 110 \rangle$ and $\langle 520 \rangle$ directions.

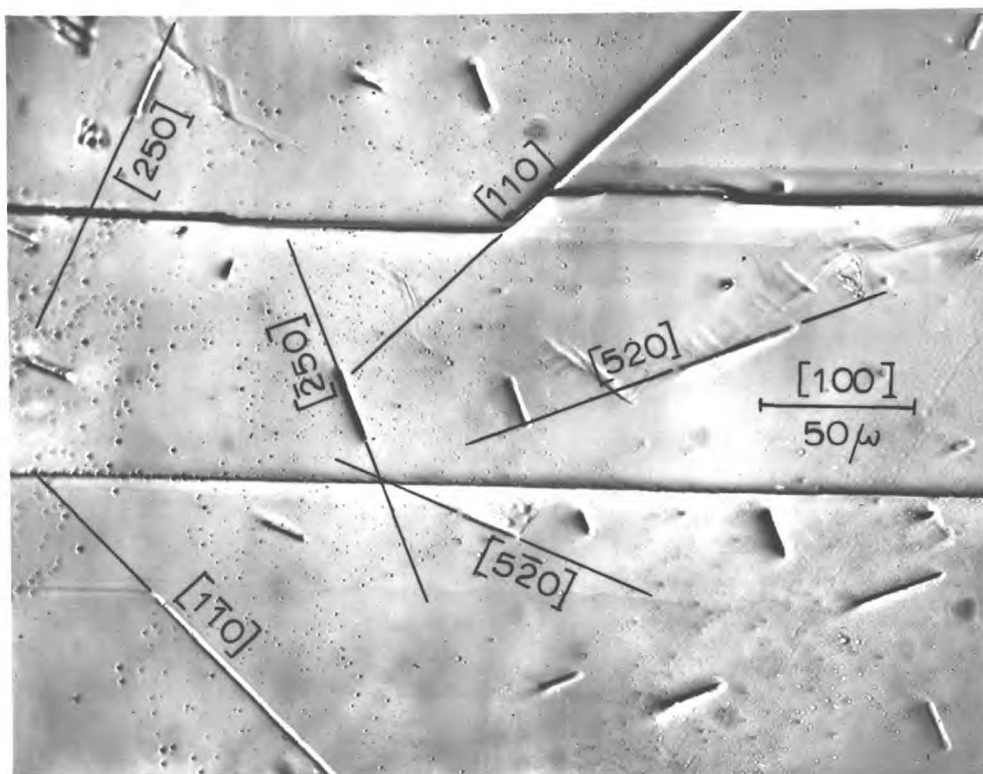


Fig. 4.22 (b). Optical micrograph of the (001) face of BaCl₂ doped (~50 mol.ppm.) NaCl, showing precipitate sections along $\langle 110 \rangle$ and $\langle 520 \rangle$ directions.

examined. The precipitates were found to cut the (110) matrix plane in $\langle 110 \rangle$, $\langle 223 \rangle$, $\langle 227 \rangle$, and $\langle 554 \rangle$ directions shown in Fig 4.23. Again the sections in $\langle 110 \rangle$ directions were fewer and larger than the sections in the other directions. When the crystal was observed under optical microscope in transmitted light the projections of the precipitates on the (100) plane were found to lie in the $\langle 100 \rangle$ and $\langle 110 \rangle$ directions, and their ends were tapered as shown in Fig 4.24.

The crystal containing 50 mol ppm BaCl_2 were heated to progressively higher temperatures and air quenched and examined. The precipitates were found to go into solution between the temperature range of 500°C to 600°C as shown in Fig 4.25.

4.6. ZnCl_2 doped NaCl :-

ZnCl_2 doping of NaCl was carried out by Dr. L. W. Barr of A.E.R.E. Harwell, by diffusion method. NaCl crystals were kept at 700°C in ^{the} presence of saturated vapour of ZnCl_2 over a period of a week. Estimated concentration of ZnCl_2 was about 200 mol ppm. But on examination no precipitates could be found in these crystals. Gold decoration replica showed the presence of voids or gas bubbles

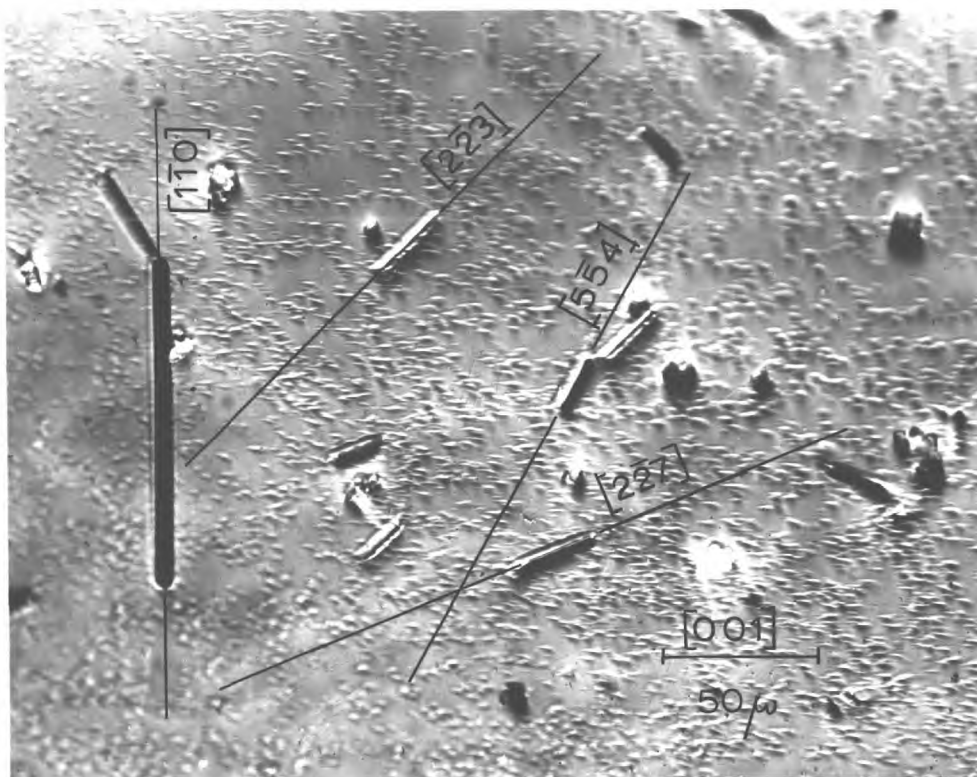


Fig. 4.23. Optical micrograph of the (110) face of BaCl₂ doped (~50 mol. ppm.) NaCl, showing the precipitate sections along $\langle 110 \rangle$, $\langle 223 \rangle$, $\langle 227 \rangle$ and $\langle 554 \rangle$ directions.

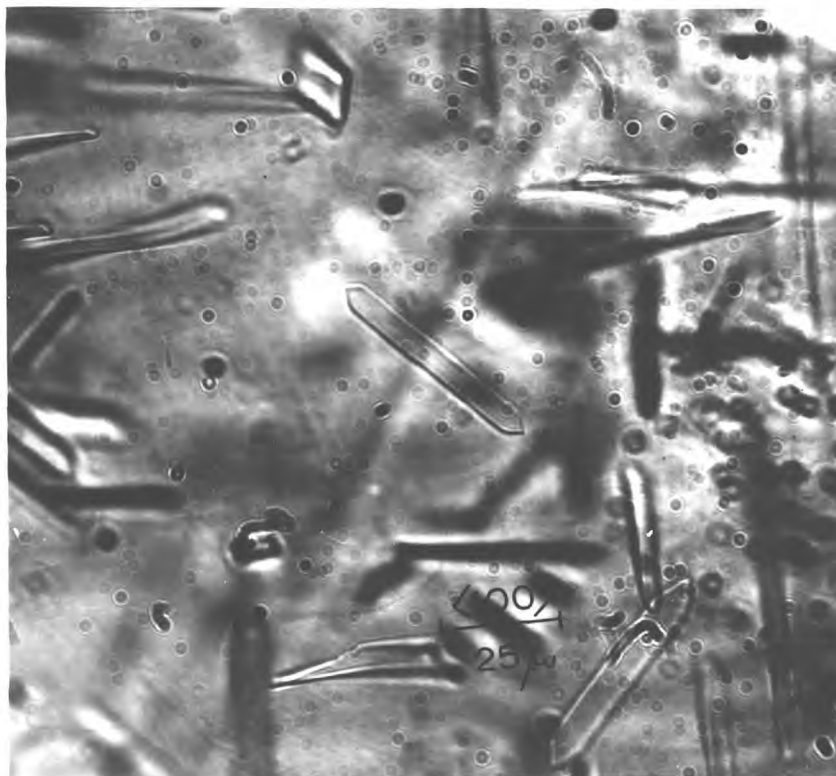


Fig. 4.24. Transmitted light micrograph of the precipitates in BaCl_2 doped (~ 50 ppm.) NaCl , showing the projections of the precipitates along $\langle 100 \rangle$ and $\langle 110 \rangle$ directions on the (100) plane.

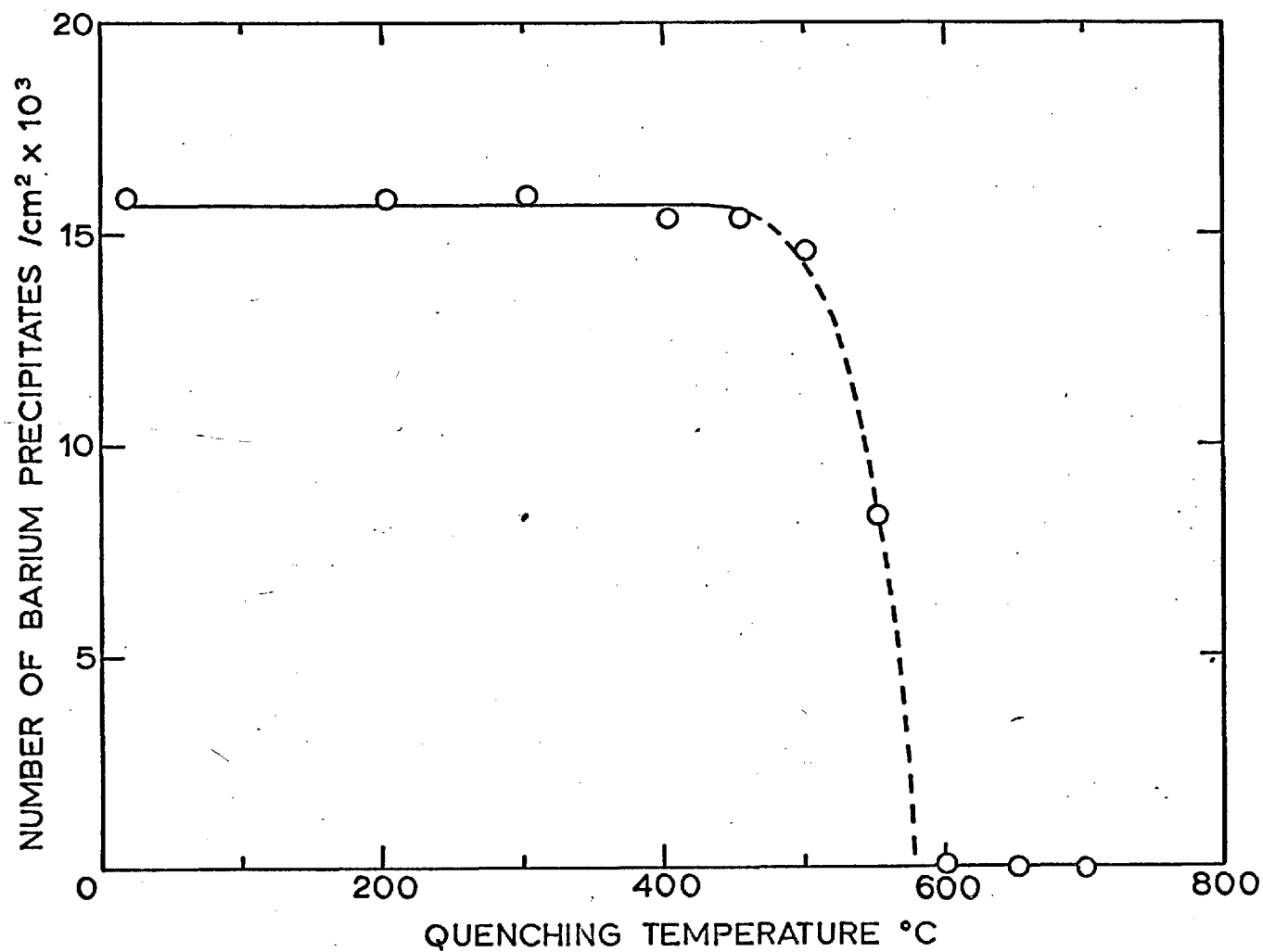


Fig.4.25. Number of precipitates in slowly cooled BaCl_2 doped NaCl as a function of subsequent quenching temperature.

in the crystals as shown in Fig 4.26. Dr Barr suggested that this may be due to NH_4Cl vapour introduced during the diffusion process. NH_4Cl was used to stop the formation of layer of Zinc Oxichloride on the surface of the crystal which prevents further diffusion of zinc into the crystal. But as our crystals were grown in air, it contained some OH^- . NH_4Cl reacted with OH^- and liberated gases which formed into bubbles.

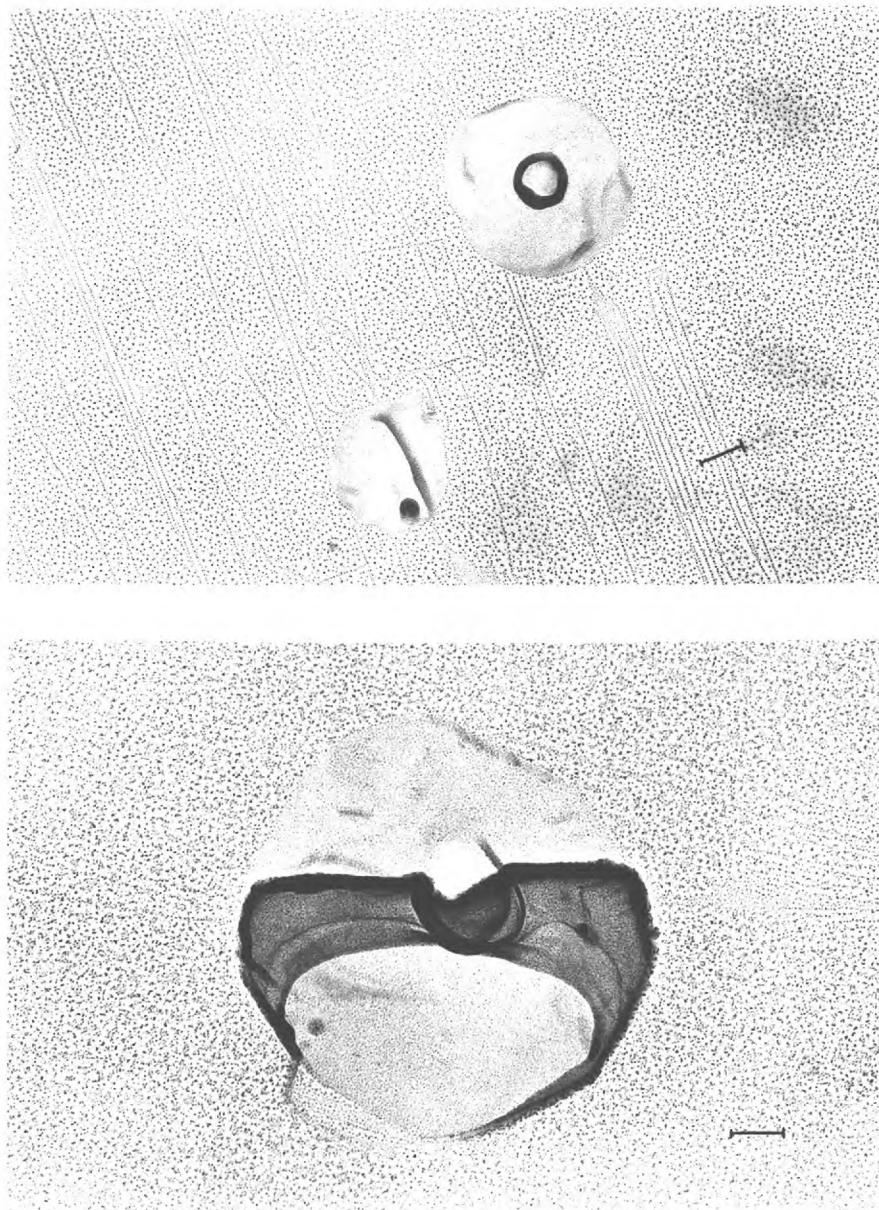


Fig. 4.26. Gold decoration replica showing 'voids' in the ZnCl_2 doped NaCl crystals. Doping was carried out by diffusion technique, in the presence of NH_4Cl vapour. (Markers, $1000 \text{ \AA}$ along $\langle 100 \rangle$.)

CHAPTER V

DISCUSSION OF THE OBSERVATIONS IN DOPED NaCl

5.1. Surface Decoration Phenomena:

Condensation of a vapour on to a substrate in general follows a nucleation and growth process. If there are preferential sites for nucleation or if there are areas where nucleation is different from rest of the substrate then these sites and areas can be made conspicuous by controlled condensation of a suitable substance.

Bassett (1958) first noted, in connection with epitaxial growth of gold on NaCl, that during the early stages of deposition there were higher density of nucleation along the molecular steps on the surface and even the presence of a monomolecular step can be made readily visible by this process as shown in Fig 5.1. This increased density of nucleation along the monomolecular steps have been used by several workers (Bethge, 1962; Schmidt, Bethge, Schutz and Keller 1964; Robins, Rhodin and Gerlach 1966) for studying the thermal etching of a cleaved surface, slip steps on the surface due to deformation, steps on the surface due to emergence of screw dislocations.

Nucleation process has been investigated theoretically by Rhodin & Walton (1964) and also by Hruska and Pound (1965). Rhodin & Walton derived an equation for the rate of nucleation

$$I = Ra^2 N(R/\gamma N)^n \exp \left[\frac{\{ (n+1)Q_{ad} + E_n - Q_D \}}{kT} \right] \dots\dots 5.1$$

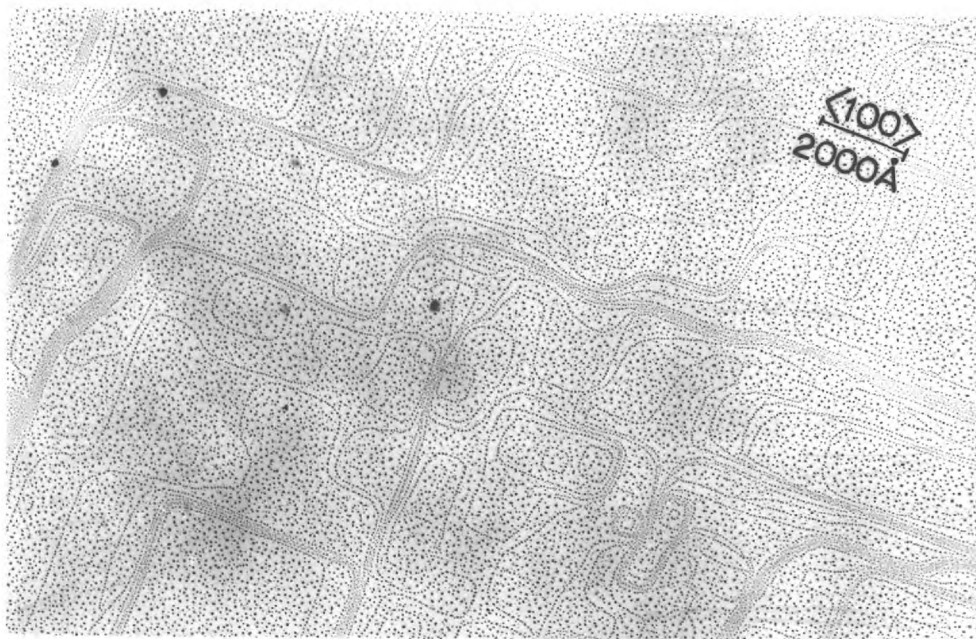
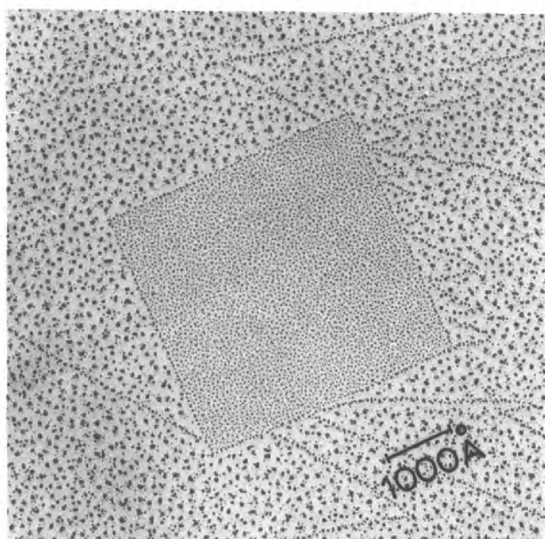
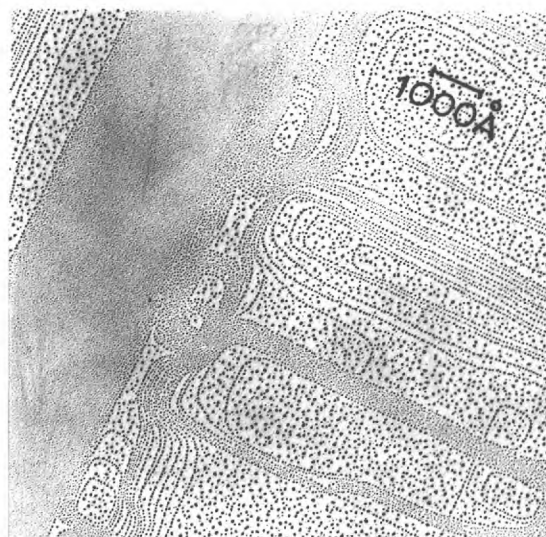


Fig. 5.1. Gold decoration replica of a thermally etched surface of NaCl, showing higher density of nuclei along the surface steps.



(A)



(B)

Fig. 5.2. Gold decoration replica showing higher density of nuclei on (A) the precipitate face; (B) the high index plane.

I = nucleation frequency

R = incidence rate of atoms of the decorating materials

a = distance between adsorption sites

N = density of adsorption sites

ν = vibrational frequency of adsorbed atoms

n = number of atoms in the critical nucleus

Q_{ad} = heat of adsorption of adsorbed atom

E_n = Energy of dissociation of critical nucleus

Q_D = Activation energy of surface diffusion

Hruska and Pound also arrived at essentially a similar equation for the rate of nucleation. However these equations do not take into account the effect of the stable nuclei present on the substrate and are therefore appropriate for only the initial stages of nucleation where the number of existing nuclei is negligible. With the progress of nucleation a situation is soon reached when the probability of an deposited atom contributing towards the formation of a new nucleus becomes very small compared to its probability to run into any of the existing nuclei. Further nucleation then practically stops and the existing nuclei grow in size. A virtual steady state is reached where by the net number of atoms arriving at the surface (number adsorbed less the number desorbed) is equal to the number of atoms

received by the growing nuclei. 'Surface decoration' corresponds to this stage in the deposition process.

The density of nuclei D_s at this stage can be given by the following relation :

$$D_s \simeq \frac{R_n}{2KC\sigma_s a \gamma} \exp (Q_D/KT) \dots\dots\dots 5.2$$

where R_n is the rate of net arrival of atoms on the substrate.

C is the 'equilibrium' concentration of atoms on the substrate.

σ_s is the average capture radius of the nuclei at the onset of the 'steady state'.

a is the distance between the adsorption sites.

γ is the vibrational frequency of the adsorbed atom.

K is a geometric factor whose value is about 4 for the cube face of NaCl structure.

Q_D is the activation energy of surface diffusion of the adsorbed atom.

Derivation of the eq 5.2 is given in Appendix I

It is to be noted however, that a complete steady state is never reached because there is always a finite probability for the formation of a new nucleus. The capture radius of the nuclei also increases as they grow. And the residual gas molecules present in a normally attained vacuum slowly contaminate the substrate and in

effect increase Q_D with time. In a good vacuum the rate of contamination can be kept sufficiently low, so that its effect is negligible for a reasonable rate of deposition.

An inspection of eq.5.2 shows that D_s increases with R_n and Q_D and decreases with the increase of substrate temperature T .

5.1.1. Decoration of a step on the substrate :-

In the case of a step on the substrate, the atoms arriving there from both sides find the foot of the step a more stable site and they are effectively trapped along the length of the step. The number of atoms arriving at the step is much higher than the number leaving the step so that R_n for the step is higher than the R_n for the surrounding flat area. Also the restriction on the movement of atoms at the step is equivalent to decreasing the geometric factor K from 4 to 2. So there is an increased density of nuclei along the step and a denuded zone on both sides comparable in width to the mean free path of the atoms in the plane.

