First-principles study of H intercalation in rutile TiO_2

Marina V. Koudriachova,^{1,2} Simon W. de Leeuw,¹ and Nicholas M. Harrison²¹*Computational Physics, Department of Applied Physics, TU Delft, Lorentzweg 1, 2628 CJ Delft, The Netherlands*²*Department of Chemistry, Imperial College of Science and Technology, London, SW7 2AZ, United Kingdom and CCLRC, Daresbury Laboratory, Daresbury, Warrington WA4 4AD, United Kingdom*

(Received 10 February 2004; published 29 October 2004)

The geometry of hydrogen intercalation sites in rutile TiO_2 has been studied using first principles calculations. A new intercalation site is predicted which is consistent with all current experimental data. The apparent contradiction between spectroscopic, diffraction and magnetic resonance data are resolved by taking into account the strong local distortions of the structure induced by localization of donated charge. In particular the predicted OH vibrational frequency is in excellent agreement with that measured. A similar local geometry is predicted in the presence of 3+ counter ions but with a preferential site occupancy which is consistent with the local symmetry implied by spectroscopic measurements of aluminium substituted titania. The local distortions of the structure are shown to result in preferential ordering of the hydrogen ions in layers over a wide range of intercalation concentrations and the consequences of this ordering for electrochemical insertion of hydrogen are discussed.

DOI: 10.1103/PhysRevB.70.165421

PACS number(s): 71.20.Tx, 66.30.-h, 82.45.-h

I. INTRODUCTION

There is a large and growing use of oxide materials, and nanostructured oxides in particular, as solid state devices such as solar cells, battery cathodes and recording materials. H impurities are usually unintentionally introduced during processing and have significant influence on material properties and thus device performance. Intentional intercalation of H into oxide materials is also of interest as it is a promising approach to hydrogen storage for fuel cells.¹ It is well established that H impurities affect the conductivity, electronic, and optical and properties of both the bulk crystal and its surfaces. The strong charge transfer from the hydrogen modifies the electronic structure of the host material and, at elevated temperatures, proton transport makes a significant contribution to the ionic conductivity. In addition, as will be discussed below, H intercalation has a significant effect on the structure of the host material.

Rutile TiO_2 is a technologically important material as a ferroelectric, in heterogeneous catalysis and as a pigment and an opacifier. Natural samples contain small amounts of hydrogen which is thought to play a role in the charge compensation of +3 cation impurities. H may also play a similar role in commercial rutile pigments, which are intentionally doped with Al^{3+} cations to suppress undesirable photoactivity. Hydrogen can also be introduced into rutile by annealing in an atmosphere containing $\text{H}_2\text{O}+\text{O}_2$ or H_2 .² Intercalation is thought to proceed through dissociative adsorption at surface defects^{3,4} although there is some evidence for molecular intercalation in the near surface region.⁵ As the insertion of H into rutile is fully reversible up to $10^{19}/\text{cm}^3$, and is easily controlled and monitored, it provides a useful probe for the variation of optical, electronic, and thermodynamic properties with donated electron concentration.⁶⁻⁹ Electrochemical insertion allows intercalation to much higher H concentrations, the exact maximum insertion concentration is not known. Upon electrochemical H-insertion rutile becomes brittle.²⁶

The clearly differentiated OH vibrational mode at around 3277 cm^{-1} means that infrared (IR) adsorption and polarized

Raman scattering can be used to obtain information about the sites adopted by H impurities. In addition to the mode frequency the total IR adsorption yields the concentration of H ions⁹ while analysis of the polarized Raman spectra yields the symmetry of the vibrational modes.^{10,11} From this data it is possible to speculate about the likely intercalation sites for H within the lattice and a number of models have been proposed. Both the large dichroism observed in the IR adsorption and symmetry analysis of the polarized Raman spectra indicate that the OH bonds are oriented perpendicular to the crystallographic c axis.^{2,11} Two structures have been suggested that are consistent with this orientation of the OH bond; the channel center (CC) and basal octahedron edge (BOE) models.^{2,12}

The rutile structure consists of TiO_6 octahedra which share edges along the c direction and corners in the ab planes. The edge sharing octahedra form pillars along c separated by channels of empty octahedra. In the channel center (CC) model the proton resides in the channel between two O ions separated by $3.33\text{ \AA}$ (Fig. 1). In its original formulation the CC model envisaged the proton equidistant from the two O ions; in the modified CC model (MCC) the proton is thought to vibrate in a double well potential with minima at

FIG. 1. Four unit cells of rutile TiO_2 viewed along the crystallographic c direction. Two possible H adsorption sites are indicated; the CC model by a closed circle, the two BOE sites are shown by an open circle. The two shown BOE sites are symmetry related.

approximately 0.98 Å from each of the O ions. In the BOE model the proton sits equidistant from the two O ions making up the shared octahedron edge (Fig. 1). There are two such edges available oriented either along the (110) or the (1-10) directions (Fig. 1). The O-H-O distance of the BOE model, 2.85 Å, is much shorter than that of the CC model (3.33 Å).