5.1.2. Decoration of a precipitate face :-

In the case of an area where Q_D is different from the Q_D in its surrounding area the density of the nuclei will also be different. Referring to the $CdCl_2 \cdot 6NaCl$

structure in Fig 5.9 it can be seen that the $\{100\}$ planes of the precipitate contain vacancies and Cd^{2+} ions in addition to Na^+ and Cl^- ions. The potential distribution on this face is therefore much more rugged than on the $\{100\}$ face of NaCl, the vacancies acting as deeper sites so that more activation is necessary for surface diffusion to take place, consequently Q_D is higher. So the density of nuclei is also higher than that on the NaCl matrix as shown in Fig. 5.2(A). . A similar consideration also applies to a close succession of monomolecular steps which is equivalent to a high index plane and a higher density of nuclei is expected as in Fig 5.2(B).

5.2. Precipitation in slowly cooled Solid Solutions :-

The theory of precipitation in binary systems with a wide miscibility gap, when cooled at a constant rate from above solution temperature, has been developed by Tappe & Kahlweit (1961) and Kahlweit (1965). The process can be explained with reference to Fig 5.3 where the logarithm of the concentration of the solute has been plotted against $1/T$ and the saturation concentration at any temperature C_s has been indicated as a dashed line. If C_0 is the concentration of the solute then as the system is cooled below T_0 where $C_0 = C_s(T_0)$, supersaturation starts to

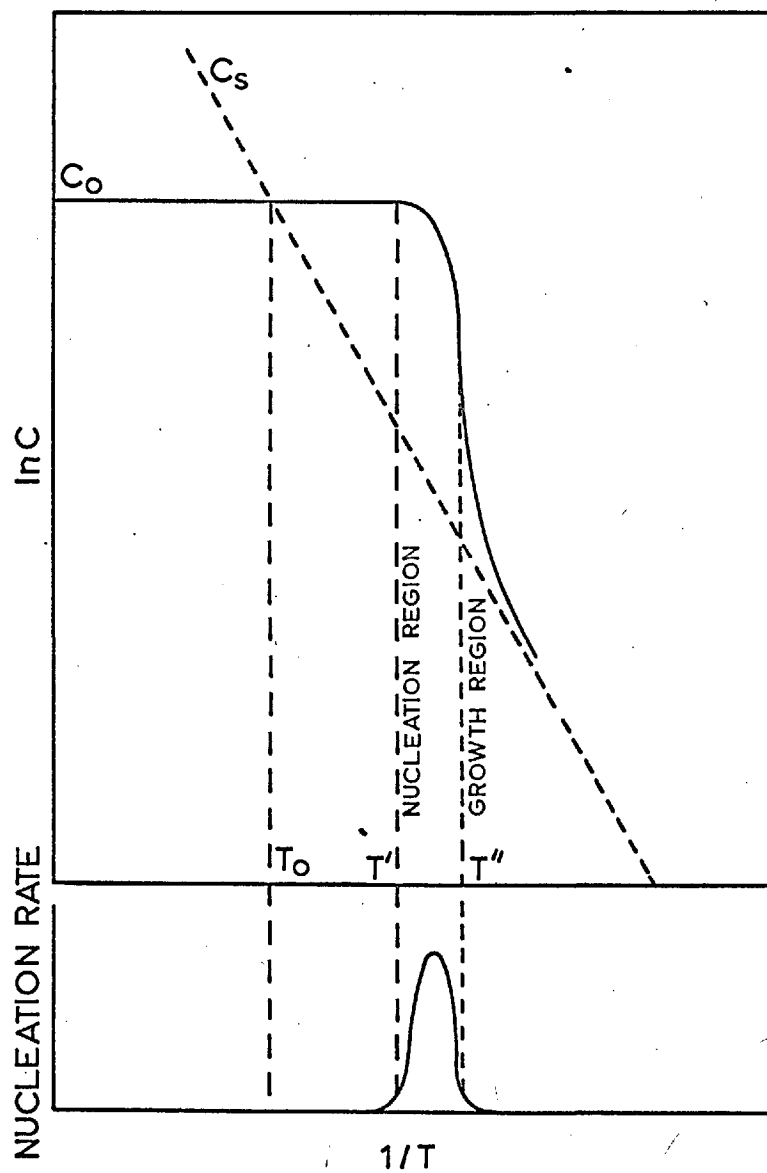


Fig.5.3. Schematic diagram corresponding to the precipitation in a binary system cooled at a constant rate.

build up until a temperature T' is reached where the rate of nucleation becomes appreciable. From then on solute is removed from the system by precipitation. As cooling continues the precipitation becomes so fast that the concentration decreases faster than the saturation build up due to cooling until the nucleation becomes negligible at T'' .

For the case where the cooling rate is slow compared to the nucleation period, the above authors derived an equation for the density of precipitates. The number of precipitate 'Z' per unit volume of the parent phase is given by the relation

$$Z = \frac{1.13 C_0 \left(- \frac{d \ln C_S}{dT} \right)_{T_0} \bar{V}^{2/3}}{4/3 \bar{V}^{1/3} [2D(C_0 - C_S)]^{3/2}} \left(- \frac{d \ln J}{d \ln C} \right)^{1/2} \dots 5.3$$

where $\bar{V}$ is the rate of cooling

$\bar{V}$ is the molar volume of the parent phase

D and C_S are the diffusion rate and saturation concentration at the temperature of maximum nucleation.

J is the nucleation rate given by the relation

$$J = A \exp(-W_D/KT) \exp \left[-B/KT \left(-\frac{T}{T_0 - T} \right)^2 \right]$$

where W_D is the activation energy of diffusion of the solute and B is the energy associated with the

formation of a nucleus.

The symbols $\left| T_0 \right|$ and $\left| \overline{\Pi} \right|$ means at the temperature T_0 and at the supersaturation $\overline{\Pi}$ of the nucleation region.

Without going into further details we can examine the qualitative features of the eq. 5.3.

It can be seen that for the same solute concentration C_0 , the number of precipitates per unit volume increases with the cooling rate so that

$$\frac{Z_2}{Z_1} \approx \left(\frac{T_2}{T_1} \right)^{3/2} \dots \dots \dots 5.4$$

The relation between the number of precipitates per unit volume for the same cooling rate but different solute concentration can be found if we make the following simplifying assumptions. That for a small difference in the solute concentration, $(C_0 - C_s)$, $\left. \frac{dC_s}{dT} \right|_{T_0}$ and $\left(\frac{d \ln J}{d \ln C} \right)^{\frac{1}{2}}$ remains unchanged. The first assumption means that the supersaturation at which the maximum nucleation occurs, remains constant for small variation in C_0 . The second and third assumptions mean that a small segment of the solvus curve and $\ln J / \ln C$ can be approximated as a straight line. As both the curves are smooth and monotonic, the assumptions are felt, not unjustified.

We then have

$$\frac{Z_2}{Z_1} = \left(\frac{C_{O1}}{C_{O2}} \right)^{\frac{1}{2}} \left(\frac{D_1}{D_2} \right)^{3/2} \left[\because \frac{d \ln C_s}{dT} \Big|_{T_0} = \left(\frac{1}{C_0} \right) \frac{dC_s}{dT} \Big|_{T_0} \right]$$

$$\text{or } \frac{Z_2}{Z_1} \approx \left(\frac{C_{O1}}{C_{O2}} \right)^{\frac{1}{2}} \exp \frac{3W_D}{2kT} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \dots\dots\dots 5.5$$

where T_2 and T_1 correspond to the temperature at which maximum nucleation occurs and W_D is the activation energy of diffusion.

From eq. 5.5. it can be seen that with the increase in the solute concentration and consequent increase in the nucleation temperature the number of precipitates per unit volume of the parent phase decreases.

5.2.1. Experimental observations of the density of precipitates :-

Different cooling rate -

Two different cooling rates were used for crystal containing 950 mol ppm CdCl_2 . The cooling rates were 6.25° per minute and 1.5° per minute. Corresponding numbers of precipitates per cubic cm. were 9.3×10^{10} and 1.1×10^{12} as shown in Table 4.1. The ratio of the numbers was 11.8 as compared to the expected ratio of

$$(1.5/0.25)^{3/2} = 14.7.$$

Different concentration of the solute :

Number of precipitates per cubic cm. in crystals containing different amount of CdCl_2 and MnCl_2 is shown in Table 4.2. The number of precipitates in this case could not be checked directly with the expected values due to lack of knowledge about the temperatures of maximum nucleation and the relevant activation energy of diffusion. However, the experimental variation in the number of precipitates was in the right direction, and also of the right magnitude, if we assume that the difference in the nucleation temperature is similar to that in the solution temperature and W_D is of the order of 1 eV.

5.3. CdCl₂ doped NaCl :-

5.3.1. Precipitate structure and shape :-

The sections of the precipitates in the slowly cooled crystals were always found to be square in shape (except those decorating sub-boundaries, which were in general oblong). The edges of the precipitate sections lay along the $\langle 100 \rangle$ directions of the NaCl matrix. Some precipitates found at large cleavage steps continued on both sides of the step, Fig 5.4. which showed that the precipitate had a thickness larger than the height of the step. Also in the etched and shadowed replicas the precipitates show a depth. Fig 5.6. As the sections of the precipitates were square, the only conclusion that is consistent with these findings is that the precipitate themselves are cubic in shape as shown in Fig 5.7.

Crystals quenched from the region of solution temperature showed that some of the precipitate sections have octagonal shape, Fig 4.8 . The cause of the octagonal shape was revealed as follows. When the freshly cleaved surface is wetted with ether, the precipitate phase, being more soluble in ether, is partly dissolved and when the ether evaporates off, solute is redeposited near the pit, Fig (5.8). The amount of deposition gave an indication

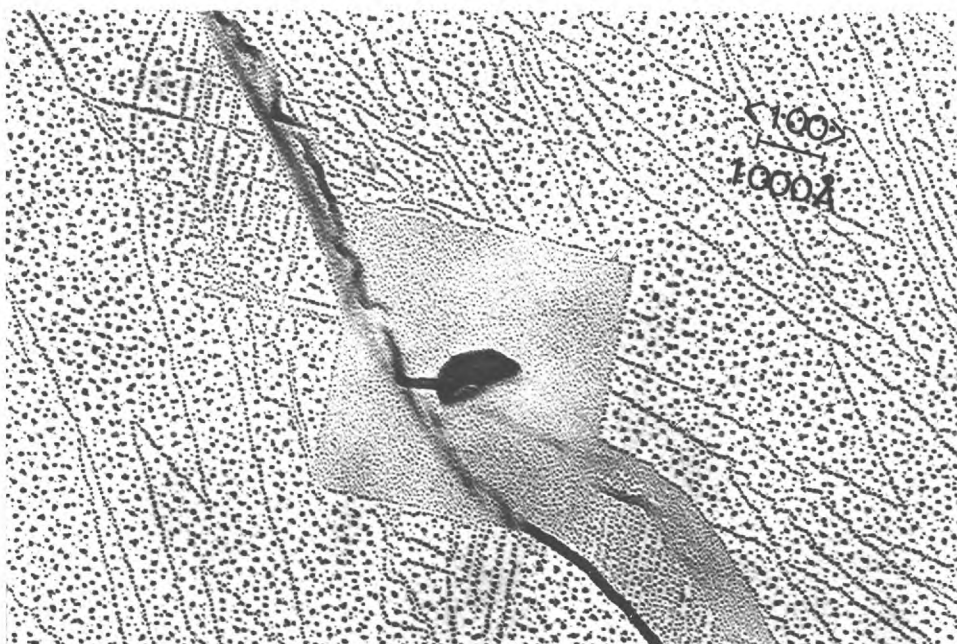


Fig. 5.4. Showing a precipitate on both sides of a large cleavage step in CdCl_2 doped (950 ppm.) NaCl .

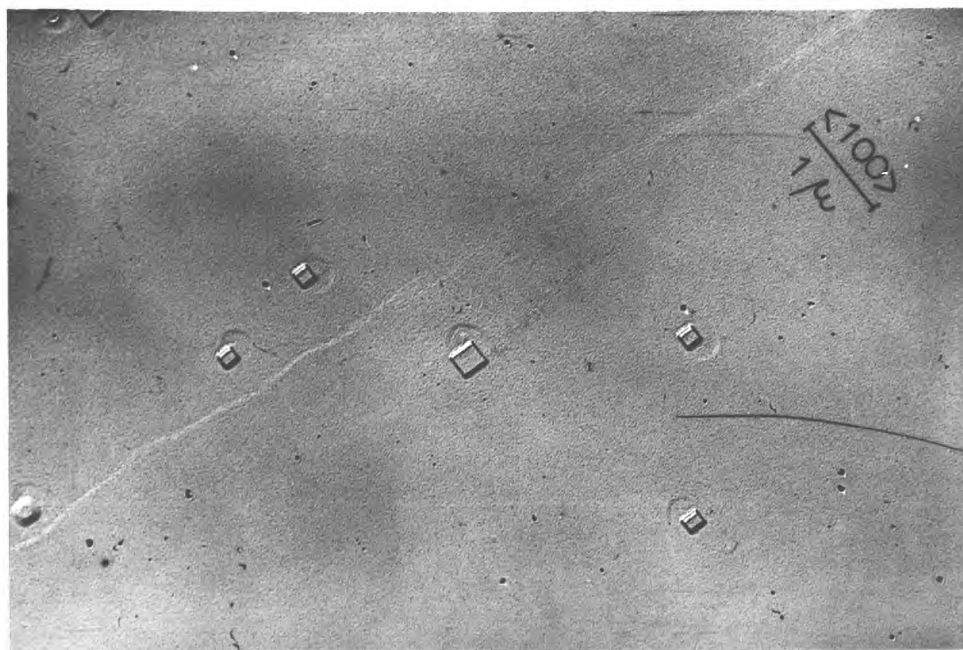


Fig. 5.6. Etched and shadowed replica of CdCl_2 doped (950 ppm.) NaCl , showing that the precipitates have a depth.

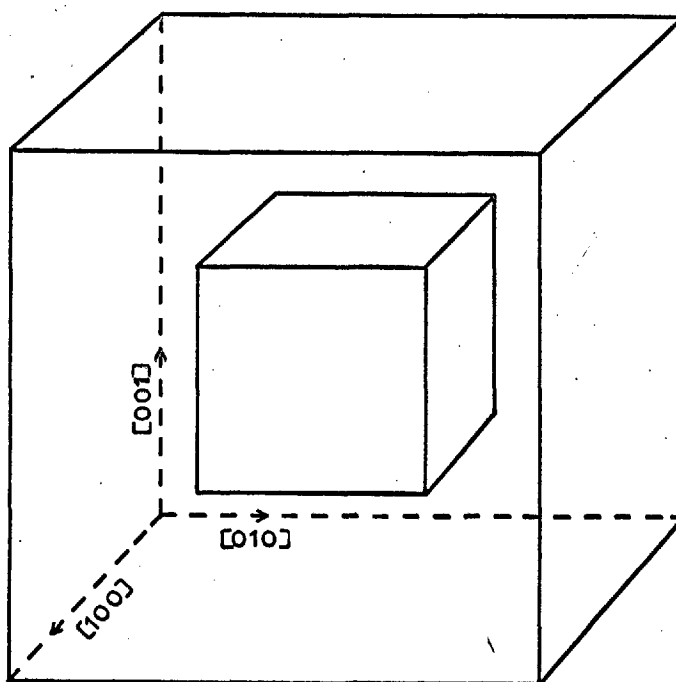


Fig.5.7. Cubic precipitates in CdCl_2 MnCl_2 and MgCl_2 doped NaCl .

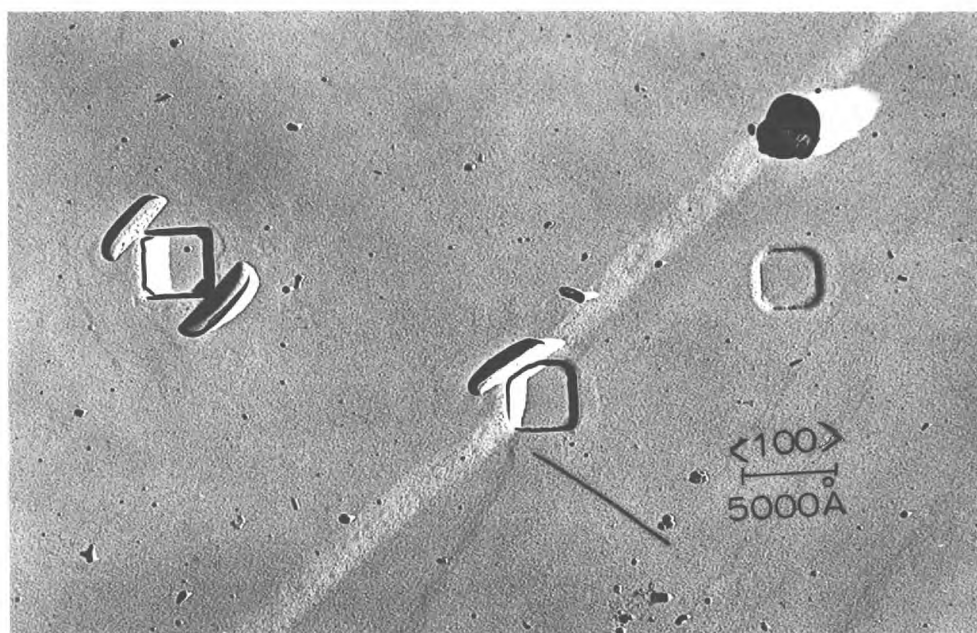


Fig.5.8. Ether etched replica of CdCl₂ doped (950 ppm) NaCl, showing that there is no redeposition near the octagonal sections of the precipitates.

as to the amount of precipitate material that was available for desolution or in other words the depth at which the particular precipitate had been sectioned. The octagonal shaped pits had practically no deposit, showing that these are due to sections very near the ends of the precipitates. The implication is that when the precipitates go into solution in the matrix, the cube corners dissolve faster than the faces and the sections near the ends of the precipitates are then octagonal in shape. Faster dissolution of the corners is understandable in terms of ease of diffusion away from the corners and also reduction of the surface energy.

5.3.2. Shape of the precipitates in quenched and aged crystals :-

The shape of the precipitate sections in quenched and aged crystals was oblong. The precipitates tended to appear in groups as opposed to randomly distributed precipitates in the slowly cooled crystals. The groups of precipitates in the quenched- aged crystals had a tendency to arrange themselves along the general $\langle 110 \rangle$ direction of the matrix.

In the slowly cooled crystals, the oblong shape is typical for the precipitates decorating the sub-boun-

daries, Fig 4.5., which suggests that the precipitates nucleated at dislocations are oblong in shape. This shape change may be due to the stress field of the dislocation and also due to the anisotropy in diffusion introduced by the dislocation.

From the shape and distribution of the precipitates in the quenched and aged crystals, it can be concluded that the nucleation had taken place heterogeneously at quenched-in dislocation loops and helices. Whereas, in slowly cooled crystals, in the absence of sufficient dislocations, the precipitates nucleated homogeneously throughout the crystals.

5.3.3. Structure of the precipitate phase :-

Suzuki (1961) made x-ray studies of precipitates in mixed crystals of NaCl and CdCl_2 . For CdCl_2 concentrations up to 5 mol %, he observed predominant reflections due to a phase which has a structure belonging to space group O_h^F and unit cell dimension twice that of NaCl. He finally identified this phase as $\text{CdCl}_2 \cdot 6\text{NaCl}$. Following Suzuki, Toman (1962) carried out an x-ray analysis of CdCl_2 doped NaCl and confirmed Suzuki's findings. One eighth of the unit cell of the $\text{CdCl}_2 \cdot 6\text{NaCl}$ phase is shown in Fig 5.9, along with the unit cell of NaCl Fig 5.10 and

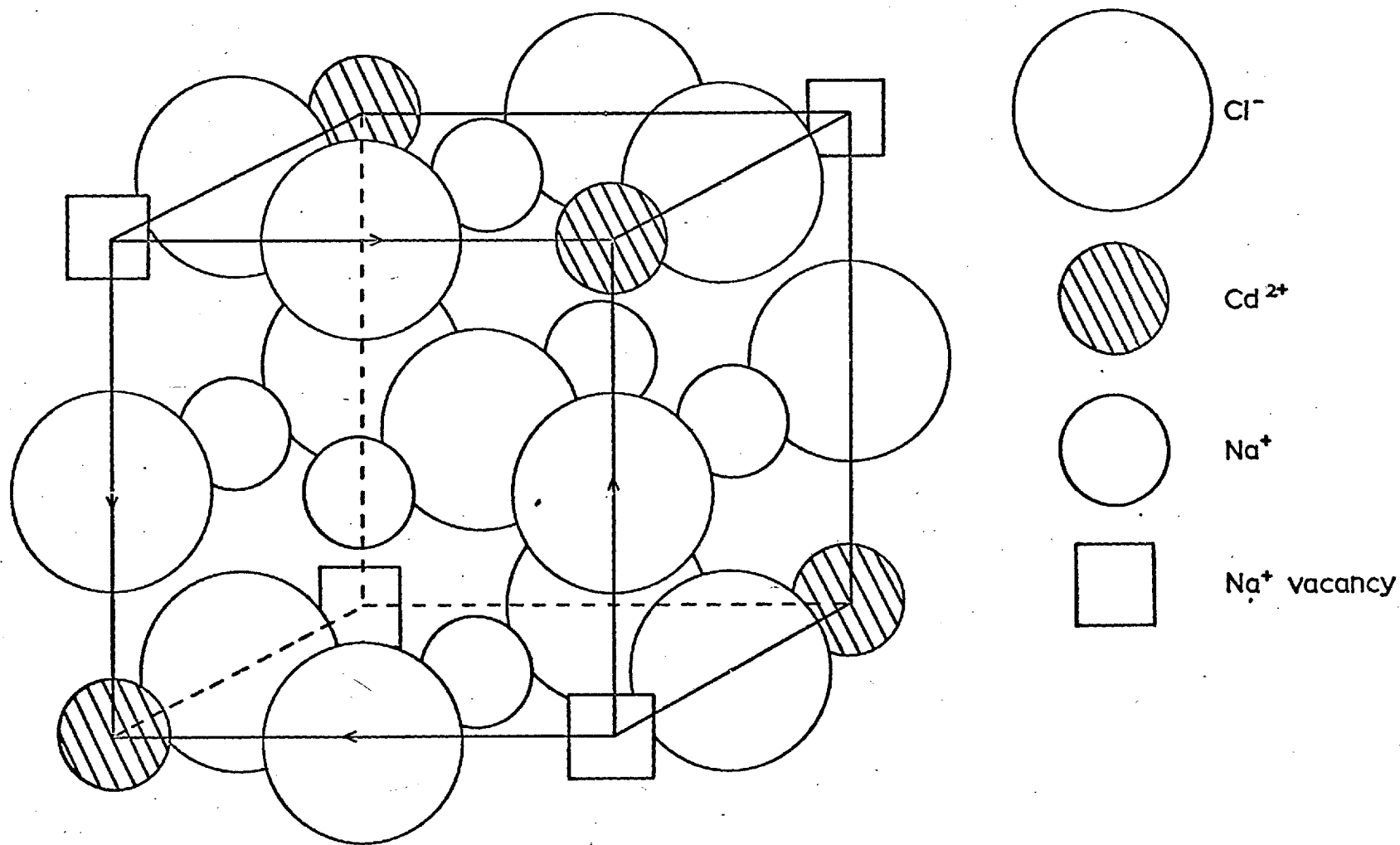


Fig. 5.9. $\frac{1}{8}$ th the unit cell of the $\text{CdCl}_2 \cdot 6\text{NaCl}$ structure

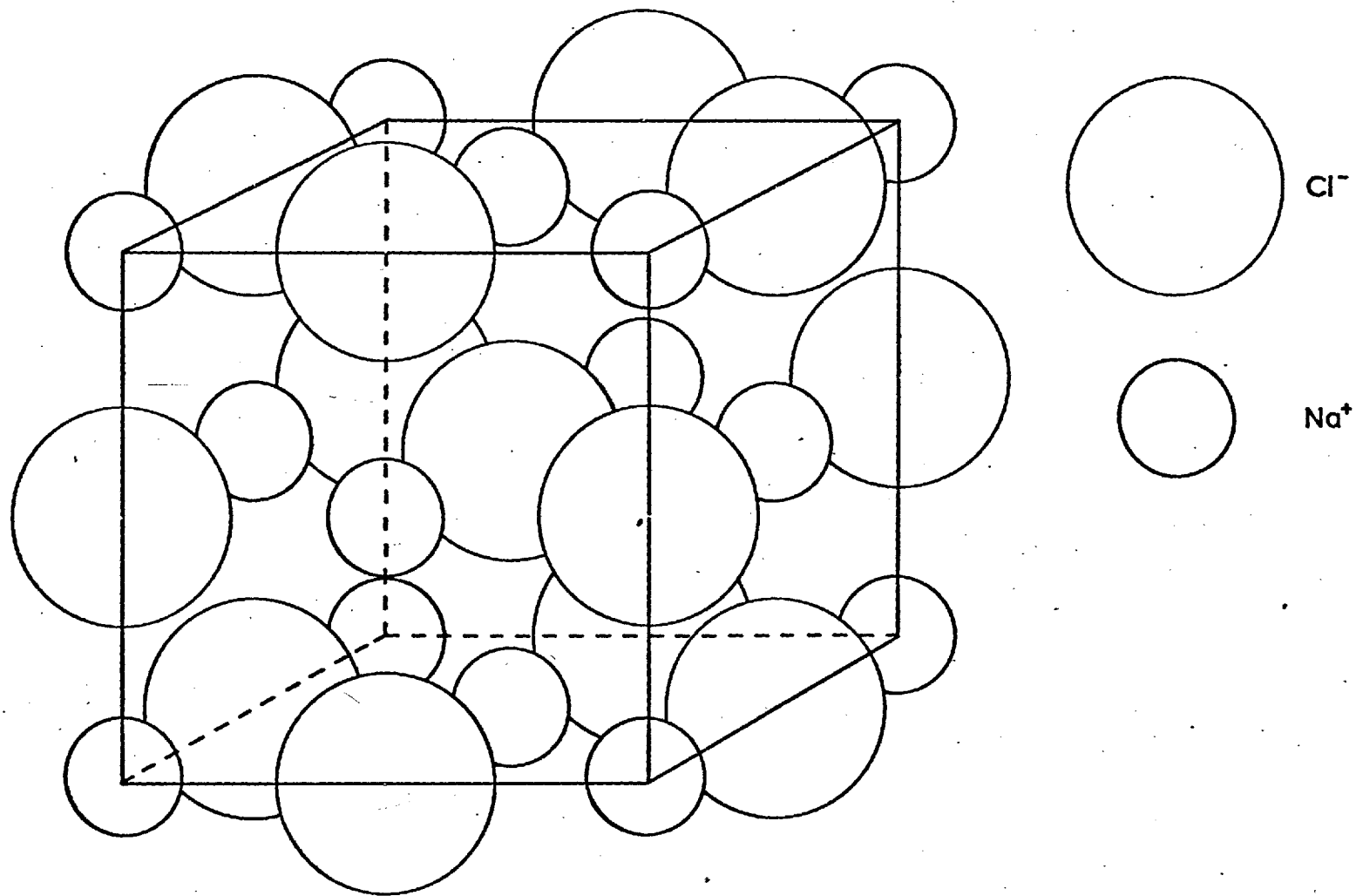


Fig.5.10. Unit cell of NaCl structure.

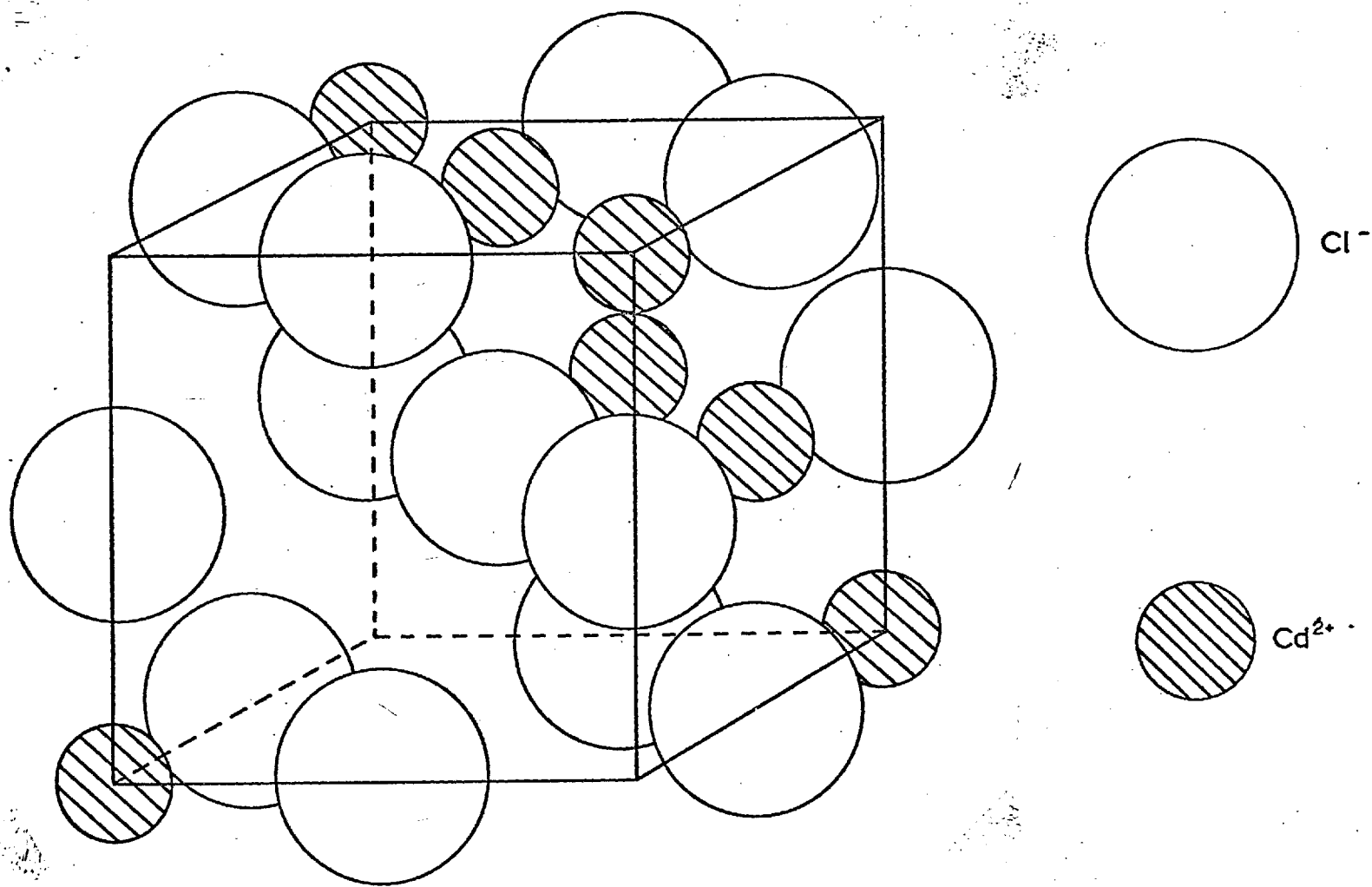


Fig. 5.11. Arrangement of ions in CdCl_2 structure.

the ionic arrangement in the CdCl_2 structure, Fig 5.11.

CdCl_2 is a hexagonal layer structure whose chloride ions are arranged in an F.C.C. lattice and whose cadmium ions are in octahedral positions between alternate closed packed layers of chlorine. The bond between cadmium and chlorine is ionic, and between the chlorine layers is Van der Waals. It can be seen from Figures 5.9 to 5.11, that the structure of the $\text{CdCl}_2 \cdot 6\text{NaCl}$ phase is intermediate between CdCl_2 and NaCl . It is a semi-layer structure in the sense that within the F.C.C. lattice of the Cl^- ions the octahedral sites between alternate close packed planes are now filled with $\frac{2}{3} \text{Na}^+$, $\frac{1}{3} \text{Cd}^{2+}$ and $\frac{2}{3} \text{Na}^+$, $\frac{1}{3}$ Vacancies instead of all Na^+ as in NaCl and Cd^{2+} and "Vacancy" as in CdCl_2 .

The chlorine ions are displaced slightly towards the Cd^{2+} ions which has been indicated by arrows in Fig 5.9. The displacement δ is of the order of $0.014a$ according to Toman (a is the dimension of NaCl unit cell). The unit cell volume of the $\text{CdCl}_2 \cdot 6\text{NaCl}$ is eight times the volume of the unit cell of NaCl and contains 4 Cd^{2+} ions, 24 Na^+ ions, 4 cation vacancies and 32 Cl^- ions as compared to 4 Na^+ and 4 Cl^- ions in NaCl unit cell. The expected volume ratio of the phase and the matrix is therefore eight times the mol fraction of CdCl_2 that has

precipitated out. The straight line fitted to the experimental points for the volume fraction of the precipitate and mole fraction of CdCl_2 , Fig 4.6. has also a slope very near to 8. This again confirms Suzuki's findings that the precipitates are of $\text{CdCl}_2 \cdot 6\text{NaCl}$ phase.

5.3.4. Solubility of CdCl_2 in NaCl :-

The experimental straight line of Fig 4.6 cuts the concentration axis at 85 mol ppm indicating that the room temperature solubility of CdCl_2 in NaCl is of that order. But from conductivity and dielectric loss experiments (Dreyfus and Nowick, 1962 ; Dryden and Meakins, 1957) we know that the equilibrium concentration of free Cd^{2+} ions and dipoles in NaCl at room temperature is very low, possibly of the order of 5 mol ppm or less. This difference can be reconciled if we also take into account the fact that in the quenched and aged crystals no precipitate was found after ageing for 96 hours at 150°C . But from the dielectric loss and paramagnetic resonance experiments (Cook and Dryden, 1960; Symmons and Kemp, 1966.) of divalent cation doped NaCl, it is known that the ageing of the crystals (i.e. formation of the dipole complexes) proceeds at an appreciable rate even at room temperature.

All these indicate that through the $\text{CdCl}_2 \cdot 6\text{NaCl}$ phase may have a lower free energy its formation has an activation barrier. This can be partly understood if we consider the structure of $\text{CdCl}_2 \cdot 6\text{NaCl}$. Referring to Fig 5.9 it can be seen that vacancies and Cd^{2+} ions are situated in next nearest neighbour positions, whereas in doped NaCl, dipoles are mostly of nearest neighbour configuration.

If the Cd^{2+} ions are already associated with a vacancy in nearest neighbour position then some activation energy ($\sim 0.3\text{eV}$) is required to break this association and incorporate them into the $\text{CdCl}_2 \cdot 6\text{NaCl}$ phase. This formation barrier controls the growth kinetics of the $\text{CdCl}_2 \cdot 6\text{NaCl}$ phase. At constant rate of cooling, below a certain temperature the growth kinetics of $\text{CdCl}_2 \cdot 6\text{NaCl}$ become too slow compared to the competing mechanism of nearest neighbour dipoles aggregating in the form of trimers and other complexes. Below this temperature the formation of the phase $\text{CdCl}_2 \cdot 6\text{NaCl}$ becomes negligible and the rest of the divalent ions in solution form into dipole aggregates like trimers etc. The ageing experiments indicated that this temperature is in the region of $150^\circ\text{--}200^\circ\text{C}$. The intercept at 85 mol ppm therefore represents the amount

of cadmium that remains in solution at the temperature where equilibrium with respect to the $\text{CdCl}_2 \cdot 6\text{NaCl}$ phase could still be reached at the cooling rate of 0.25°C per minute. (At a cooling rate of 1.5°C/minute about 300 mol ppm remained in 'solution'). This 85 mol ppm may also contain any insoluble and microscopically undetectable compounds (namely oxides or hydroxides) formed during growth and heat treatment of the crystal which had been carried out in normal atmosphere.

5.3.5. Phase diagram of $\text{NaCl}-\text{CdCl}_2$ system :-

The phase diagram of $\text{NaCl}-\text{CdCl}_2$ has been determined by Brand (1911) and is reproduced in Fig 5.12. It shows no solid solubility of Cadmium in NaCl , however in the concentration scale of this phase diagram solid solubility may not be detectable. Suzuki (1961) from his x-ray observations proposed a phase diagram shown in Fig 5.13, solubility of CdCl_2 in NaCl in this diagram has been shown to be $2.5 \text{ mol } \%$ at 200°C . In the present series of electron microscopic examinations, precipitates have been observed in NaCl for CdCl_2 concentration down to 200 mol ppm at 200°C . From the data of the precipitate volume for different concentrations of CdCl_2 at different quenching temperatures, which has been presented in Fig 4.7,

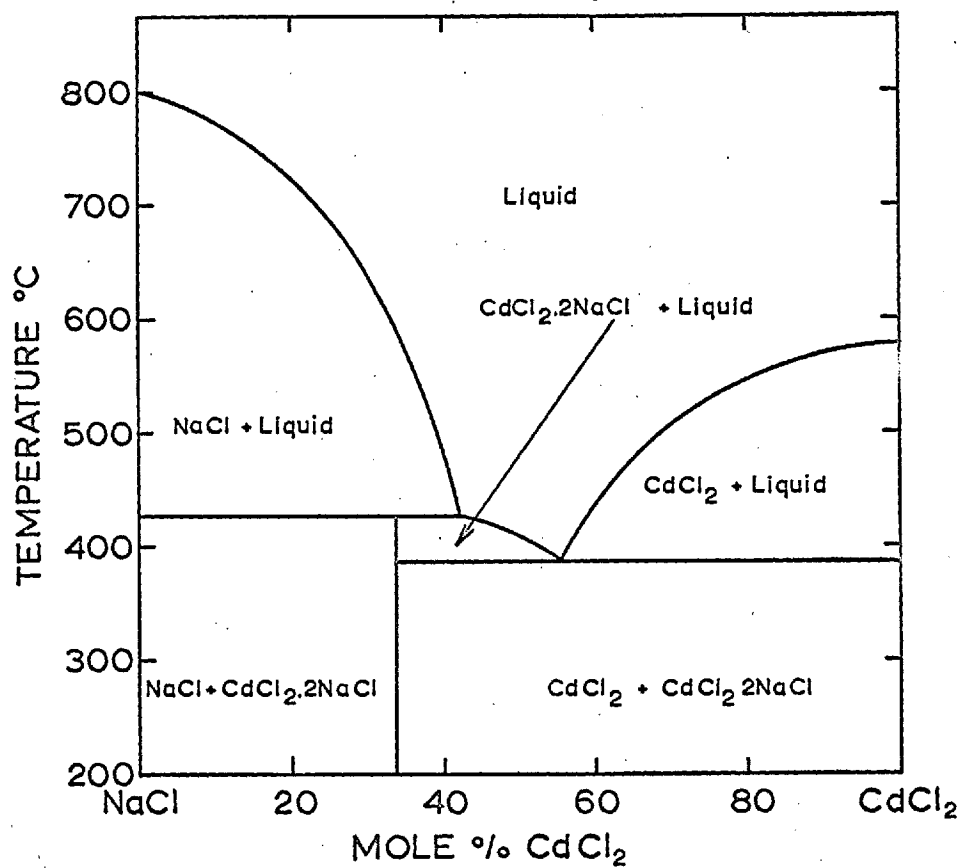


Fig. 5.12. Phase diagram of NaCl-CdCl₂ system.
(After H.Brand 1911).

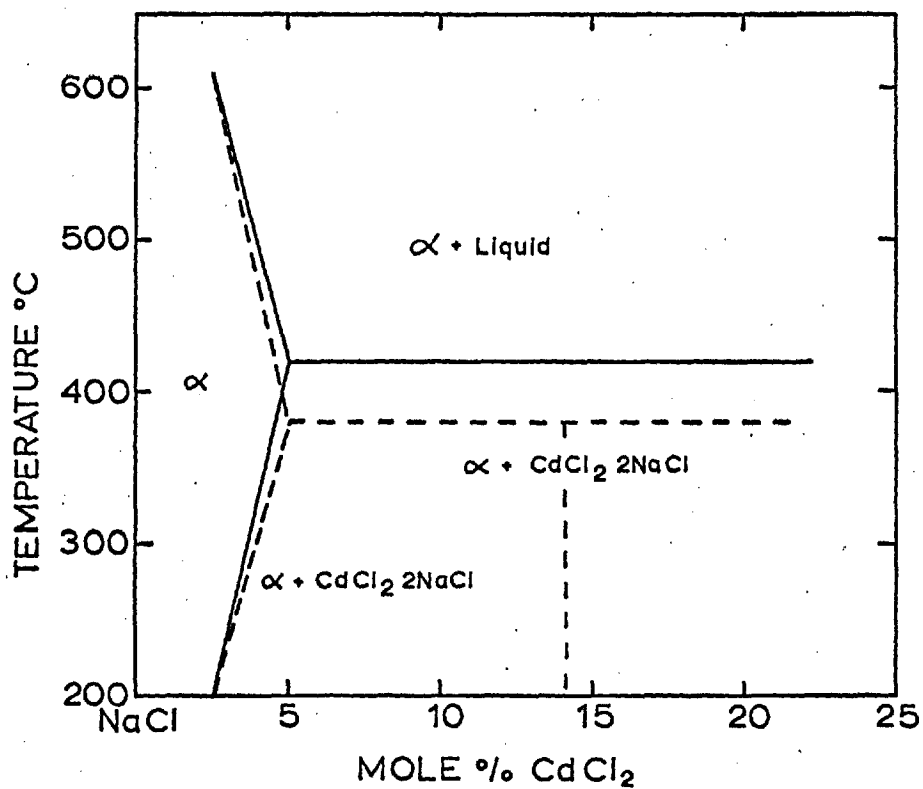


Fig. 5.13. Phase diagram for the NaCl- CdCl_2 system at a lower CdCl_2 composition (After K. Suzuki 1961)

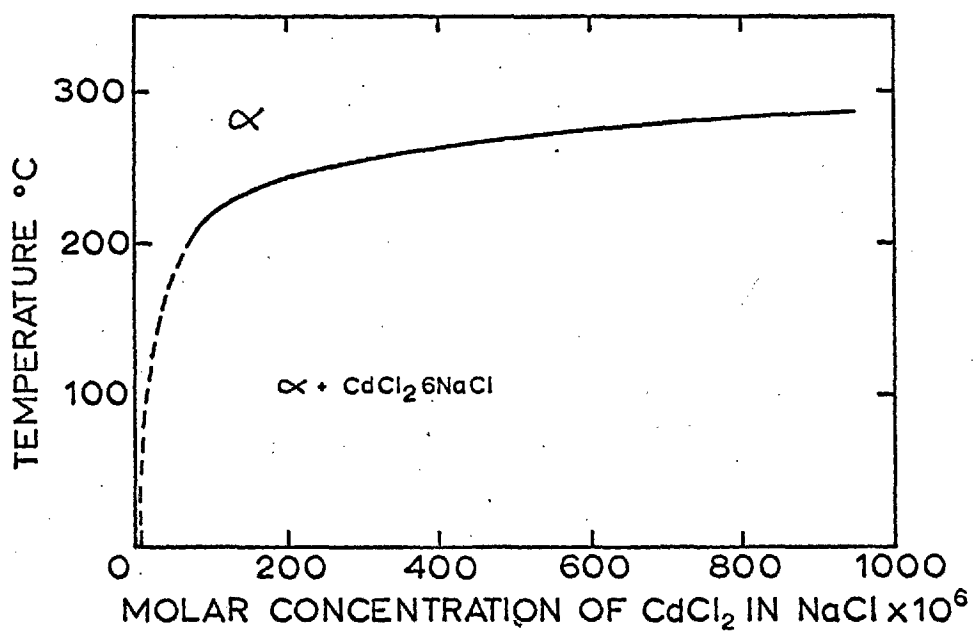


Fig.5.14. Tentative solvus for CdCl_2 in NaCl .

a tentative solvus for the $\text{NaCl} - \text{CdCl}_2$ system for CdCl_2 concentration upto 950 mol ppm has been proposed, as shown in Fig 5.14. The solvus from 200°C to room temperature has been drawn as a dotted line because the data of the present experiments in this region could not be taken for equilibrium values as discussed earlier. The dotted line is a continuation of the curve above 200°C to equilibrium solubility at room temperature as found by conductivity and dielectric loss experiments.

The enthalpy of solution of CdCl_2 in NaCl as calculated from the data in Fig 4.7, is 0.74 ± 0.1 eV. This can be compared to Haven's (1954) value of 0.62 eV. The difference may be due to the fact that in electron-microscopic observations, solubility is determined with respect to the precipitate phase only, but in the conductivity experiment the solubility was determined by Haven from the onset of stage III, where only the free ions were taken as in solution. Solubility was therefore primarily with respect to the dipoles.

5.4. MnCl_2 doped NaCl :-

5.4.1. Precipitate shape and structure :-

The observation in the manganese doped crystals

were qualitatively similar to that in the cadmium doped crystals. The observed precipitates were square in section as shown in Figure 4.10. The precipitate shape was therefore cubic as shown in Fig 5.7.

There was some difference in the size distribution. While the precipitates in the Cadmium doped crystals were in one group in size distribution with a few large precipitates decorating sub-boundaries, in the manganese doped crystals there was a somewhat higher proportion of these large precipitates and in addition there was a distribution of small precipitates shown in Fig 4.11. The reason for these small precipitates is not clear. They had the same shape and went into solution at the same temperature as the other precipitates, so it could not be established that they belonged to a different phase. It is possible that after first nucleation, with lowering of temperature there is reached a stage when the amount of MnCl_2 that could diffuse to the nuclei and precipitate out, was smaller than the super-saturation build up due to the rate of cooling, and ultimately there was sufficient super saturation to cause further nucleation.

The volume fraction of the precipitated phase has been plotted as a function of the concentration of MnCl_2

in mol fraction. The straight line fitted to the experimental data cut the concentration axis at 70 mol ppm and had a slope of 8.3 , Fig 4.12. From the similarity of the shape and the volume ratio of the precipitate with those in the cadmium doped crystals it is suggested that the precipitate phase in the manganese doped crystals has a similar structure and composition to $\text{CdCl}_2 \cdot 6\text{NaCl}$ phase i.e., $\text{MnCl}_2 \cdot 6\text{NaCl}$. It is interesting to note here that the crystallographic structure of MnCl_2 is also same as that of CdCl_2 , namely the hexagonal layer structure as shown in Fig 5.11.

5.4.2. Paramagnetic Resonance spectra of Manganese doped NaCl :-

The paramagnetic resonance spectra in manganese doped NaCl has been examined by Schneider and Guffyn (1954); Oshima, Abe, Nagano and Nagusa (1955); Oshima et al (1956); Law (1956); Watkins (1959); Bansigir and Schneider (1962); Alzetta, Crippa and Santucci (1965); Symmons and Kemp (1966) and Owston (1966). All these authors observed that the spectrum in their starting material and the final spectrum after quenching the crystals from high temperature and ageing at room temperature, consisted of a single Lorentzian absorption peak. The width of this peak has variously been described as between 130 and 220 gauss. Oshima and

his co-workers (1955) examined this room temperature spectrum more carefully by slow cooling and quenching. They found that this single peak consists of two peaks of nearly equal 'g' value, one of half width 39 ± 5 gauss in the slowly cooled crystals and other of half width 222 ± 15 gauss in the quenched crystals.

The effects of the crystal field and inter-action between neighbouring paramagnetic ions on the resonance spectra has been discussed by Pake (1962). In the structure of $\text{CdCl}_2 \cdot 6\text{NaCl}$, Fig 5.9, the divalent cations are in a position of cubic octahedral symmetry with respect to the vacancies, i.e., divalent ions are at the centers of regular octahedrons formed by the vacancies. The ground state of Mn^{2+} ion has the electronic configuration $3d^5$ and according to Hund's rule all the spins are in the same sense i.e., $S = 5/2$ and all the five d orbitals are singly occupied and therefore the charge distribution round the ion is spherically symmetric and there is no first order inter-action between the Mn^{2+} ions and the octahedral electrostatic crystal field. The sixfold degeneracy of the Mn^{2+} ground state is not lifted and no fine structure is therefore expected in the resonance spectrum. The twelve nearest neighbour Mn^{2+} ions are forming a regular dodecahedron round each Mn^{2+} ions at a distance 7.95Å in the $\langle 110 \rangle$

directions. This distribution is also isotropic and has the symmetry of face centered cubic lattice. Under these circumstances appreciable narrowing of the absorption spectrum due to spin exchange interaction, (Van Vleck, 1948) is to be expected. This will give rise to a sharp Lorentzian peak, as observed by Osima et.al. in their slowly cooled crystals. A very prominent Lorentzian peak of width 50 gauss has been observed in manganese doped KCl by Low (1956). Oshima et.al. (1956), Watkins (1958), Bansigir and Schneider (1962) and Symmons and Kemp (1966). Watkins remarked that this peak may be due to K_4MnCl_6 (possibly he meant K_6MnCl_8). The reason for such prominent exchange-narrow peak in Mn doped KCl and the rather elusive yet narrower peak in Mn doped NaCl can be found in the relative energies of the nearest neighbour and next-nearest neighbour type dipoles in KCl and NaCl. Theoretical calculations of Bassani and Fumi (1954) and Tosi and Airoldi (1958) showed that in (Strontium doped) NaCl the energy of association between the divalent cation and a cation vacancy in the nearest neighbour site, E_n , is higher than the association energy between the divalent ion and the vacancy in next-nearest neighbour site, E_{nn} , ($E_n - E_{nn}$) in NaCl is = 0.02 eV, whereas the reverse is

the case in KCl, where $(E_n - E_{nn}) = -0.11$ eV. In manganese doped NaCl and KCl, Watkins (1959) found by measuring the ratios of intensities of the E.P.R. Spectrum III_1 (due to nearest neighbour dipoles) and spectrum III_2 (due to next nearest neighbour dipoles) that in NaCl $(E_n - E_{nn}) = 0.034$ eV and in KCl $(E_n - E_{nn}) = -0.029$ eV. All these show that while the nearest neighbour type dipole is the stable configuration in NaCl it is the next nearest neighbour type dipole which is more stable in KCl. Now if a phase of $CdCl_2 \cdot 6NaCl$ structure is formed in manganese doped KCl (i.e. $MnCl_2 \cdot 6KCl$) there will be considerably less barrier for both nucleation and growth of the precipitates of the phase as the divalent ion and the vacancy are in next-nearest neighbour position in the phase and also in the stable dipoles. So the dipoles can be incorporated into the phase directly, without having to dissociate as in the case in NaCl where equilibrium dipoles are of nearest neighbour configuration. In KCl therefore, at any particular cooling rate, nucleation will occur at a lower super saturation than in NaCl, and growth will continue to a lower temperature. As a result most of the manganese in KCl will form onto the precipitate phase and precipitates themselves will be larger in size. As a result most of the Mn^{2+} ions will be in a position of cubic symmetry

as described earlier and give rise to a prominent exchange narrowed peak. But in NaCl, due to the fact that the nearest neighbour dipoles have to dissociate before going to the phase, both nucleation and growth of the phase is comparatively difficult which will result in smaller precipitate size and a considerable fraction of dipoles associating in the form of trimers and higher complexes. The effect of smaller precipitate size is to increase the surface to volume ratio and there will be a large proportion of Mn^{2+} ions at the surface of the precipitates which are asymmetrical positions. Their spectrum will be in general broader and also be a function of the orientation of the precipitate surface with respect to the applied magnetic field. Also the trimers Fig 5.15. cannot build up a three dimensional structure of local cubic symmetry. So the Mn^{2+} ions in trimers and complexes will be in a tetragonal field and will give rise to a broader spectra. In the case of super position of narrow and broad peaks, unless ^{the} narrow peak is much stronger, the width of the combined peak is very nearly equal to the width of the wider peak. This may be the reason why the experimenters who did not slowly cool the crystals from solution temperature observed just a broad peak of width between 130 - 200 gauss.