Given the current experimental data it is not possible to adopt either model as satisfactory. In pure rutile symmetry analysis of the Raman data excludes the BOE model and is consistent with the CC model^{10,11}—essentially the diagonal $\sigma(110)$ mirror plane implied by the BOE model is not consistent with the Raman data. In Al-doped rutile the Raman data is significantly different and does not exclude this symmetry element and so the BOE model may pertain in this case¹¹ while EPR measurements of Fe-doped rutile support the CC model.¹³ Neutron diffraction data from a sample of a natural mantle rutile place H ions near the BOE position in a bent O-H-O configuration.¹⁴ Natural samples contain significant impurity concentrations and so this data supports the idea that the H intercalation site is sensitive to the defect structure.

The CC(MCC) and BOE model are also not consistent with the observed vibrational frequency of the OH group. There is an empirical correlation between the O-H stretch frequency and the O-O distance of an O-H-O complex.¹⁵ The observed OH frequency of 3279 cm⁻¹ correlates with an O-O distance of 2.75–2.85 Å while the O-O distance in the MCC and BOE models are 3.33 Å and 2.52 Å, respectively. Thus one would expect a vibrational frequency of approximately that of a free OH group (3600 cm⁻¹) for the MCC model and a strongly shifted frequency (2300 cm⁻¹) for the BOE model. There have been a number of previous attempts to explain this anomaly. On the basis of empirical potential modelling it has been suggested that the hydrogen bond typical of O-H-O complexes is not formed at all in this system and that deviations from the free molecule properties result from electrostatic interaction of the proton with the surrounding lattice ions.¹⁶ Such calculations yield a frequency shift which is two times greater than that observed. The bent BOE site deduced from neutron diffraction data provides an alternative explanation. The bending of the O-H-O linkage to 166° being thought to yield a dramatic increase in the OH stretch frequency.^{14,17}

First principles simulations based on density functional theory are now sufficiently reliable and accurate that they can be used to predict intercalation sites for H in rutile. In the current study such calculations are used to determine the structures adopted on H-insertion in both pure rutile and that doped with 3-valent-ions. The importance of local deformations of the lattice induced by ion insertion and of volume expansion induced by the charge donated to the lattice are examined in detail. Currently available experimental data are discussed in the light of these results. The paper is organized as follows. The details of calculations are briefly summarized in Sec. II. In Sec. III the CC(MCC) and BOE models in pure and doped rutile are examined and the frequency of OH vibration estimated. In Sec. III the ordering of H ions is considered and the mechanism underlying the local distortions is discussed. Conclusions are drawn in Sec. IV.

FIG. 2. Eight unit cells of rutile (A) and Al-doped rutile (B) containing a H ion. Ti ions are shown in black, O ions in dark grey, an Al ion in light grey, and a H ion in white.

II. DETAILS OF CALCULATIONS

All calculations were performed with the CASTEP software within the pseudopotential plane-wave formalism^{18,19} and density functional theory. Electron exchange and correlation effects were treated within the spin polarized generalized gradient approximation (Perdew, Wang, 1991)²⁰ with ultrasoft pseudopotentials²¹ used to replace the Ti (1s,2s,2p), O(1s) orbitals. The sampling in the k space was performed on the regular grid with a spacing in the of 0.1 Å⁻¹. A plane-wave cutoff energy of 380 eV was found to converge the total energy to 0.01 eV per formula unit. The calculations were performed in a supercell containing 16 formula units of H_xTiO₂ allowing insertion concentrations ranging from $x=1/16$ to $x=1$ to be considered. The size and shape of the cell and all internal degrees of freedom were fully relaxed with respect to the total energy. For each composition a number of different initial geometries were considered and the lowest energy configuration sought.