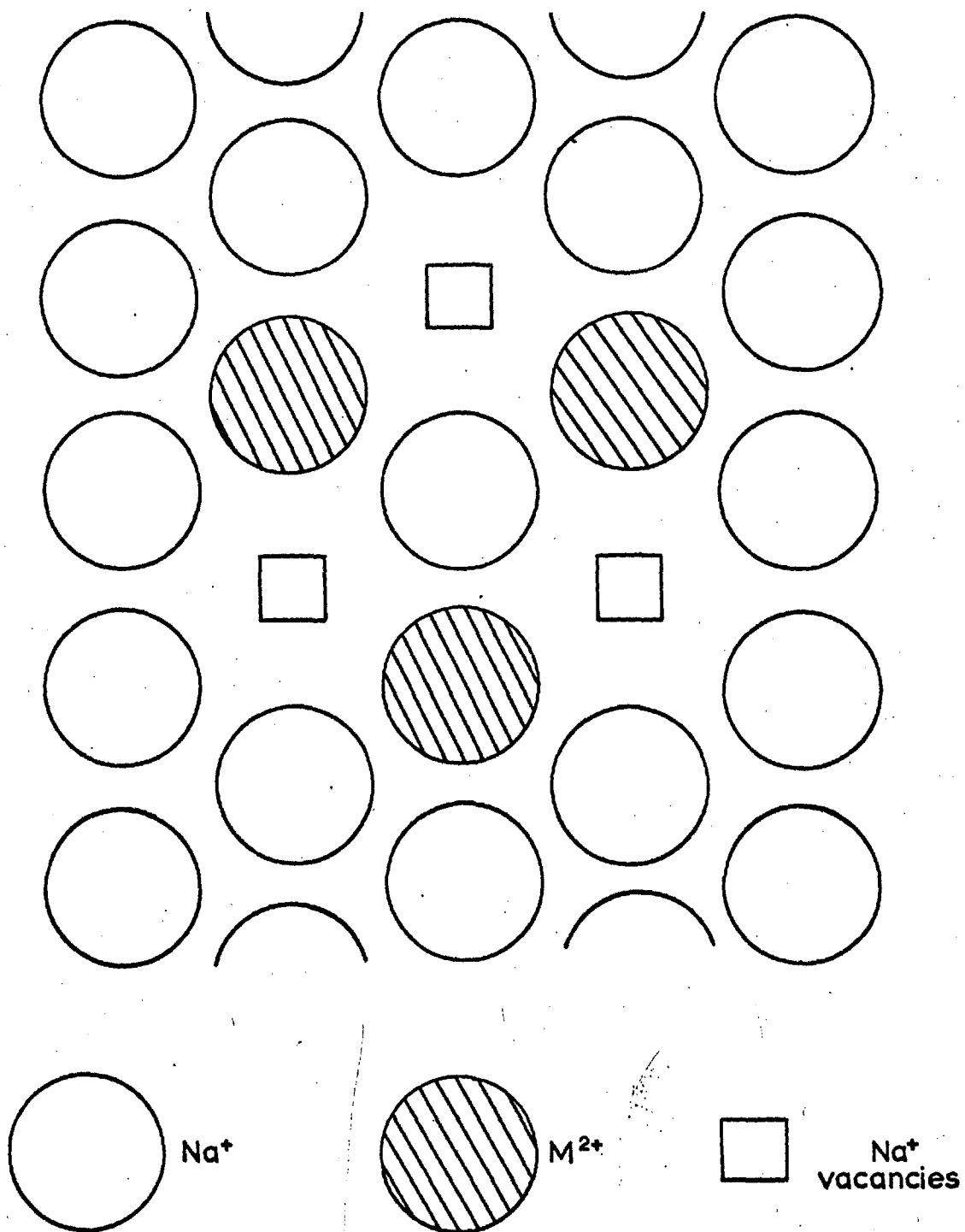


Fig.5.15. Model of a trimer in the (111) plane of NaCl.
(After Cook and Dryden, 1960)

Theoretical calculations for the width of the different absorption peaks, has not been attempted, because the difficulty in achieving quantitative agreement between the calculated and the observed widths in the Paramagnetic resonance spectra, is well known. Qualitatively, ^{the} stronger the exchange interaction ^{the} narrower is the absorption peak. The exchange interaction increases with the increase in electron wave function overlap of the interacting ions, which again increases rapidly with the decrease in the distance between the ions. The distance between the Mn^{2+} ions in a $CdCl_2 \cdot 6NaCl$ type phase in NaCl and KCl, would be 7.95 Å and 8.88 Å respectively. The widths of the absorption peaks in the slowly cooled Mn doped NaCl and KCl, as observed by Oshima et.al.(1956), are 39 ± 4 gauss and 50 ± 5 gauss respectively. The relative values of the widths are in good agreement with what would be expected if such a phase is formed in both the crystals.

5.4.3. Solubility of $MnCl_2$ in NaCl :-

The straight line fitted to the experimental data for the volume ratio of the precipitate as a function of the $MnCl_2$ concentration, cut the concentration axis at 70 mol ppm. The significance of this solubility is again similar to that in the $CdCl_2$ doped NaCl, i.e. this 70 mol ppm

represents the solubility at a temperature where equilibrium can still be reached at a cooling rate of 0.25°C per minute. From the ageing experiment it is felt that this temperature is in the region of $200^{\circ}\text{C} - 235^{\circ}\text{C}$.

Actual solubility of manganese in NaCl is very low at room temperature. E.P.R experiments do not show any spectrum due to free Mn^{2+} ions or free dipoles in well aged crystals, where a 5 mol ppm of either would be clearly detectable.

The precipitates in crystals containing 225 mol ppm to 900 mol ppm MnCl_2 went into solution in the temperature range of 250°C to 325°C as shown in Fig 4.14. From this data a tentative solvus of MnCl_2 in NaCl upto 900 mol ppm of MnCl_2 has been drawn in Fig 5.16. The phase diagram of NaCl - MnCl_2 system determined by Sandonini & Scarpa (1913), Fig 5.17, does not show any solid solubility. However in the scale of the phase diagram, solid solubility would not be detectable. The enthalpy of solution of MnCl_2 in NaCl as calculated from the data of Fig 4.14 was 0.77 ± 0.1 eV. Haven (1954), from the conductivity experiments found the enthalpy of solution to be 0.43 eV.

Oshima and his co-workers (1955) annealed the slowly cooled crystals at different temperatures between 300°C and 500°C and observed the time required to convert

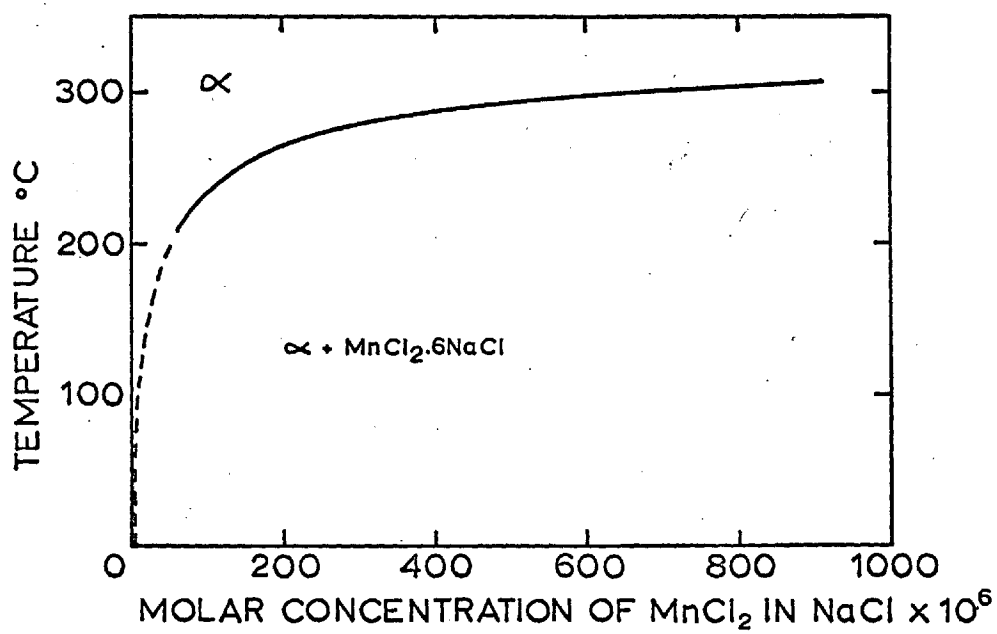


Fig.5.16. Tentative solvus for MnCl_2 in NaCl .

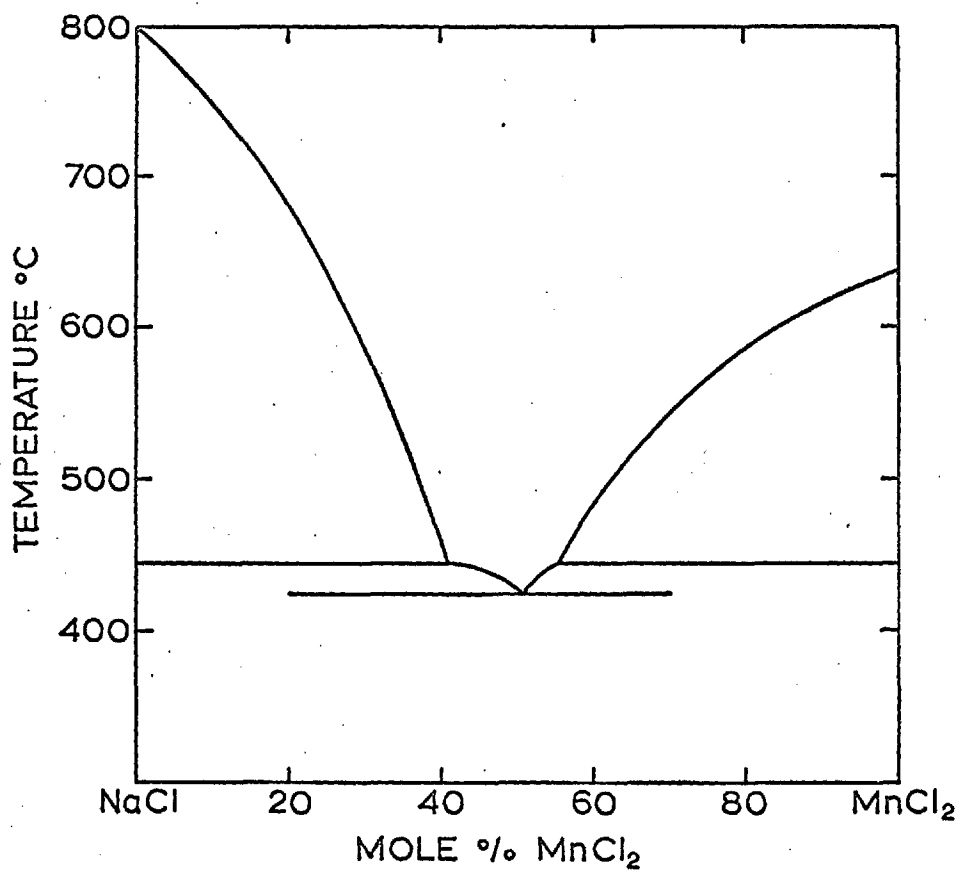


Fig.5.17. Phase diagram of the NaCl-MnCl₂ system.
(After Sandonnini and Scarpa 1913)

the narrow peak, 39 gauss to the broad peak, 220 gauss. Plotting the data as $t = t_0 \exp (Q/kT)$, they found the activation energy of the process $Q = 1.17$ eV.

5.5. $MgCl_2$ doped NaCl :-

$MgCl_2$ also has the structure of $CdCl_2$. The precipitates observed in $MgCl_2$ doped crystals also had square sections in the (100) cleavage plane of NaCl matrix, similar to the precipitates in the $CdCl_2$ and $MnCl_2$ doped crystals.

The increase in volume fraction of the precipitate with the concentration of $MgCl_2$ also followed, within its limits of error, the general trend of $CdCl_2$ and $MnCl_2$ doped crystals. It is conjectured therefore that the crystallographic structure of the precipitate is also similar to $CdCl_2 \cdot 6NaCl$.

It was noticed that compared to $CdCl_2$ and $MnCl_2$ doped crystals, there were in general more steps coming out of the precipitates in the $MgCl_2$ doped crystals, when they were cleaved through. The ionic radius of Mg^{2+} 0.65 Å, is considerably smaller than the ionic radius 0.95 Å of Na^+ . This is expected to make the unit cell dimension of the precipitate phase smaller than twice that of NaCl.

This will lead to appreciable coherency strain being set up between the precipitate and the matrix. The steps generated at the precipitates are indication of this partial loss of coherency.

The precipitates went into solution in the temperature range of $325^{\circ}\text{C} - 350^{\circ}\text{C}$ which is higher than the temperatures at which the precipitates in the CdCl_2 and MnCl_2 doped crystals went into solution.

5.6. CaCl_2 doped NaCl :-

CaCl_2 has a distorted Rutile structure. The ionic radius of Ca^{2+} is 0.99 Å. In CaCl_2 doped crystals precipitate were not observed upto a concentration of 2000 mol ppm CaCl_2 . In crystals containing 3000 mol ppm CaCl_2 , thin platelet precipitates with sections in the $\langle 110 \rangle$ directions were found along subgrain boundaries, Fig 4.19. In crystals containing 10,000 mol ppm CaCl_2 , precipitates were found randomly distributed over the whole surface. There were two types of precipitates, one thin and small and the other thicker and larger, as shown in Fig 4.20(b). Both types of precipitates cut the (100) matrix plane in the $\langle 110 \rangle$ directions. This is consistent with the findings of Miyaki and Suzuki (1954), Toman (1963) and Yagi and

Honjo (1964) that the precipitates in calcium doped NaCl are formed as platelets along the (111) plane of the matrix as shown in Fig 5.18. Two types of precipitates have also been observed by ^{the} above authors. One, found at lower doping level, has a structure coherent with NaCl lattice, Toman (1963) described this as a metastable modification of CaCl_2 with orientation relations, $\langle 100 \rangle_p \parallel (111)_m$; $[010]_p \parallel [\bar{1}1\bar{2}]_m$ and $[001]_p \parallel [\bar{1}\bar{1}0]_m$. The other, found in higher doped crystals has the structure of stable CaCl_2 which is incoherent with the NaCl lattice but has the same orientation relation as above.

On subsequent heat treatment of the crystal containing 1 mol % CaCl_2 , it was found that the thinner precipitates went into solution in the temperature range $200^\circ - 250^\circ\text{C}$ while the larger precipitates persisted and went into solution gradually in the range 300°C to 450°C . Toman found that the coherent precipitates went into solution between $200^\circ - 300^\circ\text{C}$ and Suzuki found that in quenched crystals the diffraction spots due to the CaCl_2 precipitate reappeared after annealing at 300°C .

It is likely that the thin precipitates are the coherent ones with metastable structures and the larger precipitates are of stable CaCl_2 structure.

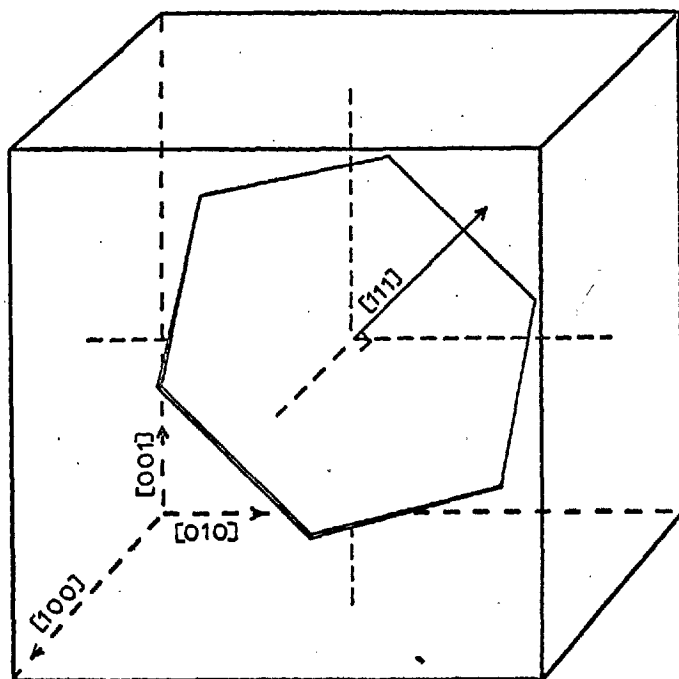


Fig.5.18. Platelet precipitate along $\{111\}$ matrix plane in CaCl_2 doped NaCl .

5.7. BaCl₂ doped NaCl :-

BaCl₂ has a Fluorite structure; ^{and the} ionic radius of Ba²⁺ is 1.35 Å. The precipitates in the BaCl₂ doped NaCl were plate like. The precipitates cut the (100) matrix plane in $\langle 110 \rangle$ and $\langle 520 \rangle$ directions as shown in Fig 4.22. As two types of planes namely $\{225\}$ and $\{552\}$ can have these intersections with the (100) plane, the (110) face of the crystals were polished and examined. The precipitates were found to cut the (110) matrix plane in $\langle 110 \rangle$, $\langle 223 \rangle$, $\langle 227 \rangle$ and $\langle 554 \rangle$ directions as shown in Fig 4.23. These intersections can be produced by $\{225\}$ planes and not $\{552\}$ planes. It was concluded therefore that the precipitate plates grew along the $\{225\}$ matrix planes. By transmitted light microscopy it was seen that the length of the precipitates were about 5 to 10 times their width. The thickness of the precipitates as seen by electron microscopy, were of the order of few hundred Angstroms. The ends of the precipitates were pointed as shown in Fig 5.19. The reason for a rather high index habit plane of the precipitates in BaCl₂ doped NaCl is not clear at the moment. X-ray analysis of the structure of the precipitate and the orientation relationship with the matrix may possibly provide an answer.

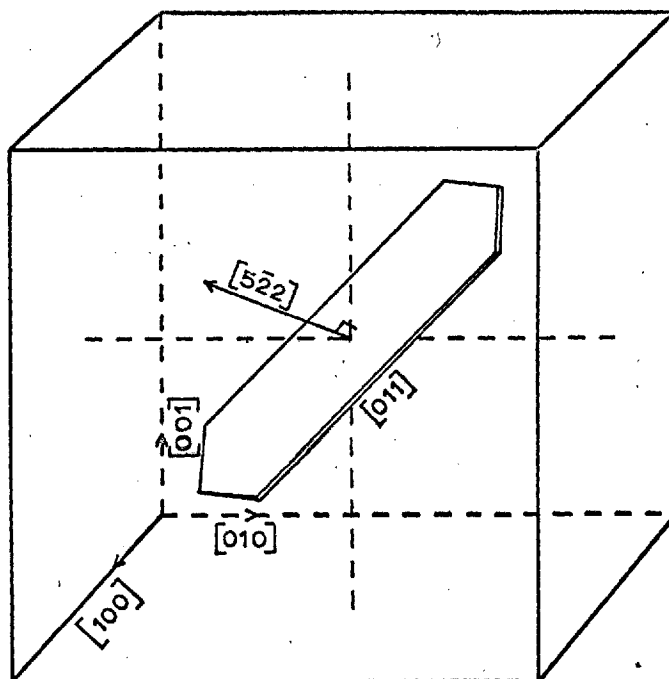


Fig.5.19. Platelet precipitates in the $\{522\}$ planes of BaCl_2 doped NaCl .

Subsequent heat treatment of the slowly cooled crystals showed that the precipitates go into solution in the temperature range 500° - 600°C .

5.8. General discussion on the Structure and Shapes of precipitates in divalent cation doped NaCl :-

Table 5. lists the divalent cations, their ionic radii, electro-negativity, structure of their chlorides, shape of the precipitates and the structure of the precipitates. It can be seen from the Table that the size of the divalent cations is not the only important factor in determining the shape and structure of the precipitates. Electronegativity of the divalent cations, also plays an important role. In fact the structure of the divalent chloride, which is determined by both the radius ratio of cation and anion and the difference in their electronegativity, provides a better guide to the structure of the precipitates. For example, Ca^{2+} and Cd^{2+} ions have nearly equal radii but different electronegativity, and the structure of CaCl_2 is different from CdCl_2 so also are the structures of the precipitates in CaCl_2 and CdCl_2 doped NaCl. On the other hand the radius of Mg^{2+} is much smaller than that of Cd^{2+} but MgCl_2 is of the same

Table 5.1

The shape and the structures of the precipitates
in NaCl doped with divalent chlorides.

Divalent chloride	Ionic radius of the divalent ion.	Electro-negativity of the divalent atom.	Structure of the divalent chloride.	Shape of the ppt. in NaCl.	Structure of the ppt.
CdCl_2	0.97 A	1.7	CdCl_2 layer structure	Cubes with faces along (100) _m	$\text{CdCl}_2 \cdot 6\text{NaCl}$
MnCl_2	0.80 A	1.5	as above	as above	Probably similar to above
MgCl_2	0.65 A	1.2	as above	as above	as above
CaCl_2	0.99 A	1.0	Rutile (distorted)	Platelets in 111 _m	CaCl_2
BaCl_2	1.35 A	0.9	Fluorite	Platelets in 522 _m	Not known

structure as CdCl_2 and the precipitates in the MgCl_2 and CdCl_2 doped crystals are also similar.

Another aspect of the structure of the precipitate is its effect on the solubility. If the structure of the precipitate is such that it is incoherent with the matrix or to maintain coherency large coherency strain is set up or if it involves a different arrangement of the anions. The energy of formation of the precipitate phase will be large. This will make precipitation difficult and consequently increase solubility. A case in point is Ca^{2+} and Cd^{2+} in NaCl . In slowly cooled CdCl_2 doped crystals precipitates are observed at Cd^{2+} concentration of 200 mol ppm whereas with a large ionic radius Ca^{2+} does not precipitate out till the concentration is as high as 3000 mol ppm. It is likely that the formation of $\text{CdCl}_2 \cdot 6\text{NaCl}$ requires less energy as it only involves incorporation of Cd^{2+} and vacancies in the cation-sublattice. But precipitation of CaCl_2 needs rearrangement of both cation and anion sublattice with consequent increase in interfacial energy and strain energy. However, it may be mentioned here that the Equilibrium constant 'K' (defined as $K = C_1/C_2$ where C_1 is the concentration of a dopant in the crystal and C_2 is the concentration of the dopant in the melt from which the crystal has been grown) for Ca^{2+}

in NaCl has been found by Andreev (1965) to be higher than Cd^{2+} in spite of the larger size of the Ca^{2+} ion. Andreev commented that this may be due to the similarity of the outer electron shell of Ca^{2+} and Na^+ ions. Both consist of 2 s and 6 p electrons, whereas Cd^{2+} has 10 d electrons. This may also lead to lower free energy for the Ca^{2+} ion in solution and contribute towards its higher solubility.

5.9. Precipitation and the mechanical properties of doped NaCl :-

The room temperature flow stress of slowly cooled NaCl containing Cadmium, Manganese, Magnesium and Barium has been found by Harrison (1965) and Pratt, Harrison and Newey (1964, 1966) to increase considerably when subsequently quenched from above certain temperatures. The temperatures at which this quench hardening occurred, corresponds very closely to the temperatures at which precipitates were found to go into solution in the present experiments (comparisons are shown in table 5.2).

The above authors also found that crystals doped with about 1000 mol ppm Calcium, or lightly doped with

TABLE 5.2.

Solution temperatures for the precipitates and the
quench-hardening temperatures for divalent chloride doped NaCl.

Divalent chloride used as dopant	Solution temperature for the precipitates	Temperature at which quench-hardening has been observed by Harrison (1965)
CaCl_2	$225^{\circ}\text{C} - 275^{\circ}\text{C}$	$225^{\circ}\text{C} - 300^{\circ}\text{C}$
MnCl_2	$275^{\circ}\text{C} - 325^{\circ}\text{C}$	$275^{\circ}\text{C} - 350^{\circ}\text{C}$
MgCl_2	$325^{\circ}\text{C} - 375^{\circ}\text{C}$	$300^{\circ}\text{C} - 400^{\circ}\text{C}$
BaCl_2	$500^{\circ}\text{C} - 600^{\circ}\text{C}$	$475^{\circ}\text{C} - 600^{\circ}\text{C}$

Cadmium (35 mol ppm) did not show any quench hardening. It may be mentioned that no precipitates were observed in these crystals.

From these, it is seen that the observed quench hardening is due to the precipitate going into solution and the divalent cations being distributed throughout the matrix in the form of dipoles or aggregates of dipoles. The interaction between the dipoles and moving dislocations have been discussed by the above authors. Due to electrostatic attraction between the vacancy and the divalent ions it is difficult for a dislocation to cut through a dipole. Also the dipoles provide strong resistance to dislocation motion by setting up a tetragonal strainfield in the matrix. In ionic solids therefore most efficient hardening is achieved when the divalent impurities are dispersed throughout the matrix in the form of dipoles. Precipitation as observed in slowly cooled crystals, therefore, essentially softens the crystals by taking the divalent cations out of solution and leaving most of the matrix free from obstacles for dislocation motion. The precipitates themselves do not cause appreciable hardening as the distance between precipitates in slowly cooled Cadmium and Manganese doped crystals is of the order of 5 - 10 microns. Orowan type hardening from

such a distribution of rigid obstacles would be $\Delta p \simeq g \times 10^{-4}$ where Δp is the increase in flow stress due to the precipitates, g is the shear modulus of NaCl.

However even in slowly cooled crystals about 70 - 90 mol ppm of manganese and cadmium do not precipitate out but remain distributed in the matrix in the form of, probably, dipole-aggregates (trimers etc.) which contribute to the temperature dependent part of the flow stress as has been observed by Pratt, Harrison and Newey (1966). They also observed a considerable increase in the temperature dependent flow stress in quenched crystals. Alzetta et. al (1965) found in Mn doped NaCl that after deformation six hyper-fine lines of spin resonance spectra of isolated manganese ions could be found superimposed on the single broad peak of the undeformed crystal. The intensity of the hyperfine lines increased with deformation. These show that the obstacles in quenched crystals are small so that dislocations can overcome them by thermal activation. Observation of hyperfine lines after deformation in MnCl doped crystals shows that the state of aggregation of the Mn^{2+} ions in the crystal which initially displays a single broad peak, is such that the passage of dislocations through these aggregates can move

individual Mn^{2+} ions sufficiently away from other Mn^{2+} ions and the vacancies as to give rise to hyperfine lines, which is characteristic of isolated Mn^{2+} ions. This again suggests that the aggregates are small and probably planar (such as trimers in the $\{111\}$ plane).

Pratt, Harrison and Newey (1964) observed that the flow stress of Cadmium doped NaCl showed a small but definite peak and a yield drop in quenched crystals at about 215°C and a larger peak with smaller yield drop in slowly cooled crystals at about 245°C . Similar peaks and yield drops were also observed in quenched and slowly cooled Mn doped crystals at about 270°C and 300°C . The peaks were supposed to be due to increased number of dipoles in the crystals. In other words those peak temperatures can be looked at as the solution temperatures for the dipole aggregates and the precipitates. This is also confirmed by the present ageing experiments of quenched crystals where precipitates could only be found when ageing was carried out above the solution temperature of the aggregates.

Harrison (1967) determined the room temperature flow stress of quenched NaCl crystals containing 600 mol ppm CdCl_2 , as a function of subsequent ageing temper-

ature. He observed a minimum in the flow stress for ageing temperatures around 200°C . All these observations coupled with the fact that dipole aggregation in the form of trimers is the most important process in the quenched crystals, (Cook and Dryden, 1960; Owston, 1966; Symmons and Kamp, 1966) all suggests that, at least Cd and Mn (and it may also be true for other divalent cations) doped NaCl behaves very similarly to some metal systems such as Al - Cu where rapid cooling leads to the formation of metastable Zones (G.P. Zones) and precipitates are formed on subsequent ageing above the metastable solvus.

Quench-ageing experiments suggested that precipitates nucleate preferentially on the dislocations. This is in agreement with Cottrell type locking of dislocations, observed by Pratt and Brown (1963) during strain ageing experiments with Cd doped NaCl.

Precipitation strengthening :-

The precipitation in Calcium and Barium doped crystals were found to offer considerable resistance to propagation of cleavage cracks through them. This is evident from the large number of extra cleavage steps that

have been introduced at the precipitate and the way the precipitates modified the courses of the cleavage steps as shown in Fig 5.20. This is possibly due to the difference in the crystallographic orientation and the mechanical properties of the precipitate and the matrix. The precipitate plane which is parallel to the cleavage plane of the matrix may be a difficult one to cleave through. The cleavage front is held up at the precipitate and a considerable stress build-up is required before the precipitate can actually be broken and the cleavage is allowed to proceed. (It may be mentioned in this connection that the precipitates in the Cd, Mn and Mg doped crystals offer little such resistance. The cleavage steps were found to propagate through them with little or no modification, and no large steps are originated at the precipitates as shown in Fig 5.4. This is due to the identical structure and orientation of the precipitate and the matrix, in fact the anion sublattice of the precipitate and the matrix are practically the same. So the cleavage can continue through the precipitate with comparative ease.).

It is seen that in the systems like $\text{NaCl} - \text{BaCl}_2$, where precipitates have a complex relation with the

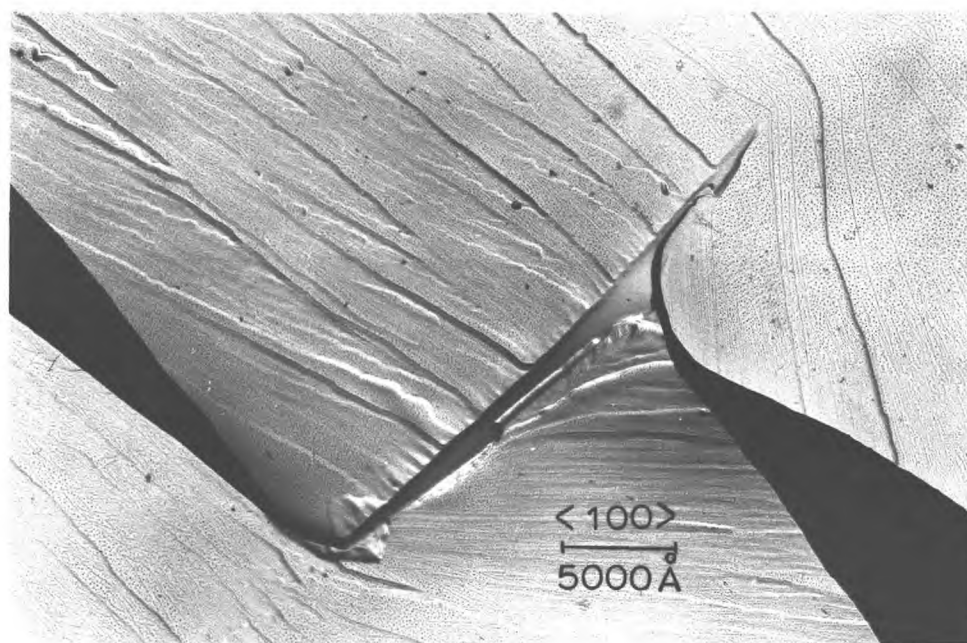


Fig.5.20. Gold decoration replica of BaCl₂ doped NaCl, showing large scale irregularities caused on the cleaved surface due to the presence of the precipitates.

matrix and precipitation occurs at a low concentration (<20 mol ppm. BaCl_2) it may be possible by adjusting the doping level and the heat treatment, to achieve considerable increase in the fracture strength of the matrix.

CHAPTER VI

MICROSTRUCTURE OF ELECTRON

IRRADIATION DAMAGE IN PURE NaCl

Micro structure of Electron irradiation damage in pure NaCl.

An attempt to study NaCl by transmission electron-microscopy was met with very limited success. It was found that the beam of the electronmicroscope readily damage the specimen and made it difficult to investigate the original micro structure. The damage process itself was therefore studied in the hope of understanding the mechanism and possibly minimising its effects in the future.

6.1. Specimen preparation :-

To produce specimens for transmission electron-microscopy crystals were first cleaved into plates of size 3mm x 3mm x 0.3mm. Then a drop of distilled water was placed on each side of the plates with a fine dropper. Due to its surface tension, distilled water formed a hemispherical drop and produced a corresponding dimple on the surface as in Fig 6.1. The plates were then passed in quick succession through solutions of 50% H_2O + 50% Ethanol, pure Ethanol and anhydrous ether and examined under^{an}optical microscope. The process was repeated till a hole just appeared in the middle and there were interference fringes round it as shown in Fig 6.2.

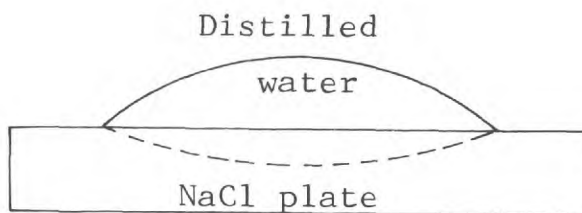


Fig.6.1. Diagram showing the method of producing dimples on the NaCl plates by placing droplets of distilled water.

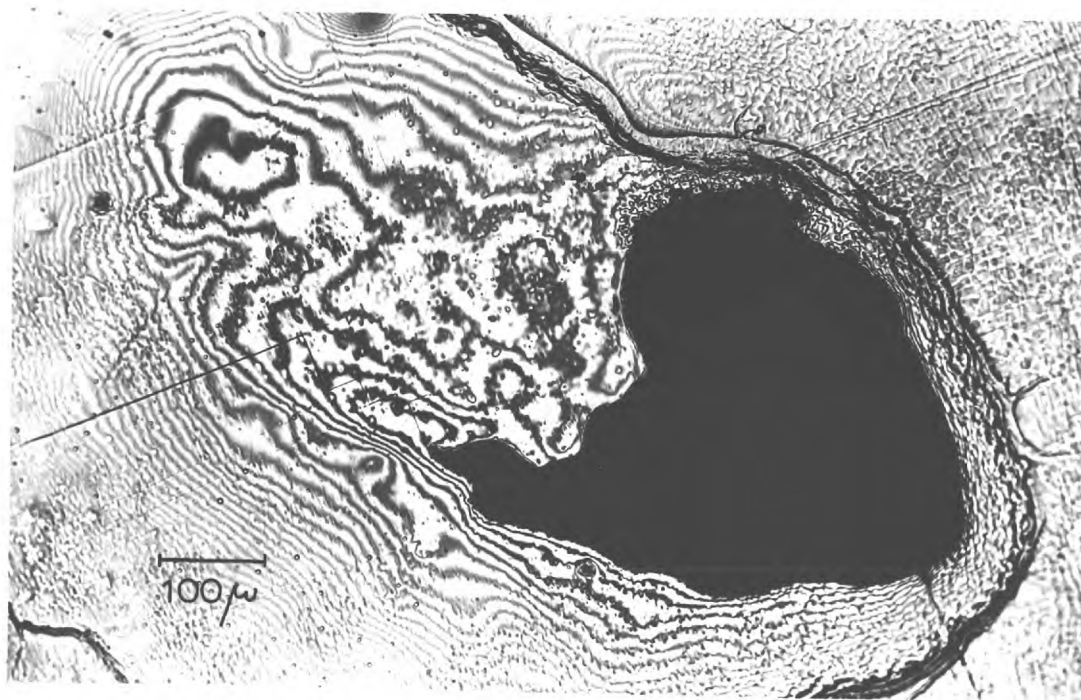


Fig.6.2. Thinned specimen of NaCl, showing interference fringes.

6.2. Beam Analysis :-

In view of the possibility that negative ions might be present in the beam, which could cause the damage an electromagnet was designed as shown in Fig 6.3, and was introduced between the Intermediate and the Projector lens of the Electronmicroscope. The electrons of the beam were then deflected away by the magnet but no negative ion could be detected on the photographic plate even after an exposure of 30 minutes to one hour.

6.3. Determination of beam intensity :-

To obtain an accurate measurement of the intensity of the beam, a beam collector was used. The second specimen stage of the microscope was modified for this purpose by insulating it from rest of the microscope body and by placing an aluminium disc in the position of the specimen. The collected beam current was then passed through a 'Vibron' electrometer.

6.4. Measurement of the density change in NaCl due to electron irradiation :-

To measure the change in density of NaCl due to electron irradiation, an ethelene dibromide density

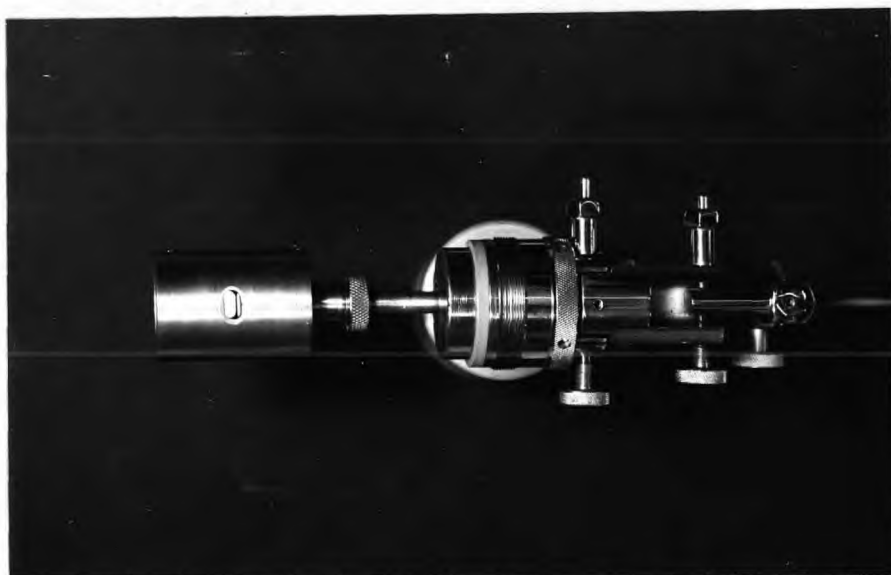


Fig.6.3(a) Photograph of the beam deflecting magnet.



Fig.6.3(b) Exploded view of the deflecting magnet.

column was used. The apparatus has been described in detail by Silverstone (1960). Essentially it consists of a vertical column of ethelene dibromide, which is a liquid of similar density as NaCl and doesnot react with it. A nearly constant temperature gradient is maintained along the hught of the column (by suitable arrangement of heaters and thermostats) which results in a density gradient along the height of the column. A density gradient of $2 \times 10^{-5} \text{ gm/cc/cm}$ was used for the present experiment. NaCl specimens were cleaved to 3mm x 3mm x 1mm in size and polished in distilled water and Ethanol. After irradiation in the microscope to known doses these specimens were floated in the column along with similar unexposed standards shown in Fig 6.4. From the difference in height at which the standard and the irradiated specimen floated, the density change due to irradiation was found.

6.5. Determination of the depth of penetration of the electrons in NaCl :-

The depth of penetration of 50KV, 75KV and 100KV electrons in NaCl was determined by exposing NaCl plates to the electrons of above energies in the electronmicroscope and then cleaving the plates in the middle and



Fig.6.4 Showing irradiated NaCl specimens in the density column.

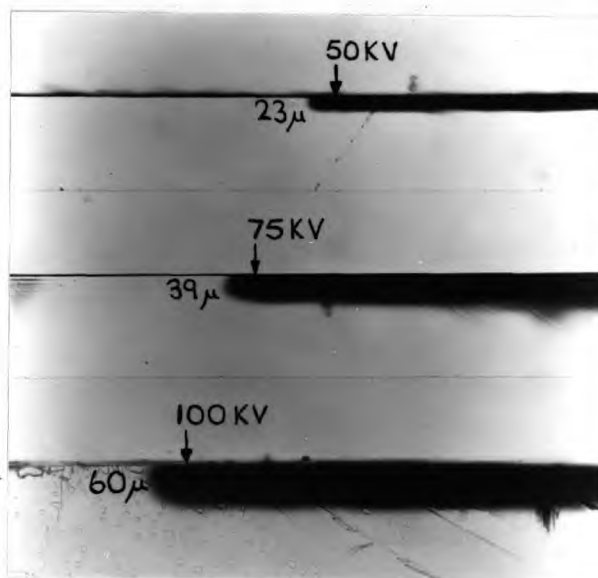


Fig.6.5 Showing the depths of penetration of 50 KV, 75 KV and 100 KV electrons in NaCl.

photographing them edge on, under an optical microscope. The depth of electron penetration was indicated by the depth of coloration as shown in Fig 6.5.

6.6.1. Early stages of damage :-

To observe the early stages of damage, a very low beam intensity was used. A beam intensity of 2×10^{-10} amp was obtained by introducing a 25μ aperture at the condenser and operating the electron gun below saturation. To photograph at this low beam intensity, Kodak high speed x-ray film 'Kodirex' was used which allowed exposures ten times faster than the B-2 plates normally used. Though the photographs were grainy none the less they were quite satisfactory. To reduce the total irradiation of the area to be photographed, focusing was carried out on an adjacent area and the area of interest was moved in just before the exposure was made.

At an irradiation dose of 1.5×10^{-11} coulomb/ μ^2 of 100KV electrons, defect clusters, ^{were} about 100 - 200 Å in size, and assuming a foil thickness of about 3000 Å the density of clusters was of the order of 2×10^{15} per cubic centimeter. The projection of these clusters lay along the $\langle 100 \rangle$ directions on the (100) plane and they

produced strong strain contrast, as shown in Fig 6.6. The diffraction pattern at this stage showed spiking in the cube directions Fig 6.7. indicating strains normal to the cube planes. With the increase of irradiation the defects grew in size Fig 6.8. The strain contrast and the associated spikes in the diffraction pattern reduced. Fig 6.9. The process continued till the defects overlapped one another and were no longer distinguishable individually. Fig 6.10.

6.6.2. Damage at higher beam intensity :-

When beam intensity was increased to about 1×10^{-6} amp, rapid movement of the defects could be seen, in some cases local melting and evaporation of the specimen was also observed. Diffraction pattern first showed arcing, indicating start of polygonization, Fig 6.11a. And as the irradiation continued, arcing also increased, Fig 6.11b and finally a ring pattern, corresponding to nearly complete polygonization was observed Fig 6.11c.

6.7. Possible mechanism for the damage of the NaCl specimens in the electron beam :-

The damage of the specimen in the beam may be

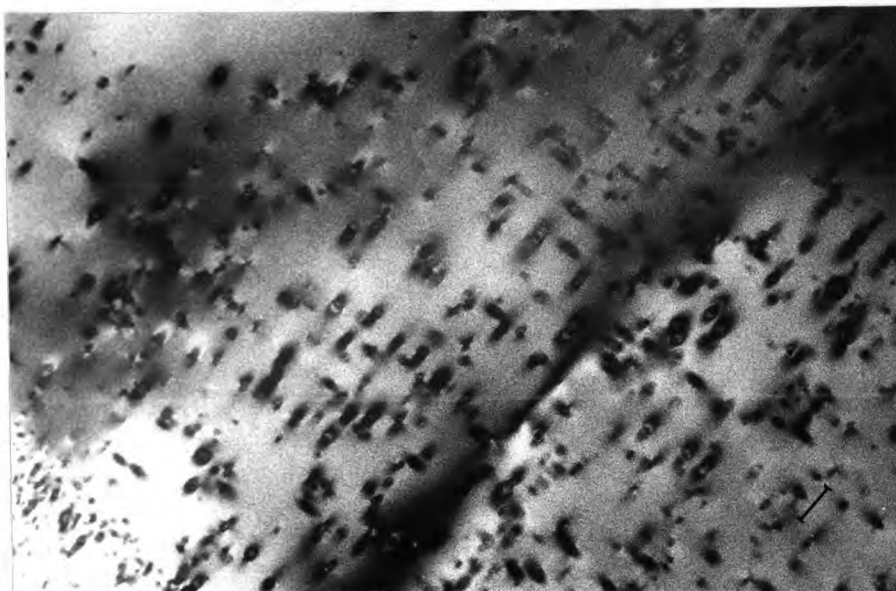


Fig.6.6 Showing defect clusters in the NaCl specimen after an irradiation dose of 1.5×10^{-11} coulomb/ μ^2 . (Marker: 1000 Å along $\langle 100 \rangle$)

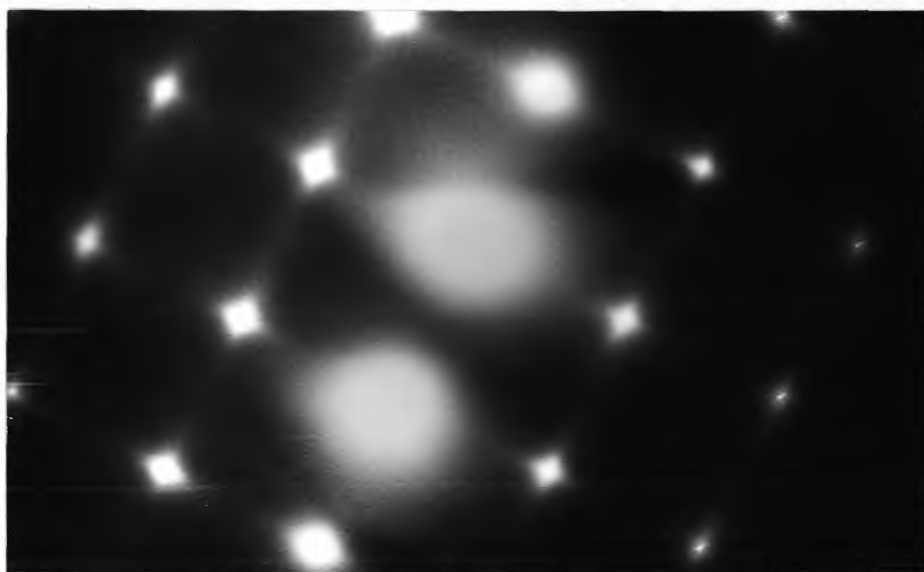


Fig.6.7 Diffraction pattern of the above area showing spiking along $\langle 100 \rangle_r$.

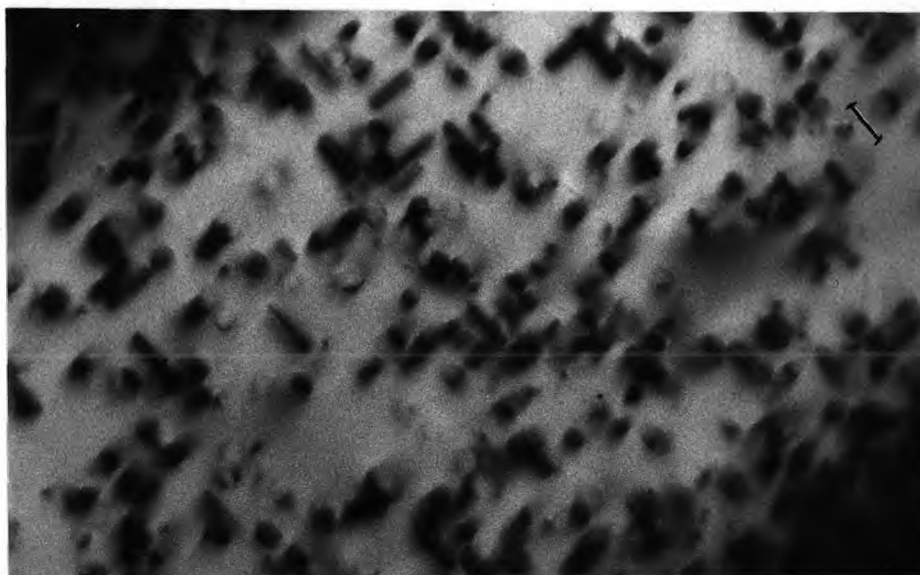


Fig.6.8 Showing the increase in size of the defect clusters. (Marker: 1000 Å along $\langle 100 \rangle$)

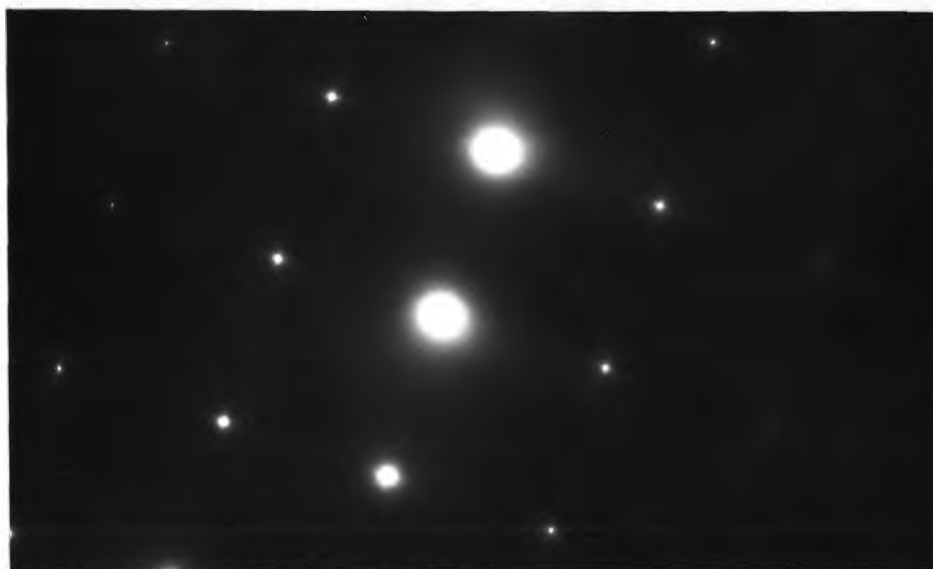


Fig.6.9 Diffraction pattern of the above area showing decrease in the spiking.