III. RESULTS AND DISCUSSION

A. Position of a proton

Rutile is a tetragonal crystal with lattice parameters $a=b=4.59$ Å and $c=2.95$ Å (Ref. 22) (calculated values $a=b=4.63$ Å and $c=2.96$ Å). At $x=1/16$ ($x=\text{H}/\text{Ti}$), initial configurations based on the BOE and MCC models were examined and the structures fully relaxed. The BOE structures were found to be unstable and upon relaxation H ions leave the octahedron edge and move into the c channel. The fully relaxed configurations correspond essentially to the CC model (Fig. 2). H ions occupy sites symmetry equivalent to (0.54a, 0.09b, 0c) of the primitive cell of rutile. In these sites the hydroxyl group has a bond length of 1.00 Å and is oriented close to either the [110] or [1-10] directions. There is considerable local distortion of the lattice which results in the hydrogen bond distance across the c channel being 1.86 Å rather than 2.35 Å of the CC model. This distortion immediately removes one of the main difficulties of the CC model discussed above. The empirical frequency expected for the predicted O-H-O distance is 3300 cm⁻¹.¹⁵ The frequency obtained by fitting the computed energy surface for the O-H bond is 3280 cm⁻¹, in excellent agreement with that observed (3288 at 10 K²). It is clear from Fig. 2 that the size and the shape of the c -channels are significantly modified by H insertion. The mechanism for this is discussed further below.

Upon substitution of a Ti^{+4} ion by a trivalent ion (Fe, Al) at $(0.5a, 0.5b, 0.5c)$ the stable configurations for intercalated H ions remain locally similar to the distorted CC structure. However, the substitution and subsequent relaxation breaks the local symmetry and generates preferred O sites for H adsorption. In these sites H is bonded to O ions sitting on the edge shared by Al/Fe-substituted octahedra and all OH bonds are therefore oriented along the (110) direction rather than along both the $(1-10)$ and (110) directions as in pure rutile. This preferential site occupancy restores a $\sigma(110)$ mirror plane and thus the modified CC model is consistent with the symmetry observed in Raman measurements of Al-doped rutile which was previously interpreted as evidence for the BOE model.¹¹ The $(1-10)$ oriented sites are coplanar with Al/Fe in the ab plane. The computed energies of adsorption reveal that bonding at (110) oriented sites is strongly preferred over bonding at the $(1-10)$ oriented sites; by 0.22 eV in the Al case and 0.4 eV in the Fe case. The computed H-ion position for the Al case is $(0.54a, 0.12b, 0c)$ and has not been determined experimentally. In the Fe case the computed position of $(0.54a, 0.10b, 0c)$ is in excellent agreement with that deduced from EPR measurements $(0.56a, 0.11b, 0c)$.¹³

The preference of the H ions for bonding at the shared edge of Ti and Al octahedra is largely electrostatic in origin. The Al^{+3} ion is more electronegative than the Ti^{+4} ions and thus its nearest neighboring Ti ions (which are along the c directions) are partly oxidized having charges of $1.41|e|$ compared to $1.36-1.37|e|$ on other Ti ions. The O ions of the shared edge also lose some of their charge to the Al^{+3} ion (charge $-0.74|e|$ compared to $-0.78|e|$ on the neighboring O ions coplanar with the Al ions in the ab planes). Thus the intercalated H, as an electron donor, is stabilized at the shared edge as it donates charge to these charge deficient ions. The computed O-H-O distance is $3.13 \text{ \AA}$ for Al-doped rutile significantly longer than that for pure rutile ($2.86 \text{ \AA}$) and this corresponds to a higher OH frequency as observed in IR and Raman experiments ($3331-3325 \text{ cm}^{-1}$ on Al doping^{2,10}).

This example of Fe and Al impurities demonstrates that the H intercalation site is very sensitive to the defects present in rutile. Additional calculations on a number of model defect structures were performed in order to explore the influence of the nature of the defect on the H site. Three simple models for O vacancies have been considered, namely, neutral, doubly ionized, and reconstructed vacancies. A doubly ionized O vacancy creates a charge depletion on Ti and O sites which are second neighbors to the vacancy and it is at these sites that the OH bond is preferentially formed. In the neutral O vacancy charge is trapped in the vacancy site as the H occupies essentially the center of the site; this has been suggested previously by (Bursill *et al.*²⁷). There is a strong interaction between impurities and vacancies and in Al(Fe)-doped rutile the lowest energy position for neutral O vacancy is located on the shared edge between a substituted and Ti-occupied octahedron.

Perhaps a more realistic model of the O-vacancy site is the reconstructed vacancy in which one of the Ti ions neighboring the O vacancy along the c direction moves to an

FIG. 3. Eight unit cells of rutile containing an aggregation of Al dopants and O vacancy with the H ion in a metastable state near the BOE.

interstitial site. The energy of this model is computed to be 0.07 eV lower than the unreconstructed vacancy and the computed barrier for the dislocation of the Ti ions required to reconstruct the vacancy is computed to be 0.16 eV which is easily accessible at room temperature. The reconstruction produces twofold coordinated O ions neighboring to charge depleted Ti ions and these provide the preferential adsorption site for H—0.2 eV lower than trapping at the vacancy center.