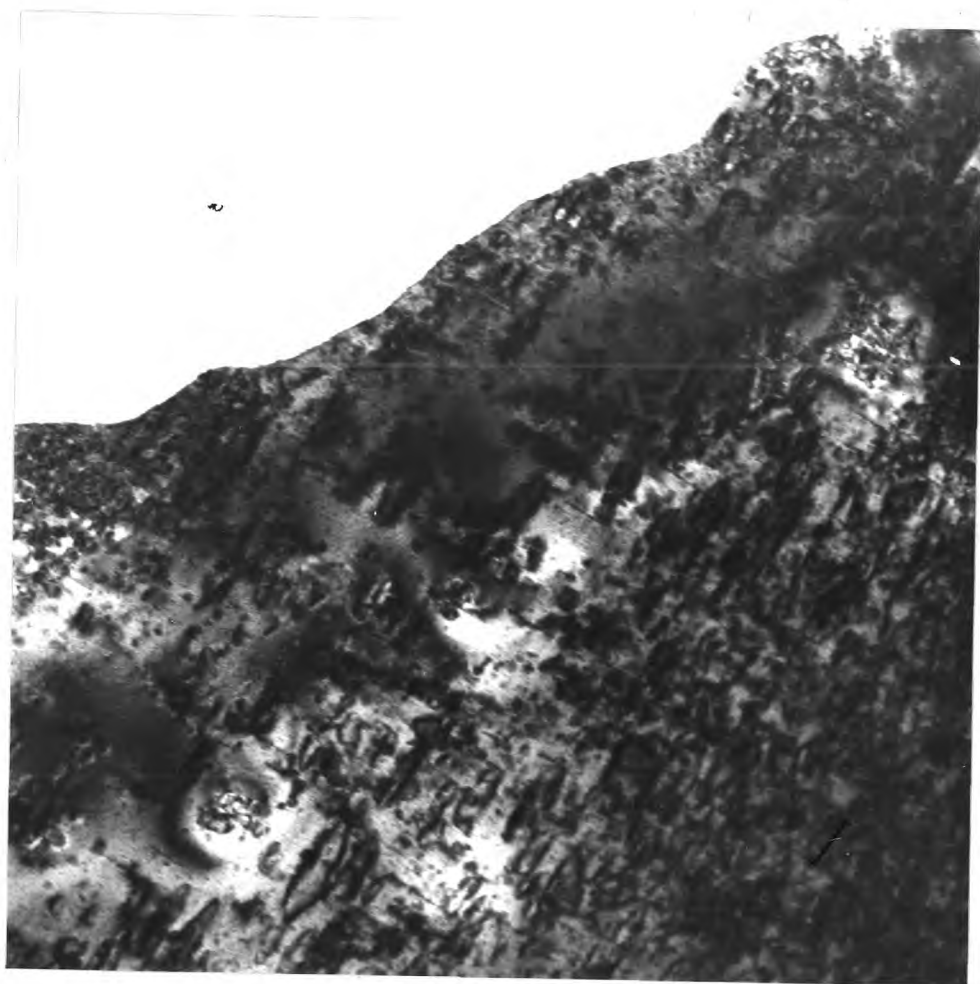
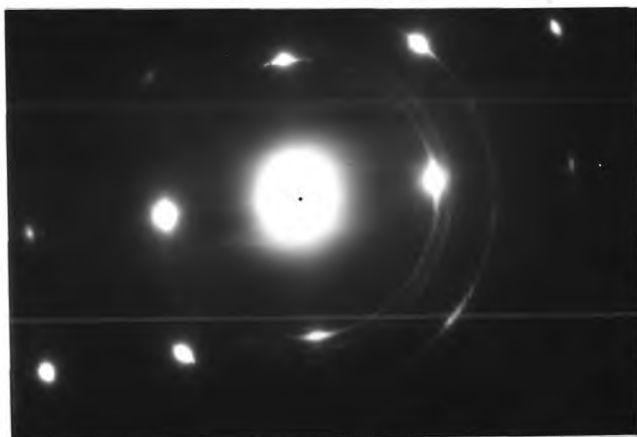
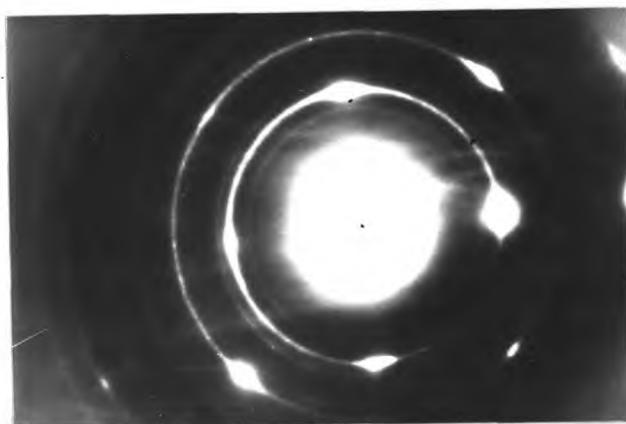


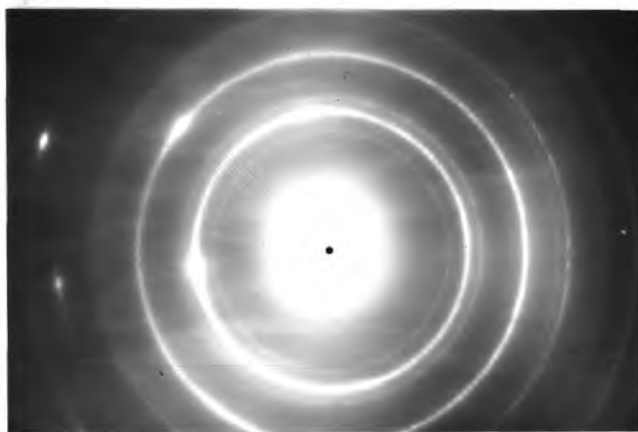
Fig. 6.10 Showing the defect clusters overlapping one another. (Marker, 1000 Å, along $\langle 100 \rangle$)



(a) Showing the beginning of polygonization.



(b) Progress of polygonization.



(c) Nearly complete polygonization.

Fig.6.11 Showing the polygonization of NaCl specimen in the electron microscope, due to high beam intensity.

caused by any one or a combination of the following mechanisms. (1) Rise in the temperature of the specimen due to the absorption of the beam energy. (2) Direct knock-out of the ions from their lattice sites by the beam electrons. And (3) Removal of one or more of the valance-electrons from the ions due to interaction with the beam electrons and thus rendering ions unstable in their lattice sites which is followed by the displacement of the ions and creation of point defects.

6.7.1 Rise of specimen temperature due to the absorption of beam energy :-

At the conditions of the early stages of the damage, i.e. due to a beam of 2×10^{-10} amp spread over an area of $\sim 100 \mu^2$, the calculated rise in the specimen temperature, assuming that the whole of the beam energy has been converted to heat and conducted out through the specimen, is of the order of 5°C (calculation has been shown in Appendix II). In practice however, only a fraction of the beam is absorbed and actual rise of the specimen temperature is possibly of the order of $2 - 3^\circ\text{C}$. It is seen therefore that the damage observed at the low beam intensities is not likely to be caused by the rise

in the specimen temperature.

However, it may be noted that by deliberate increase of the beam intensity and by focusing the beam it is possible to raise the temperature sufficiently to cause local melting and evaporation of the NaCl specimen.

6.7.2. Direct knock-out of ions from their lattice sites by the beam electrons :-

To knock an ion out from its lattice site and to put it into an interstitial position, the bombarding electron must be able to transfer energy above the minimum energy for displacement ' E_d ' to the ion. A simple method for estimating this energy ' E_d ' has been suggested by Seitz (1949). If ' E_c ' is the energy of sublimation, that is the energy required to remove an atom or an ion from a surface site, then twice as much energy will be required to remove an ion from an internal site because twice as many bonds have to be broken. To overcome the lattice opposition in moving and placing the ion in an interstitial site, additional energy of the order of $2E_c$ will be needed. So E_d is about four times E_c . In most solids E_c is in the region of 5 - 6 eV and E_d therefore in the region of 20 - 25 eV. The values of E_d found

experimentally in metals and semiconductors are in good agreement with the above estimate.

The experimental values of E_d for ionic solids are not available. Balarin (1964) pointed out that in the rock salt structure there is a possibility of E_d being substantially lowered due to the focussing collision of anions in the close-packed $\langle 110 \rangle$ directions. He argued that if the colliding anion can overcome the repulsive interaction of the two cations lying midway between the next anion in $\langle 110 \rangle$ directions, a replacement can take place. Balarin calculated the height of this barrier at the saddle-point. Assuming Born-Mayer type repulsive potential he found the barrier height for displacement of Cl^- in NaCl to be 1.69 eV.

Pooley (1965) carried out a machine calculation for $\langle 110 \rangle$ replacement sequence taking into account also the long range coulomb interaction and using Born-Mayer potential with parameters deduced by Fumi & Tosi (1964). The replacement threshold was calculated by giving increasing ^{amount of} energy to the ion till a stable defect configuration was achieved. The minimum distance of separation between the anion vacancy and the interstitial for a stable defect was found to be twice the distance of

the ions in $\langle 110 \rangle$ directions. The replacement threshold energy for Cl^- in NaCl ^{was} found by this machine calculation to be between 7 and 8 eV.

The maximum energy that an electron can transfer to an ion is given by the relation (Dienes & Vineyard, 1957)

$$E_{\text{max}} = 2E (E + 2mc^2) / Mc^2$$

where E and m is the energy and the mass of the electrons, M is the mass of the ion and c is the velocity of light.

The maximum energy that an 100 KeV electron can transfer to an Cl^- ion is 6.2 eV. So even with the help of focussing collision, the probability of direct displacement of a Cl^- ion in NaCl due to 100 KeV electrons is very small.

Focussing type collision in the cation sublattice of NaCl is not envisaged, because focussing can not take place if the effective radius of the colliding ions is less than a quarter of the distance between the ions. The effective radius of Na^+ ions is $< 0.95 \text{ \AA}$ and the distance between the Na^+ ions is $3.98 \text{ \AA}$.

However due to the small mass and size of the cations one would expect it to be easier to produce defects by direct displacement in the cation sublattice.

But cationic defects are not found in the normally irradiated alkali halides. It is only in irradiated LiF that there is some evidence (Kenzig, 1960) for centers associated with cation vacancies.

The main difficulty for the direct displacement to be the operating mechanism in the amount of defect yield. Even assuming that each beam electron succeeds in displacing an ion the number of point-defects produced (either vacancies or interstitials) would be equal to the number of electrons absorbed. But the number of point defects that are necessary to account for the observed damage at the early stages and specially the density change of the irradiated specimens is much higher than the total number of electrons absorbed. A more efficient mechanism than the direct displacement, must be operative to produce the observed damage.

6.7.3. Defect production through ionization or excitation of the lattice electrons :-

The bombarding electrons interact strongly with lattice electrons raising the lattice electrons either to a higher bound state or to the conduction level and thereby removing them from the parent ions. The mechanisms through

which lattice defects are produced from this excited and ionised states have been examined by several workers. Seitz (1954) first suggested that if electron-hole recombination or exciton-decay takes place near a dislocation jog, sufficient energy is released (5 - 8 eV) to create a vacancy pair (Schottky defect) and these vacancies are assisted to diffuse away from the dislocations by the excess thermal energy generated by this process. The mechanism is essentially inhomogeneous, such that higher density of defects are expected around the dislocations. But in practice coloration is found to be homogeneous throughout the irradiated crystals. Also there is lack of evidence for dislocation climb during vacancy production, which is an essential feature of this mechanism.

Varley (1954) then suggested that if an anion loses more than one electron through interaction with the ionising radiation it is left in a positively charged state. A positively charged ion is highly unstable in an anion site and it is ejected to an interstitial position creating a Frenkel defect in the anion sub-lattice. However for the Varley mechanism to be operative the probability of multiple ionisation should be sufficiently high to account for the observed defect yield, the duration

of the lifetime in multiply-ionised state should be longer than the lattice vibration period (10^{-13} sec) for ejection to take place and the ejection distance should be sufficient to result in a stable defect configuration.

Multiple ionisation can take place in two ways. By successive stripping of the outer electrons or by Auger process (i.e. removal of an inner shell electron which is then filled by an outer shell electron with simultaneous ejection of one or more outer electrons).

For multiple ionisation cross section Varley proposed a semi empirical relation $\sigma_n = \sigma 10^{-n+1}$, where σ_n is the cross section for n-fold ionisation and σ is the cross section for single ionisation. This relationship is in good agreement with the data for ionisation in rare gases (Massey & Burhop, 1952). A calculation on the assumption that each multiple ionisation leads to the formation of a stable Frenkel-type defect, yields a value of 600eV to 1100 eV per defect which is also in good agreement with Rabin and Klick's (Rabin & Klick, 1960) experimental value of 1000eV absorbed per F center in KCl, KBr, NaF, LiF. However if centers are also taken into account this value becomes too large compared to 190 eV per vacancy found by Ritz (1966) in KBr irradiated at 5°K with

unfiltered 50KV x-rays.

To calculate the life time of the doubly ionised state of the halide ion Howard and Smoluchowski (1959) treated the problem as the time needed to capture a conduction electron and arrived at a value of $\sim 10^{-12}$ sec which they considered long enough for ejection to occur. Dexter (1960) however treating the problem as a separation of two holes localised on a single lattice site found that the holes will separate within 10^{-15} sec. In other words a doubly ionised halide ion will capture an electron from one of the neighbouring anions in a much shorter period than is necessary for ejection to take place. And this will render ^{the} Varley mechanism inoperative. Klick (1960) then suggested an alternative way of vacancy formation. After the capture of an electron from a neighbouring anion by the positive halide ion a halogen molecule will be formed. Halogen molecule has a small volume and will move into one of the anion sites leaving a vacancy. ^{The} subsequent jump of an anion into the vacancy will separate the vacancy from the halogen molecule. Capture of an electron each by the halogen molecule and the vacancy will convert them to an H-center and an F-center. It is to be noticed that Klick mechanism will also account for defect formation by

simultaneous single ionisation of two adjacent anions.

Both multiple ionisation of single anion and simultaneous single ionisation of two adjacent anions have experimental support for being the initial condition of defect production.

Sharma and Smoluchowski (1965) found appreciable increase in F center yield in KCl as the energy of irradiating x-ray just exceeded the K edge (2.826KeV) for chlorine which they attributed to higher efficiency of double ionisation through Auger process for K-shell ionisation.

Ritz (1964) on the other hand, after careful study of defect yield in KCl, KBr, NaCl, LiF with x-rays of different energies and electron at 2MeV came to the conclusion that his result is more in accord with defect production by simultaneous ionisation of adjacent anions.

However as Dexter's (1960) calculation showed that a double ionisation will within 10^{-15}sec lead to the condition similar to single ionisation of adjacent ions (except for the energy term due to electron exchange) it is possible that both multiple ionisation and single ionisation of adjacent ions are capable of producing defects.

Another mechanism of defect production have been

suggested by Konitzer and Hersh (1966) and Poole (1966). This is through the non-radiative decay of excitons. F center yield in uv and x-ray irradiated KI has been found to increase very rapidly between 90° to 110°K with corresponding decrease in luminescence efficiency. Pooley calculated the probability of non radiative decay of exciton as a function of temperature and found that in the above mentioned temperature range there is also a sharp increase in the probability of non radiative decay in KI. In NaCl, KCl and KBr however this probability is already high at 4°K and increases slowly with temperature so the effect is not discernable.

An exciton has a $\langle 110 \rangle$ structure with an excited electron bound to two neighbouring anions. Return of the electron to the ground state in a non radiative mode will convert the electronic energy to kinetic energy which will initiate a replacement collision in $\langle 110 \rangle$ direction.

Pooley made computer calculation for threshold energy of replacement for alkali halides, assuming Born Mayer interaction between colliding anions and also taking into account long range coulomb interaction with other ions. He found that except for LiBr, LiI and NaI, replacement is possible in all other alkali halides.

V centers (a hole is bound to two neighbouring anions) when recombining with an electron will also behave similarly to exciton decay.

Pooley pointed out that the above mechanism is consistent with the observation that late stage coloration is suppressed by the presence of divalent cations like Pb^{++} , Ca^{++} , Sr^{++} . He argued that if direct electron V center recombination is necessary for late stage F-center production then the divalent cations by providing an alternative path for recombination can reduce the F center yield. Divalent cations are known to be good electron traps and can act as recombination centers where holes are mobile. At low temperature (below 78°K) however, this inhibiting property is lost because the holes are no longer mobile and cannot reach divalent ions before direct recombination takes place.

It is seen that multiple ionisation of an anion, simultaneous single ionisation of two adjacent anions and also exciton and V-center decay can lead to the formation of Frenkel type defects in anion sublattice of alkali halides.

The mechanisms for the production of defects in the cation sublattice have not been so well investigated,

probably because cationic defects are not normally encountered in irradiated alkali halides.

Ionisation of a cation makes it more positive and increases its Madelung energy and this makes more difficult for it to leave its lattice site. However, Varley (1962) suggested that a multiple ionised anion can some_time replace a cation, forcing the cation into an interstitial position. After electron capture, ^{the}anion will fall back to its vacancy creating a Frenkel defect in the cation sublattice.

Another possibility is that, where bonds are already broken due to the presence of one or more anion vacancies, the energy released after a cation returns to the ground state from the ionised or excited state may be sufficient to displace it into an interstitial position and thus create a cationic Frenkel defect.

6.8. Defect yield due to ionisation process :-

Varley (1962) estimated that about 600 eV need be absorbed to produce a double ionisation in NaCl. Ritz (1964) calculated that 400-800 eV is absorbed to produce a pair of singly ionised anions. Observed efficiency of

point defect (namely F-center) production from these initial conditions has been found to vary with the temperature of the specimen (Rabin and Klick, 1960), the rate of irradiation (Etzel, 1962) and the energy of the irradiation (Ritz, 1964). An extrapolation of Etzel's data for the present rate of irradiation yields a value of about 5,000 eV per F-center.

From the change in density of the irradiated specimens Fig 6.12, the increase in volume due to the absorption of each 100 KeV electron was found to be about $24a^3$, where a is the interionic distance. Volume increase per F-center in irradiated KCl has been determined by Blackmann and Thomman (1966). They found a volume increase of $1.36 \pm 0.04 a^3$ per F-center. If it is assumed that a similar volume change also takes place in NaCl then the energy absorbed per F-center is about 5,600 eV.

6.8.1. The rate of energy dissipation of beam electrons in NaCl :-

The rate at which accelerated electrons lose energy in a solid through electron-electron inter-actions, is given by the well known Bethe (1953) equation.

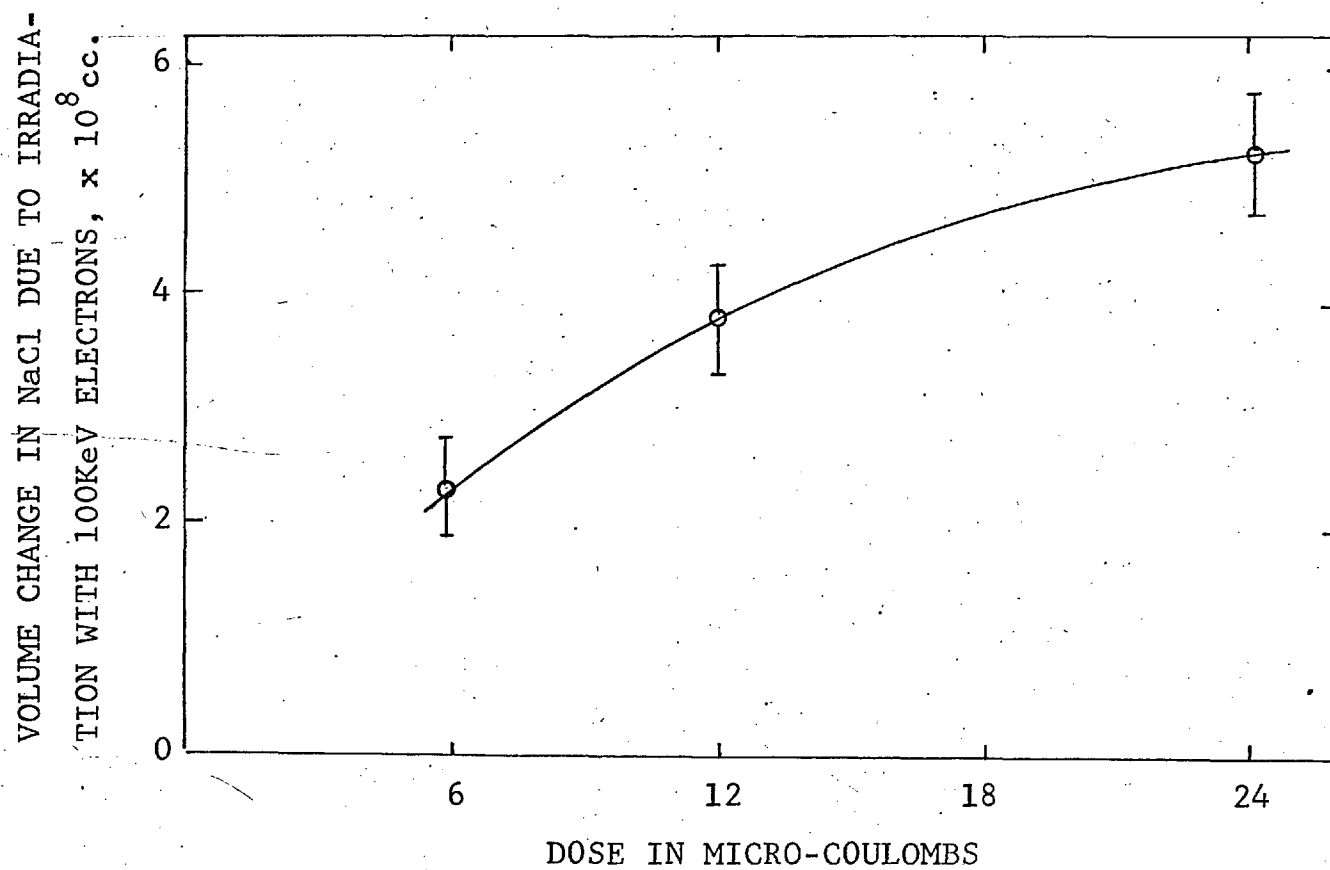


Fig. 6.12. Volume increase in the irradiated NaCl specimens as calculated from the density changes.

$$\frac{dE}{dx} = 4\pi n_e Z e^4 / m V^2 \cdot \ln\left(\frac{m V^2}{\bar{I}} \cdot c/2\right)$$

where dE/dx is the rate at which energy is dissipated by the electron per unit path length, $n_e Z$ is the number of electrons per unit volume, e , m & V are the charge, mass and velocity of the accelerated electrons, $\bar{I}$ is the average ionisation potential and e is the exponential constant.

A plot of dE/dx vs x in NaCl (assuming $\bar{I} = 160\text{eV}$) has been shown in Fig 6.13. However, energy dissipation as a function of depth as calculated from the Bethe equation does not take into account the effect of scattering of the electrons away from the initial direction of the beam. Spencer (1955) has examined theoretically the effect of scattering and slowing down of the electrons on the rate of energy dissipation at different depth. Huffman, Cheka, Saunders, Ritchie and Birkhoff (1957) have experimentally determined the energy dissipation of 57 KeV to 126.5 KeV electrons in aluminium. They found that their data agreed satisfactorily with Spencer's theory. The general feature of Spencer's theory is that the effective range of the accelerated electrons is about 80% of that predicted by the Bethe equation and the

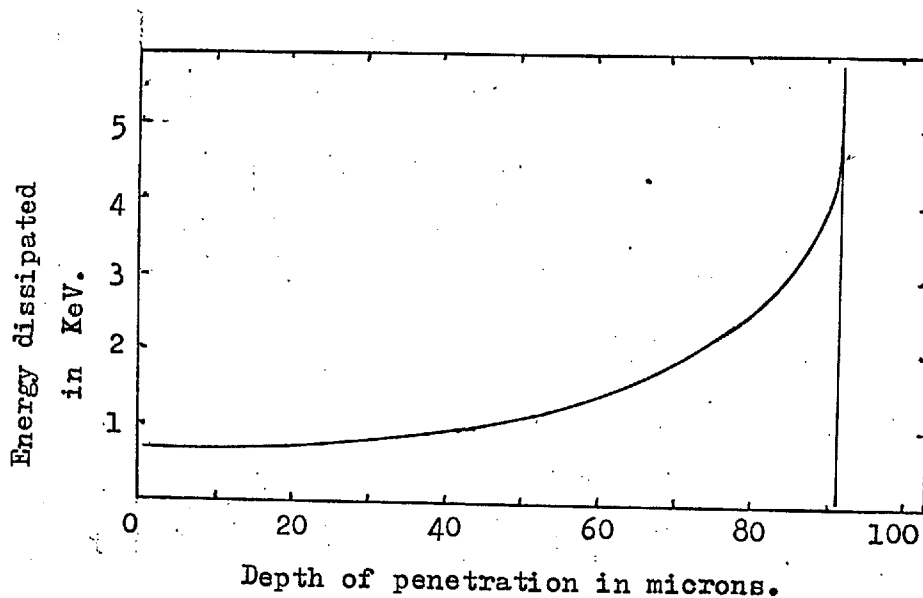


Fig.6.13 Energy dissipation of 100 KeV electrons in NaCl, According to Bethe equation.

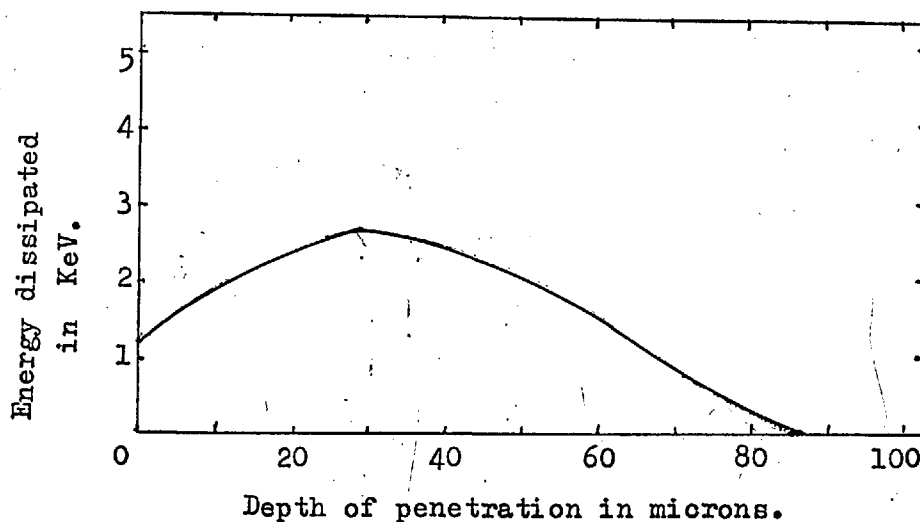


Fig.6.14 Showing the energy dissipation of 100 KeV electrons, in NaCl. According to Spencer's (1955) theory, (Schematic).

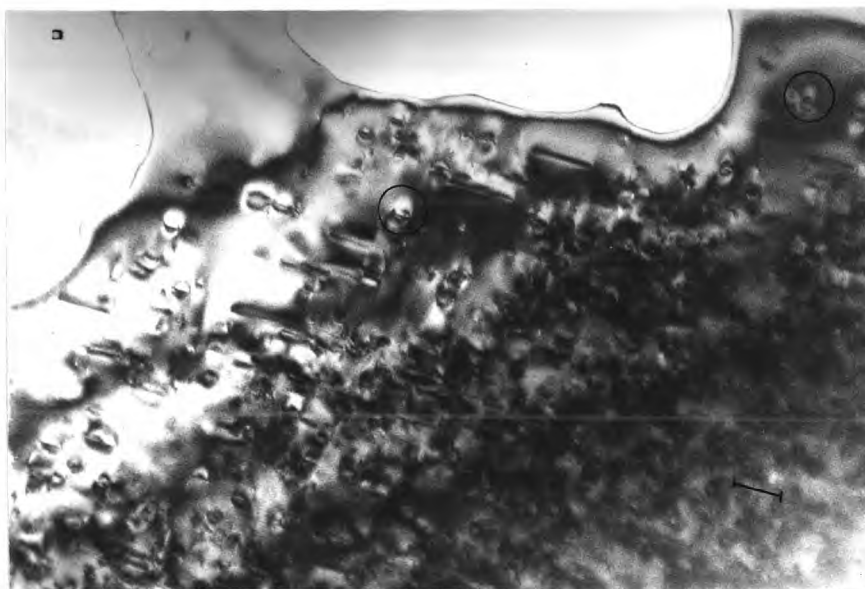
energy dissipation reaches a maximum at a depth of between $0.25-0.3$ of the total range of the electrons as shown in Fig 6.14.

The range of 50 KeV, 70 KeV and 100 KeV electrons in aluminium ($I = 150$ eV) has been calculated by Spencer to be 0.0056 gm/cm², 0.01 gm/cm² and 0.018 gm/cm² respectively. Equivalent depths in NaCl would be 25μ , 45μ and 82μ respectively. The depths of penetration of 50 KeV, 75 KeV and 100 KeV electrons in NaCl have been found to be 23μ , 39μ and 60μ respectively Fig 6.5.

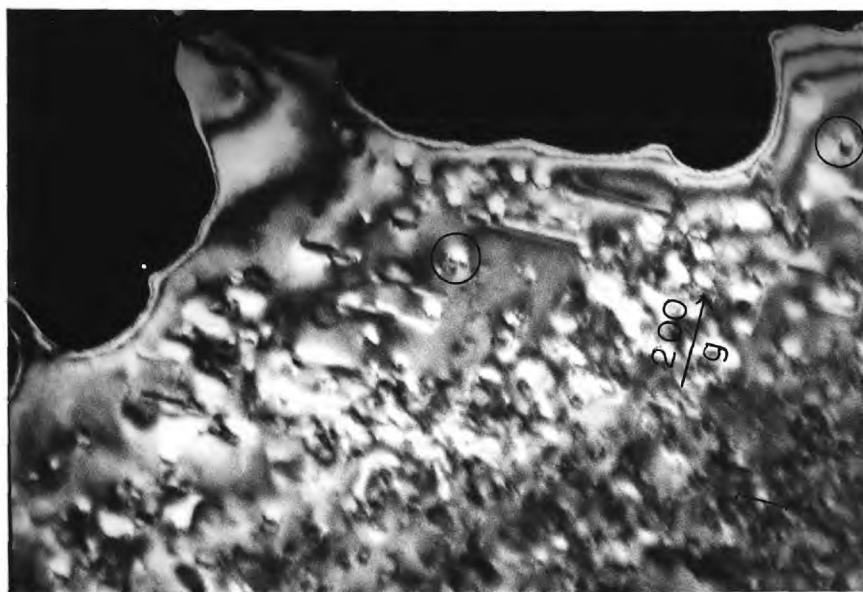
The initial rate of energy dissipation of 100 KeV electrons in NaCl as calculated from the Bethe equation is about 0.75 KeV/ μ and from the Spencer's theory, about 1.2 KeV/ μ . The number of point defects that would be generated due to a dose of 1.5×10^{-11} coulomb/ μ^2 of 100 KeV electrons (assuming 5,600 eV is needed to produce a point defect) is of the order of 2×10^{19} per cubic cm. The number of defect clusters that has been observed due to the above dose is about 2×10^{15} per cubic cm. Assuming they are loops due to the point defects, the clusters would account for about 10^{19} point defects per cubic cm.

6.9. The nature of the defect clusters :-

Whether the defect clusters are due to vacancies or interstitials that could not be determined with certainty, as the beam continually damage the specimen a proper Ashby-Brown type analysis was not practicable; because, during the time required to tilt and adjust the gun assembly to obtain high resolution dark field picture, the extra damage caused to the specimen will make the comparison with the bright field picture very difficult. A low resolution dark field was therefore tried. Fig 6.15. Low resolution dark field is not always reliable due to the effects of the spherical aberration. However if the evidence of this low resolution dark field is taken at its face value, the contrast shown at some of the asymmetrical images are of the vacancy type. It is possible that when a thin specimen is irradiated, the more mobile species of the defects may diffuse to the surface (chlorine interstitials in NaCl may diffuse easily by interstitialcy mechanism) leaving predominantly the less mobile species inside the specimen and with the progress of irradiation the concentration of the less mobile species builds up sufficiently to cause clustering.



(a)



(b)

Fig.6.15 (a) Bright-field and (b) Dark-field picture of the defect clusters, showing that the contrast at some of them are of vacancy type. (Markers:1000 Å along $\langle 100 \rangle$).

6.10. Possible ways of reducing the specimen damage :-

6.10.1. Increasing the beam potential :-

It may be seen from the Bethe equation that the rate of energy dissipation of the electrons to a first approximation varies inversely as the velocity of the electrons. Spencers calculation also shows that the initial rate of energy dissipation decreases with increasing beam voltage. Bahr, Kobayashi and Zeitler (1966) have found that the damage caused in polyethylene crystals by the electrons from 75 KeV to 300 KeV is inversely proportional to the beam voltage. Yagi and Honjo (1964) have been successful in observing dislocations and precipitates in NaCl by using 150 KV accelerating potential. They thinned their specimens by beam flashing technique and claimed that the defects observed by other workers are due to amorphous surface layer caused by solution thinning. That the observed damages are not surface features can easily be seen for the strain contrast due to the defect clusters and its effect on the diffraction spots. Very thin regions are also comparatively damage free even in solution thinned specimens as shown in Fig 6.16. This is because the beam electrons dissipate less energy in the thin area and also there is less probability for the beam

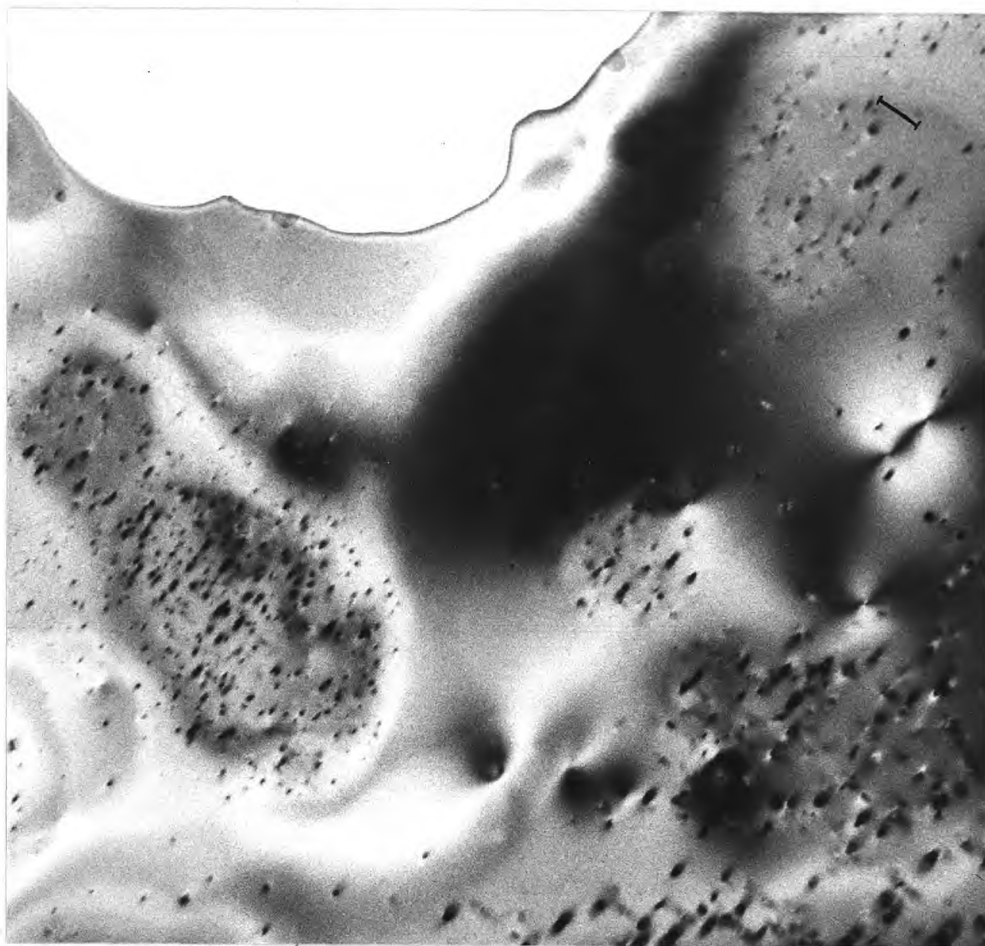


Fig.6.16 Electron micrograph of NaCl specimen showing that the thinner areas are comparatively damage free. (Marker: $1000\text{ \AA}$ along $\langle 100 \rangle$).

electrons to suffer large angle scattering. The smaller number of defects thus produced, can easily reach the surface and therefore do not attain a sufficient supersaturation in the specimen, to produce clusters. Increasing the beam voltage will allow observations through increased thickness of the specimen, without causing this supersaturation build-up.

6.10.2. Lowering the specimen temperature :-

Lowering the specimen temperature can reduce the damage in two ways. First, by reducing the thermal activation necessary to produce the point defects from the ionized and excited states and second, by reducing the mobility of the defects produced and thereby prevent them from clustering. Hirsch (1967) has found that, cooling the NaCl specimen to liquid Helium temperature appreciably reduces the damage due to the beam in the electron microscope.

S U M M A R Y A N D C O N C L U S I O N S

It has been found in NaCl doped with divalent chlorides that the precipitate structures bear a close correlation with the structure of the divalent chloride used for doping. In the case of crystals doped with CdCl_2 , MnCl_2 and MgCl_2 , all of which have the layer structure of CdCl_2 , the precipitates are also similar in shape and volume ratio and presumably have the same structure i.e. that of $\text{CdCl}_2 \cdot 6\text{NaCl}$. While CaCl_2 which has a distorted Rutile structure, produce platelet precipitates in $\{111\}$ plane of NaCl and the precipitate has a structure similar to CaCl_2 . BaCl_2 on the other hand, has a Fluorite structure and the precipitates are thin, long plates in the $\{522\}$ plane of the NaCl matrix.

The solution temperatures of the precipitates coincide with the temperatures at which quench hardening has been observed in doped NaCl. This confirms the view that quench hardening is due to divalent ions going into solution from the precipitate and being dispersed throughout the matrix in the form of dipoles or dipole-aggregates.

Ageing of the quenched crystals show that precipitates do not appear until ageing temperature is fairly high (within about 50°C of the solution temperature of the

precipitates). From this observation and the observations by other workers in dielectric loss, paramagnetic resonance, and mechanical properties, it is evident that divalent chlorido doped NaCl behaves similarly to some metal systems where quenching produces metastable clusters and stable precipitates can be obtained after ageing above the metastable solvus.

The precipitates in the quench-aged crystals appeared to have nucleated on the quenched in dislocation loops and helices. This indicates that the dislocations act as preferential sites for the nucleation of the precipitates.

The damage of the NaCl specimens in the electron-microscope has been indicated to be, primarily due to the generation of point defects through the ionization and excitation processes, and the subsequent clustering of those point defects. The damage may possibly be reduced by lowering the specimen temperature. This will reduce the availability of the thermal activations required for the conversion of electronic higher energy states into lattice defects and the migration of these defects to form clusters. The damage may also be reduced by increasing the beam voltage (within the sub-relativistic range) and thereby

decreasing the amount of energy dissipated in the specimen foil, by the beam electrons.

SUGGESTED FUTURE WORKS

Natural follow-up to the present investigations are the x-ray crystallographic studies of the precipitates in MnCl_2 , MgCl_2 and BaCl_2 doped NaCl . Also, as it has been found in the cases of CdCl_2 , MnCl_2 and MgCl_2 doped crystals that the divalent chlorides with CdCl_2 structures when added as a dopant in NaCl , form precipitates which are similar in shape and volume ratio and probably have the same crystallographic structure, namely that of $\text{CdCl}_2 \cdot 6\text{NaCl}$, it may be worthwhile to investigate NaCl doped with other divalent chlorides which have the CdCl_2 structure such as CoCl_2 , FeCl_2 , NiCl_2 and ZnCl_2 , to find out whether this trend continues.

It has been suggested in the Discussion that the precipitates in MnCl_2 doped KCl also probably has the structure of $\text{CdCl}_2 \cdot 6\text{NaCl}$. X-ray investigation of MnCl_2 doped NaCl may be under taken to confirm or contradict this suggestion.

It has been found that the size and number of the precipitates and also the amount of dopant that precipitate out depends upon the cooling rate. It may be worthwhile to study how the cooling rate effects the mechanical proper-

ties of the doped crystals.

Finally, the differential density of nucleation that has been observed and exploited in the present investigations, may itself be studied with reference to the epitaxial growth of thin films.

A P P E N D I X I

Derivation of the expression for the equilibrium density of nuclei during surface decoration, Eq. 5.2.

Eq. 5.2 can be derived in two ways.

(a) From the mean life time of an adsorbed atom on the substrate before it is captured by a growing nucleus.

At the 'steady state' the net number of atoms reaching the substrate over unit area in unit time, R_n is equal to the number of atoms captured by the existing nuclei during the same time. If the average capture radius of the nuclei be σ and the density of the nuclei on the substrate be D_s then the mean free path of a moving atom is $1/(2\sigma D_s)$, and if 'V' is the velocity of the atoms on the substrate, then their mean life time before running into a nucleus is

$$\tau = 1/(2\sigma D_s V) \dots\dots\dots I.1$$

If the density of atoms on the substrate is maintained at C_0 the 'equilibrium' density, i.e. the density at which nucleation probability is low for the time scale of evaporation, then the number of atoms reaching the nuclei is

$$C_0/K = R_n = 2C_0 \cdot \sigma_s \cdot D_s \cdot V$$

$$\text{or } D_s = R_n / (2C_0 \cdot \sigma_s \cdot V) \dots\dots\dots \text{I.2}$$

The velocity of the atoms on the substrate is given by the jump frequency 'f' times the jump distance 'a'.

$$V = f \cdot a.$$

The jump frequency 'f' is again given by

$$f = K \cdot \nu \cdot \exp (Q_D/kT) \dots\dots\dots \text{I.3}$$

where K is the number of available jump sites,

ν is the vibrational frequency of the adsorbed atom and Q_D is the activation energy of a jump or in other words the activation energy for surface diffusion.

Substituting I.3 in I.2 we have

$$D_s = \frac{R_n}{2C_0 \cdot \sigma_s \cdot K \cdot a \cdot \nu} \exp (Q_D/kT) \dots\dots \text{5.2.}$$

(b) Derivation of Eqn. 5.2 from the diffusion of atoms to the nuclei.

For the purpose of this calculation we can imagine that the substrate is divided into equal squares and the nuclei are at the center of each square, as in Fig. I.1.

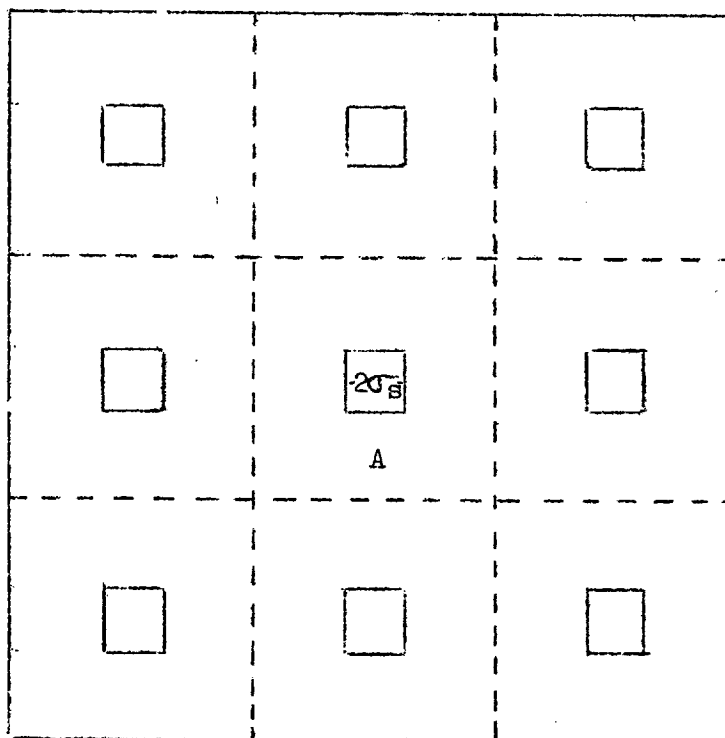


Fig. I.1

At the 'steady state' the net number of atoms reaching each square ' r_n ' is equal to the number of atoms diffusing to the nucleus.

Now, the number of atoms diffusing to the nucleus in unit time is equal to the number of atoms within a jump distance from the nucleus times half their jump frequency. This is because the atoms within the jump distance

of a nucleus have a probability of $\frac{1}{2}$ for jumping into the nucleus and a probability of $\frac{1}{2}$ for jumping away from the nucleus.

As the atoms on the substrate can approach the nucleus from only one side the density of atoms close to the nucleus 'c' will be about half the average density of atoms on the substrate, or 'c' = $C_e/2$

Therefore the number of atoms within the jump distance of the nucleus is

$$n = 8\sigma_{s.a.}C_e/2$$

and the number of atoms jumping into the nucleus is

$$n.f/2 = 2\sigma_{s.a.}C_e.f = R_n.A$$

where A is the area of the squares.

The density of nuclei

$$D_s = \frac{1}{A} = \frac{R_n}{2\sigma_{s.a.}C_e.f} \dots\dots\dots I.4$$

Substituting I.3 in I.4 we have

$$D_s = \frac{R_n}{2\sigma_{s.a.}C_e.K.v) \exp (Q_D/kT) \dots\dots\dots 5.2$$

A P P E N D I X I I

Calculation of the rise of temperature of the specimen due to absorption of the beam energy.

The upper limit of the specimen temperature can be estimated by assuming that whole of the beam energy is converted to heat and conducted out through the specimen without any loss at the surface by radiation or convection.

A situation which is most commonly met in practice is a wedge shaped specimen with the beam near the edge as in Fig II.1 (Heating is likely to be maximum in this condition of the transmission of the beam through the thin areas is not allowed for).

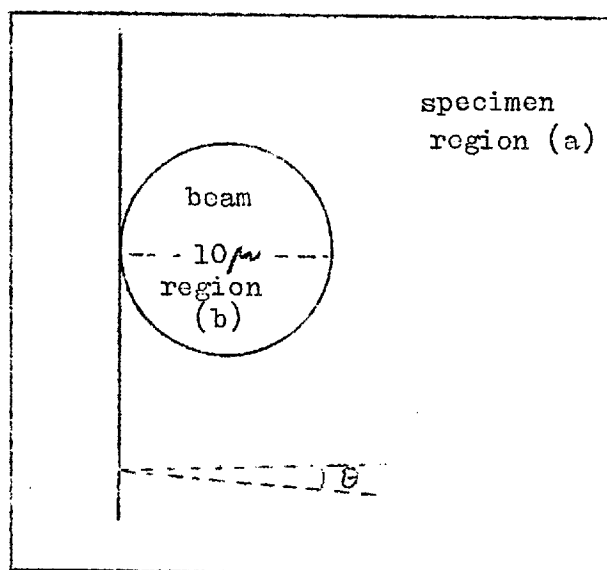


Fig. II.1

The diameter of the beam is about 10μ and typical wedge angle θ is about 0.05 radian. For the purpose of calculation the specimen can be divided into two regions, (a) outside the beam and (b) within the beam.

The surfaces of equal temperature gradient to a first approximation can be taken as cylindrical with the axis through the center of region (b).

For the region (a) then

$$Q = -2\theta\sigma(r + \delta)^2 \frac{dt}{dr} \dots\dots\dots \text{II.1}$$

where Q is amount of thermal energy received by the specimen from the beam in unit time.

σ is the thermal conductivity of the specimen.

r is the distance from the center of the beam.

δ is the correction term which has a value of about 3.86μ for the distance between the edge of the specimen and center of the beam of 5μ

Integrating eqn (II.1)

$$T_{5\mu} = -Q/(2\theta\sigma) \int_{5\mu}^{\infty} dr/(r + \delta) + T_0 \dots\dots\dots \text{II.2}$$

$$\text{or } T_{5\mu} = Q/(2\theta\sigma) \cdot 1/(8.86) + T_0 \dots\dots\dots \text{II.3}$$

where $T_{5\mu}$ is the temperature at the edge of the beam and T_0 is the temperature of the specimen when $Q = 0$

For region (b) Q_r the amount of energy received within

a radius r is $= Q \times r^2 / (5\mu)^2$

and the flow eqn is $Q \cdot r^2 / (5\mu)^2 = -2\pi\sigma \cdot r \cdot 5\theta \cdot \frac{dt}{dr} \dots \text{II.4}$

Integrating eqn II.4 we have

$$T_c = - Q / (2\pi\sigma 5\mu^3 \theta) \cdot \int_0^{5\mu} r \cdot dr + T_5 \dots \text{II.5}$$

$$\text{or } T_c = Q / (4\pi\sigma 5\mu \theta) + T_5 \dots \text{II.6}$$

Value of Q for a beam of 2×10^{-10} amp at 100 KV if we

assume whole of its energy is converted to heat, is than

$$2 \times 10^{-10} \times 10^5 \times 2.39 \times 10^{-1} = 4.78 \times 10^{-6} \text{ caloric/sec}$$

σ the thermal conductivity of Sodium chloride at 30°C

is 1.5×10^{-2} caloric/sec/cm/degree (Ballard, McCarthy and Davies. 1950).

Combining eqn(II.3) and (II.6) and putting the values of the parameters we have

$$T_c = 4.63^\circ\text{C} + T_0$$

or in other words, at the low beam intensity the temperature rise in the irradiated area is less than 5°C ,

However it is to be noticed that the temperature rise is proportional to the beam intensity and inversely proportional to the beam diameter. So, by increasing the

beam intensity by 2 to 3 magnitude and by focussing the beam it is possible to cause sufficient temperature rise to melt and evaporate the specimen locally.

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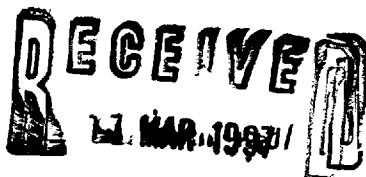
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Ministeriet for Fødevarer, Landbrug og Fiskeri
Statens Planteavlsforsøg

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Jørn Nygaard Sørensen, Kaj Henriksen & Holger Hansen
Afdeling for Frugt og Grønsager
Kirstinebjergvej 6
5792 Årslev

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Sammendrag

Udbyttet og optagelsen af tungmetaller i issalat, hvidkål, gulerod og porre er undersøgt 1, 2 og 9 år efter tilførsel af 0, 5, 100 og 200 t tørstof ha^{-1} af komposteret dagrenovation og spildevandsslam i 1978.