Overall these calculations on model defects demonstrate that the H-ion site is sensitive to the nature of the cation impurities and the charge of vacancy sites but that such point defects do not stabilize the BOE site. The BOE site is also unstable with respect to CC type sites in calculations of Ti and Al interstitial defects.

The robust stability of the CC type sites is closely related to the local geometry. In rutile the three Ti-O bonds formed by each O ion lie either in the (110) or $(1-10)$ planes. Chemical bonding of an H ion to O ions perpendicular to these planes produces the maximum separation of the Ti and H ions and thus minimize their electrostatic repulsion. This geometry corresponds to the CC model. In the BOE model OH bonds bisect Ti-O-Ti angles causing strong repulsion. In order to stabilize the BOE model the local structure must be strongly distorted and it does not appear that point defects are capable of producing sufficient distortion of the local geometry.

Spectroscopic data on heavily Al-doped rutile (1 wt % of Al_2O_3) suggest that at high concentrations dopants and structural defects form complicated aggregates. Here, a simple model of a complex defect is studied in which two Al impurities are present in face sharing octahedra with an O vacancy as a second neighbor as suggested by Gesenhues *et al.*²⁸ In the presence of this defect the BOE site is metastable (Fig. 3). Natural mantle rutile contains 5 wt % of different impurities including Al_2O_3 , Fe_2O_3 , etc., and its defect structure is not known. As the agglomeration of defects into complex structures is likely it appears that the observation of H in BOE-like geometries in natural samples is related to its interaction with complex defects.¹⁴

B. Ordering of protons and charge localization

The ordering of H ions in the rutile lattice has also been investigated as it has important consequences for the electro-

TABLE I. The intercalation energy E of H into rutile TiO_2 for various concentrations.

x	E, eV
1/16	0.66
1/8	0.47
1/4	-0.03
1/2	-0.44
3/4	-1.04
1	-1.57

chemical insertion of H ions. The lowest energy configurations were sought for H_xTiO_2 with concentrations ranging from $x=1/16$ to $x=1$. At all insertion concentrations the distorted CC site was found to be stable with respect to the BOE site. Intercalation energies (Table I) were estimated from the total energy of the most stable configuration with respect to the bulk rutile and molecular hydrogen. These energies correspond to intercalation at $P_{\text{H}_2}=0$ and $T=0$. One can conclude that in this limit the maximum insertion concentration is close to $x=1/4$. At higher partial pressure of hydrogen and high temperature intercalation will proceed beyond $x=1/4$.

At $x=1/8$, $1/4$, and $1/2$ the lowest energy configurations are layered structures with rumpled ab layers of H ions separated in the c direction. The layered configuration shown in Fig. 4 is the lowest energy configuration for $x=1/4$. The cell parameters of this structure are $a=4.61 \text{ \AA}$, $b=4.87 \text{ \AA}$, and $c=11.91 \text{ \AA}$ corresponding to a 2% increase of volume over pure rutile which is very similar to the expansion observed in lithiated rutile at $x=1/4$ though the nature of inserted ions and the local geometries of the adsorption sites are different.²³ The predicted volume of the layered hydrogenated structures remains close to that of lithiated structures up to $x=1/2$ (Fig. 5). This indicates that the expansion of the structure in this concentration regime occurs because of accommodation of extra electron density donated by guest ions rather than short range repulsions.²³

The volume expansion and ordering of the H ions in the ab planes can be understood in terms of a simple ionic model if the elastic distortion of the lattice is taken into account. The role of the donated electron density is analyzed here

FIG. 4. The lowest energy configuration of $\text{H}_{1/4}\text{TiO}_2$ viewed along the b axis (A) and the c axis (B). H ions form rumpled ab planes separated in the c direction. Ti ions are shown in black, O ions in dark grey, H ions in white.

FIG. 5. The volume of the lowest energy configurations of H rutile (open circles) and Li rutile (closed circles) as a function of insertion concentration x .