Hverken udbyttet eller indholdet af Mn, Cu, Zn, Pb og Cd var påvirket af komposttilførslen på nogen entydig måde. Indholdet af Cd og i visse tilfælde også Pb faldt dog ved stigende tilførsel af kompost. Tilførsel af store mængder kompost med en pH-værdi på 8 har øget jordens pH og dermed reduceret tilgængeligheden af Cd og Pb.

Nøgleord: bly, cadmium, dagrenovation, forurening, gulerod, hvidkål, issalat, kobber, mangan, porre, slam, spormetal, tungmetal, zink

Summary

Yield and uptake of heavy metals in crisphead lettuce, white cabbage, carrots, and leeks were measured 1, 2 and 9 years after application of 0, 5, 100, and 200 tonnes dry matter ha^{-1} of a compost made of municipal waste and sewage sludge in 1978.

The yield and the content of Mn, Cu, Zn, Pb, and Cd in the vegetable crops were not influenced in any consistent manner. The most obvious result was a decreased content of Cd and in some cases also Pb at an increased application of compost. This effect was caused by a decreased plant availability at increased pH following application of the rather large amounts of alkaline compost.

Key words: cadmium, carrots, crisphead lettuce, copper, heavy metal, lead, leeks, manganese, municipal waste, pollution, sewage sludge, trace element, white cabbage, zinc

Introduktion

Da planter kan optage tungmetaller tilført jorden med komposteret dagrenovation eller spildevandsslam, er der stigende bekymring for, om disse metaller vil indgå i den humane fødekæde (Ekeblad 1982; Hardiman et al. 1984; Thornton og Jones 1984; Crews og Davies 1985). Et myndighedskrav om at slam og andet affald skal deponeres på agerjord vil ofte være i konflikt med et forbrugerkrav om at fødevarer skal være fri for uønskede tungmetaller (Fritz og Venter 1979; Hansen et al. 1986; Knudsen og Kristensen 1987).

Optagelsen af tungmetaller i planter påvirkes af mange forskellige forhold, blandt andet planteart, tilførselsmængde, typen af slam og jordens egenskaber (Sonoda og Hara 1983; Bruemmer et al. 1986; Chu og Wong 1987). Jordens pH er den parameter, der oftest kontrollerer opløseligheden og tilgængeligheden af tungmetaller (Öborn et al. 1995, Brallier et al. 1996).

Målet med nærværende forsøg var at undersøge hvorledes tilførsel af komposteret dagrenovation og spildevandsslam påvirkede udbyttet og indholdet af tungmetaller i den spiselige del af en række forskellige grønsager.

Materialer og metoder

En kompost blev lavet ved at blande dagrenovation og spildevandsslam. Når temperaturen inde i blandingen nåede 65 °C blev komposten stukket om. Denne proces blev gentaget indtil temperaturen var konstant. Den kemiske sammensætning af komposten fremgår af tabel 1. Indholdet af Pb, Cd og Hg var relativt højt og overskrider gældende grænseværdier for anvendelse af kompost til jordbrugsformål (Miljøministeriet 1989). Efterår 1978 blev 0, 5, 100 eller 200 tons kompost-tørstof ha⁻¹ indarbejdet i jorden. Mængden af næringsstoffer og tungmetaller, der således blev tilført fremgår af tabel 2. Forinden komposttilførsel var jordens pH 6.1, Kt 14.8, Ft 7.9 og Mgt 4.4, hvor 1 t-enhed svarer til henholdsvis 1 mg K, 3 mg P og 1 mg Mg pr. 100 g tør jord. Jordens pH blev bestemt efter opslemning i en opløsning af kalciumklorid, K blev ekstraheret med ammoniumacetat, P med svovlsyre og Mg med ammoniumklorid.

I 1979 og 1980 blev der etableret forskellige arter af grønsager, og 3 N-mængder blev tilført. Forsøgene blev anlagt i et split-plot design med 2 gentagelser. Hovedparcellerne, hvortil der blev udbragt kompost, var 20 x 20 m. Disse blev opdelt i delparceller á 100 m² og tilført kvælstof. I hver delparcel blev der dyrket 4 forskellige afgrøder i parceller á 24 m². Afgrøderne var issalat, hvidkål, gulerod og porre. I 1979 blev alle afgrøder tilført 0, 45 eller 90 kg N ha⁻¹. I 1980 blev issalat og gulerod tildelt 0, 67 eller 134 kg N ha⁻¹; hvidkål og porre blev tildelt 0, 105 eller 210 kg N ha⁻¹.

Tabel 1. Tørstof og pH af den i forsøget anvendte kompost samt kemisk sammensætning af tørstoffet i ppm.

Dry matter and pH of the compost and the chemical composition of the dry matter in ppm.

pH	8.0
Tørstof, %	64.5
Aske, % i tørstof	75.3
HCl-uopløselige bestanddele, % i tørstof	41.7
Kvælstof (N)	6440
NH ₃ -N	70
Fosfor (P)	3380
Kalium (K)	2040
Magnesium (Mg)	1520
Jern (Fe)	9600
Zink (Zn)	2080
Mangan (Mn)	600
Kobber (Cu)	440
Bly (Pb)	304
Krom (Cr)	60
Kviksølv (Hg)	6.5
Cadmium (Cd)	2.4
Nikkel (Ni)	12.0
C:N	25

Tabel 2. Mængden af næringsstoffer og tungmetaller i kompost indarbejdet i jorden efterår 1978.

Amount of nutrients and heavy metals in compost incorporated in the autumn 1978.

Kompost t ha ⁻¹	kg ha ⁻¹								
	K	Zn	Mn	Mg	Cu	Pb	N	P	Cd
5	10	11	3	8	2.2	1.5	32	17	0.012
100	204	208	60	152	44.0	30.4	640	338	0.240
200	408	416	126	304	88.0	60.8	1280	676	0.480

Til vurdering af langtidseffekten af de tilførte kompostmængder blev der i 1987 sået gulerod og porre. Til disse blev der tilført henholdsvis 52 og 114 kg N ha⁻¹. Parcelstørrelsen var 50 m² og antallet af gentagelser var 2. Af tabel 3 fremgår hvilke sorter af grønsager, der blev anvendt i de enkelte år.

Parceludbyttet blev bestemt ved at høste 10-20 planter af issalat og hvidkål eller ved at høste 3-4 m række af gulerod og porre. I 1987 blev udbyttet af gulerod og porre registreret på 10 m² pr. parcel. Friskvægten af salgbart produkt blev herefter bestemt. I issalat fra 1979 var det dog alene vægten af hele planter, der blev registreret. I hele planter eller i den spiselige produktandel, rengjort for jord, blev der bestemt tørstof efter 14-16 timers tørring ved 80 °C. Prøver til analyse for tungmetaller blev frysetørret på Al-folie og opbevaret i lufttætte flasker

indtil analysering. Koncentrationen af Mn, Zn, Cu, Pb, og Cd blev bestemt ved atomabsorption-spektrofotometri. Der blev ikke analyseret for Zn i 1980. Efter høst i 1987 blev der udtaget jordprøver til analyse for pH, gødningstilstand og indhold af tungmetaller.

De statistiske beregninger er foretaget ved hjælp af Statistical Analysis System (SAS Institute Inc. 1988). Signifikante forskelle er angivet ved $P=0.05$.

Resultater og diskussion

Tabel 4, 5 og 6 viser at tilførsel af kompost ikke signifikant påvirkede udbyttet af grønsager. En undtagelse var issalat dyrket 1980, hvor udbyttet af hoveder øgedes med stigende tilførsel af kompost (Tabel 5). Set i forhold til de store N-mængder, der blev tilført med komposten er det overraskende, at der ikke er større effekt på udbyttet. En forklaring kan eventuelt være, at kvælstoffet i komposten er bundet i tungtopløselige forbindelser. Dagrenovationen bestod kun i ringe grad af madrester og planteaffald. En væsentlig del bestod af emballage af papir og plast. Det tilførte spildevandsslam hidrørte fra klaringsbassiner og var altså de uopløste partikler i spildevandet. I hvidkål dyrket 1979 reduceredes tørstofprocenten med stigende komposttilførsel. Denne effekt ses ofte ved stigende N-tilførsel.

Tabel 3. Oversigt over gennemsnitlig friskvægt-udbytte, tørstof-procent og indhold af tungmetaller i prøver af grønsager fra 1979, 1980 og 1987.

A summary of mean fresh-weight yield, dry-matter percentage and content of heavy metals in vegetable crops grown in 1979, 1980, and 1987.

Planteart og år	Sort	Udbytte kg m ⁻²	Tørstof %	ppm i friskvægt				
				Zn	Cu	Mn	Cd	Pb
Issalat, hele planter 1979	Pennlake	4.5	6.0	2.274	0.365	1.451	0.047	0.037
Issalat, hoved 1980	Great Lake	1.8*	5.2	-	0.385	0.870*	0.025*	0.022
Hvidkål, hoved 1979	Hidena	4.5	11.6*	1.475*	0.372	1.137	0.010	0.027*
Hvidkål, hoved 1980	Hidena	4.4	12.0	-	0.221	1.203	0.007	0.018*
Gulerod 1979	Amtou	4.4	11.2	1.945	0.617	0.889	0.070	0.046
Gulerod 1980	Amtou	2.5	10.8	-	0.446	0.856*	0.039	0.018
Gulerod 1987	Fancy	8.5	10.7	1.288	0.362	0.617	0.021*	0.011
Porre, top 1979	Odin	1.6	11.1	2.907*	0.821*	4.154	0.064*	0.228
Porre, skaft 1979	Odin	1.4	14.1	2.389	0.518	1.842	0.047	0.090
Porre, skaft 1980	Odin	1.0	13.3	-	0.457	2.307	0.033	0.094
Porre, top 1987	Longina	1.1	11.0	2.108	0.592*	2.356	0.016	0.094
Porre, skaft 1987	Longina	2.3	10.7	2.345	0.533	1.600	0.022	0.042

*) signifikant effekt af komposttilførsel

Stigende tilførsel af N-gødning øgede udbyttet i alle forsøg. Denne effekt vil dog ikke blive diskuteret videre i nærværende rapport, som alene skal belyse effekten af kompost. Der blev ikke fundet nogen vekselvirkning mellem tilførsel af kompost og N-gødning.

Tabel 4. Friskvægt og indhold af tørstof og tungmetaller i grønsager 1979, 1 år efter tilførsel af kompost.

Fresh weight and content of dry matter and heavy metals in lettuce (A), white cabbage (B), carrots (C), trimmed leek leaves (D), and leek stems (E), grown in 1979, one year after application of compost.

A. Hele planter af issalat.

Kompost t tørstof ha ⁻¹	Friskvægt g stk ⁻¹	Tørstof %	ppm i friskvægt				
			Zn	Cu	Mn	Cd	Pb
0	650	6.1	2.276	0.346	1.507	0.050	0.051
5	670	5.9	2.100	0.349	1.439	0.047	0.034
100	709	5.9	2.218	0.376	1.370	0.043	0.032
200	660	6.2	2.500	0.393	1.487	0.047	0.030
LSD	n.s. ¹	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.

1) n.s. = ikke signifikant

B. Hoveder af hvidkål.

Kompost t tørstof ha ⁻¹	Friskvægt g stk ⁻¹	Tørstof %	ppm i friskvægt				
			Zn	Cu	Mn	Cd	Pb
0	1542	12.1	1.227	0.377	1.108	0.010	0.033
5	1516	11.7	1.318	0.403	1.124	0.010	0.027
100	1705	11.5	1.585	0.366	1.203	0.008	0.025
200	1717	11.3	1.771	0.243	1.112	0.011	0.025
LSD	n.s.	0.5	0.296	n.s.	n.s.	n.s.	0.007

C. Gulerod.

Kompost t tørstof ha ⁻¹	Friskvægt g m ⁻²	Tørstof %	ppm i friskvægt				
			Zn	Cu	Mn	Cd	Pb
0	4049	11.4	1776	0.776	0.955	0.079	0.066
5	4527	11.3	1732	0.555	0.828	0.076	0.041
100	4327	11.1	2214	0.550	0.948	0.067	0.041
200	4616	11.0	2057	0.587	0.827	0.059	0.037
LSD	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.

D. Top af porrer.

Kompost t tørstof ha ⁻¹	Friskvægt g m ⁻²	Tørstof %	ppm i friskvægt				
			Zn	Cu	Mn	Cd	Pb
0	1530	11.2	2.995	0.954	4.517	0.081	0.227
5	1697	11.0	2.631	0.863	3.930	0.064	0.197
100	1552	11.1	2.887	0.724	4.068	0.056	0.246
200	1653	11.0	3.114	0.741	4.095	0.055	0.240
LSD	n.s.	n.s.	0.163	0.052	n.s.	0.014	n.s.

E. Skaft af porrer

Kompost t tørstof ha ⁻¹	Friskvægt g m ⁻²	Tørstof %	ppm i friskvægt				
			Zn	Cu	Mn	Cd	Pb
0	1430	14.1	2.271	0.535	2.026	0.059	0.104
5	1510	14.0	2.170	0.509	1.722	0.051	0.088
100	1413	14.2	2.373	0.515	1.620	0.043	0.094
200	1412	14.2	2.743	0.512	2.000	0.035	0.074
LSD	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.

Tabel 5. Friskvægt og indhold af tørstof og tungmetaller i grønsager 1980, 2 år efter tilførsel af kompost.

Fresh weight and content of dry matter and heavy metals in lettuce (A), white cabbage (B), carrots (C), and leek stems (D), grown in 1980, two years after application of compost.

A. Hoveder af issalat.

Kompost t tørstof ha ⁻¹	Friskvægt g stk ⁻¹	Tørstof %	Cu	ppm i friskvægt		
				Mn	Cd	Pb
0	357	5.5	0.393	0.944	0.035	0.024
5	416	5.3	0.294	0.917	0.026	0.023
100	471	5.0	0.396	0.920	0.021	0.025
200	473	5.0	0.457	0.738	0.019	0.017
LSD	62	n.s. ¹	n.s.	0.175	0.016	n.s.

1) n.s. = ikke signifikant

B. Hoveder af hvidkål.

Kompost t tørstof ha ⁻¹	Friskvægt g stk ⁻¹	Tørstof %	Cu	ppm i friskvægt		
				Mn	Cd	Pb
0	1468	12.4	0.246	1.193	0.011	0.015
5	1516	12.4	0.217	1.192	0.009	0.023
100	1662	11.8	0.217	1.213	0.005	0.019
200	1708	11.5	0.202	1.214	0.005	0.015
LSD	n.s.	n.s.	n.s.	n.s.	n.s.	0.007

C. Gulerod.

Kompost t tørstof ha ⁻¹	Friskvægt g m ⁻²	Tørstof %	Cu	ppm i friskvægt		
				Mn	Cd	Pb
0	5214	11.2	0.378	0.976	0.040	0.014
5	2710	10.6	0.424	0.760	0.044	0.019
100	2423	10.7	0.481	0.660	0.040	0.021
200	2545	10.8	0.499	1.029	0.032	0.018
LSD	n.s.	n.s.	n.s.	0.226	n.s.	n.s.

D. Skaff af porrer.

Kompost t tørstof ha ⁻¹	Friskvægt g m ⁻²	Tørstof %	Cu	ppm i friskvægt		
				Mn	Cd	Pb
0	982	13.4	0.442	2.440	0.041	0.076
5	952	13.8	0.400	2.518	0.039	0.080
100	1030	12.9	0.479	2.140	0.026	0.130
200	990	13.0	0.511	2.110	0.027	0.090
LSD	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.

I tabel 3 er anført de gennemsnitlige koncentrationer af Zn, Mn, Cu, Pb og Cd i de forskellige grønsagsarter. Generelt er indholdet af Zn, Cu, Mn og Pb højt i porre, især porretop, mens indholdet af Cd er højt i gulerod. Indholdet af Zn, Cu, Cd og Pb er lavt i hvidkål, mens gulerod har et lavt indhold af Mn. Noget entydigt billede aftegner der sig dog ikke ved sammenligning mellem de forskellige arter. Ved sammenligning af de forskellige

år ses at indholdet af Cu, Cd og Pb generelt falder med tiden. Som det fremgår af tabel 3 er der kun signifikant effekt af komposttilførsel på indholdet af tungmetaller i 11 af de i alt 56 sammenligninger. Ekeblad (1982), Chu og Wong (1987) og Brallier et al. (1996) har vist at indholdet af tungmetaller kan variere meget mellem arter og sorter af grønsager.

Tabel 6. Friskvægt og indhold af tørstof og tungmetaller i grønsager 1987, 9 år efter tilførsel af kompost.

Fresh weight and content of dry matter and heavy metals in carrots (A), trimmed leek leaves (B), and leek stems (C), grown in 1987, nine years after application of compost.

A. Gulerod.

Kompost t tørstof ha ⁻¹	Friskvægt g m ⁻²	Tørstof %	ppm i friskvægt				
			Zn	Cu	Mn	Cd	Pb
0	8260	10.7	1.127	0.376	0.590	0.031	0.012
5	8830	10.7	1.288	0.322	0.645	0.028	0.013
100	8650	10.7	1.175	0.374	0.481	0.013	0.011
200	8450	10.8	1.563	0.337	0.756	0.014	0.010
LSD	n.s. ¹	n.s.	n.s.	n.s.	n.s.	0.012	n.s.

1) n.s. = ikke signifikant

B. Top af porrer.

Kompost t tørstof ha ⁻¹	Friskvægt g m ⁻²	Tørstof %	ppm i friskvægt				
			Zn	Cu	Mn	Cd	Pb
0	3050	11.1	2.158	0.553	2.801	0.023	0.089
5	2172	11.2	2.065	0.502	2.846	0.022	0.092
100	2398	11.0	2.088	0.659	2.198	0.009	0.096
200	2914	10.9	2.118	0.652	2.791	0.008	0.098
LSD	n.s.	n.s.	n.s.	0.108	n.s.	n.s.	n.s.

C. Skift af porrer

Kompost t tørstof ha ⁻¹	Friskvægt g m ⁻²	Tørstof %	ppm i friskvægt				
			Zn	Cu	Mn	Cd	Pb
0	2392	11.0	2.307	0.483	1.663	0.034	0.034
5	1996	11.2	2.371	0.552	1.710	0.029	0.039
100	2424	11.0	2.218	0.528	1.426	0.012	0.042
200	2472	10.9	2.482	0.569	1.603	0.011	0.052
LSD	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.

Tilførsel af store mængder kompost har i visse tilfælde fremkaldt lavere koncentration, end hvor der er tilført lidt eller intet. Denne effekt er særlig udpræget med hensyn til Cd og til dels også for Pb, som det ses af tabel 4-6. I porre er der dog en tendens til at indholdet af Pb øges med stigende komposttilførsel. Indholdet af Zn, Cu og Mn er ikke entydigt påvirket af komposttilførslen. Der er dog en svag tendens til at Zn-indholdet øges ved stigende tilførsel. Ved at se på forholdet mellem Zn og Cd træder disse resultater

tydeligere frem. Af tabel 7 ses at Zn/Cd stiger signifikant med stigende tilførsel af kompost. Årsagen hertil kan måske skyldes at Zn optages lettere end Cd. Disse har nær samme position i det periodiske system og kan derfor eventuelt erstatte hinanden. Stigende Zn/Cd kan også skyldes at kompostens indhold af Zn er betydeligt større end Cd. Som det ses af tabel 1 indeholdt komposten da også ca. 1000 gange mere Zn end Cd. Ganske vist er de i tabellen anførte værdier totalindholdet af de forskellige stoffer og siger intet om tilgængeligheden af disse. Jordprøver udtaget 1987 viser imidlertid at Znt er steget væsentligt med stigende komposttilførsel (Tabel 8).

Tabel 7. Forholdet mellem indhold af Zn og Cd i prøver af grønsager fra 1979 og 1987. *Ratio between Zn and Cd in vegetable crops grown in 1979 and 1987.*

Planteart og år	Kompost, t tørstof ha ⁻¹			
	0	5	100	200
Issalat 1979	45	45	69	53
Hvidkål 1979	121	136	189	162
Gulerød 1979	22	23	33	35
Gulerød 1987	36	46	92	112
Porre, top 1979	37	41	52	57
Porre, skaft 1979	39	42	55	77
Porre, top 1987	93	93	240	279
Porre, skaft 1987	67	83	191	218
Gennemsnit	57	64	115	124

Opløseligheden af Zn og andre tungmetaller reduceres med stigende pH (Herms og Brümmer 1977; Brallier et al. 1996). Tilførsel af store mængder kompost med en pH-værdi på 8.0, som i dette forsøg, vil øge jordens pH og dermed reducere opløseligheden af tungmetallerne. Jordprøver udtaget 1987 viser da også at jordens pH øgedes med stigende komposttilførsel (Tabel 8). Om tilgængeligheden reduceres ved tilførsel af alkalisk kompost med et stort indhold af tungmetaller afhænger dog også af mængderne af de tilførte tungmetaller. Øget pH er sandsynligvis forklaringen på at indholdet af Cd i mange afgrøder i nærværende undersøgelse reduceredes med stigende tilførsel af kompost. Chu og Wong (1987) har således fundet at planter optog færre tungmetaller efter tilførsel af komposteret dagrenovation med en pH-værdi på 8.0 end efter tilførsel af slam med en pH-værdi på 6.0. undersøgelser med grønsager har Jackson og Alloway (1991), Guttormsen et al. (1995) og Brallier et al. (1996) vist at såvel indholdet af plantetilgængeligt Cd i jord som optagelsen i planter reduceres med stigende pH. Af tabel 8 fremgår endvidere at koncentrationen af Cd og Pb samt tilgængeligheden af Cu og P i jorden er øget, mens plantetilgængeligt indhold af Mn er reduceret 9 år efter tilførsel af kompost. Koncentrationen af Cd og Pb i jorden er ikke nødvendigvis et udtryk for tilgængeligheden af disse.

Tabel 8. Effekt af kompost tilført efterår 1978 på jordens pH, gødningstilstand og indhold af tungmetaller efterår 1987.

Effects of compost applied in the autumn 1978 on the soil pH, soil fertility, and content of heavy metals in the autumn 1987.

Kompost t ha ⁻¹	pH	Ft (1)	Kt (2)	Mgt (2)	Mnt (3)	Cut (3)	Znt (3)	Cd ppm	Pb
0	6.1	8.3	12.0	8.2	1.5	2.0	3.4	0.24	14.9
5	6.3	8.5	12.1	7.7	1.5	2.2	4.1	0.24	15.5
100	6.8	10.2	11.6	6.7	0.3	5.1	11.5	0.28	17.9
200	7.0	11.9	12.4	7.2	0.2	8.1	18.6	0.35	22.1

1) 1 enhed svarer til 3 mg P pr. 100 g tør jord

2) 1 enhed svarer til 1 mg K eller Mg pr. 100 g tør jord

3) 1 enhed svarer til 1 mg Mn, Cu eller Zn pr. 1000 g tør jord

Af de her omtalte tungmetaller er Cd og Pb uønskede i kosten. Sammenlignes de fundne koncentrationer af disse tungmetaller i nærværende undersøgelse med indholdet i prøver af dansk producerede grønsager i perioden 1977-80 (Hansen og Andersen 1983) ligger maksimumkoncentrationen i nærværende undersøgelse kun i et enkelt tilfælde over maksimumværdierne i prøverne fra 1977-80 (Tabel 9). De i dette forsøg fundne maksimumkoncentrationer overskrider dog ikke de i Tyskland vejledende grænseværdier for højeste Cd- og Pb-indhold i bladgrønsager, henholdsvis 0.1 og 0.8 ppm i friskvægt (Anonym 1996).

Tabel 9. Maximale værdier for indhold af tungmetallerne Cd og Pb i grønsagsprøverne sammenlignet med maksimale værdier i prøver af dansk producerede grønsager i perioden 1977-80 (Hansen og Andersen 1983).

Maximum values of Cd and Pb in the vegetable crops compared to the maximum values of crops grown in 1977-80 (Hansen and Andersen 1983).

	ppm i friskvægt			
	Cd		Pb	
	1977-80	Dette forsøg	1977-80	Dette forsøg
Issalat, hoved	0.051 ¹	0.035	0.280 ¹	0.025
Hvidkål, hoved	0.032	0.011	0.093	0.033
Gulerod	0.190	0.079	0.400	0.066
Porrer, top	0.048	0.081	0.035	0.246
Porrer, skaft	0.180	0.059	0.350	0.130

1) Inkluderer også hovedsalat.

Konklusion

Tilførsel af komposteret dagrenovation og spildevandsslam påvirkede ikke udbyttet eller indholdet af tungmetaller på nogen entydig måde i de undersøgte grønsagsarter. Tilførsel af forholdsvis store mængder let basisk kompost øgede jordens pH selv 9 år efter

indarbejdning. Herved reduceredes opløseligheden og dermed tilgængeligheden af tungmetallerne, især Cd og Pb. Øget pH er derfor forklaringen på, at indholdet af Cd i de fleste afgrøder i nærværende undersøgelse faldt med stigende tilførsel af kompost.

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