using population analysis. At all insertion concentrations examined here the intercalated H donates about 32% of an electron to the lattice in good agreement with what one would expect from the electronegativities of H and O atoms. This charge is not distributed homogeneously, it is mainly localized on the O ions forming the hydroxyl group (about 28%) and on O ions across the c channel forming hydrogen bonds (about 12%). The remainder of the charge is accommodated by neighboring Ti ions in the ab planes and neighboring O ions in the c direction. The accommodation of this donated charge leads to a strong increase in the ionic radius of these O and Ti ions and a considerable elongation of the Ti-O bonds (by 7–13 %). This elongation grows linearly with the insertion concentration. At $x=1/4$ the length of Ti-O bonds reaches 2.15–2.20 $\text{\AA}$, which is beyond the typical bond length for the $\text{Ti}^{+3}-\text{O}^{-2}$ bonds (2.06–2.1 $\text{\AA}$) and thus H-insertion becomes thermodynamically unfavorable. The elongation of Ti-O bonds leads to strong local deformations which are only partially alleviated by the relatively modest volume expansion. The deformations reshape the c channel containing the H ions [Fig. 2(A)]. The c channel closes in the direction of the O-H-O complex ([110]), but opens in a perpendicular direction ([1-10]). The corresponding atomic displacements are reminiscent of the low frequency B_{1g} mode at 142 cm^{-1} .²⁴ These deformations affect the size and the shape of the neighboring empty channels and create an ideal neighboring site for further H insertion and thus the formation of ab layers of H ions (Fig. 4).

The ab layers which contain H ions expand in the c direction due to the charge donation. This resultant stress is accommodated by the lattice as a sequence of alternating long and short Ti-O bonds in unoccupied ab layers. This distortion pattern is similar to an excitation of the soft ferroelectric vibrational mode A_{2u} mode at 176 cm^{-1} .²⁴ The magnitude of the distortion decays rapidly with distance. At $x=1/8$ the shorter and the longer bonds in the neighboring unoccupied ab layers are 1.86 $\text{\AA}$ and 2.10 $\text{\AA}$, respectively, and within six atomic layers return to the unperturbed Ti-O distance of 1.94 $\text{\AA}$. As the GGA is known to overestimate the ferroelectric distortions of rutile²⁵ these calculations were repeated within the LDA which yielded similar distortions.

The formation of the layered structure provides a trapping mechanism for inserted H ions. The diffusion of H ions is dominated by that in the c direction. The experimental value

for the diffusion barrier at low H concentrations is 0.59 eV in the c direction and 1.28 eV in the ab planes.⁹ The barrier for diffusion out of the layered structures is estimated here by constrained minimization in which the position of the H ion is fixed along an assumed diffusion pathway in the c direction while the rest of the structure is fully relaxed. The computed barrier grows quickly with the H concentration; at $x=1/8$ it is two times higher than at $x=1/16$ (1.6 eV and 0.8 eV, respectively). It is the slow diffusion of H ions out of their thermodynamically favorable sites that leads to the rapid aging of rutile electrodes upon H insertion. In addition the strong elongation of the Ti-O bonds in the rumpled planes predicted here may lead to the breaking of interlayer bonds and thus be responsible for the embrittlement of the material at high insertion concentrations.²⁶

IV. CONCLUSIONS

The hydrogen intercalation sites in rutile TiO₂ have been determined using first principles calculations. The predicted

site is similar to the channel center model with strong local lattice distortions which remove all inconsistencies between this model and existing experimental data. The primary cause of the distortions is found to be the localization of the charge donated upon insertion of H ions. Upon doping with 3+ cations the channel center position is retained but preferential site occupancy leads to a different symmetry for the OH-stretching vibration which was previously interpreted as evidence for the basal octahedron edge model. Local deformations of the lattice upon substitution are also predicted to result in a frequency shift of the OH stretching vibration which is in excellent agreement with spectroscopic measurements. The lattice deformations lead to the thermodynamic stability of ordered layered structures of H ions. The stress induced in the lattice is accommodated in long range distortions of the lattice reminiscent of soft ferroelectric vibrational modes. The consequent elongation of Ti-O bonds may play a role in both the rapid aging of rutile electrodes and in the hydrogen embrittlement of rutile at high insertion concentrations.

-
- ¹P. Wang, A. M. Wang, H. F. Zhang, B. Z. Ding, and Z. Q. Hu, *J. Alloys Compd.* **313**, 218 (2000).
 - ²O. W. Johnson, W. D. Ohlsen, and P. I. Kingsbury, *Phys. Rev.* **175**, 1102 (1968).
 - ³W. Göpel, G. Rocker, and R. Feirabend, *Phys. Rev. B* **28**, 3427 (1983).
 - ⁴J.-M. Pan, B. L. Maschhoff, U. Diebold, and T. E. Madeym, *J. Vac. Sci. Technol. A* **10**, 2470 (1992).
 - ⁵J. V. Cathcart, R. A. Perkins, J. B. Bates, and L. C. Manley, *J. Appl. Phys.* **50**, 4110 (1979).
 - ⁶O. W. Johnson, J. W. DeFord, and J. W. Shaner, *J. Appl. Phys.* **44**, 3008 (1973).
 - ⁷J. W. DeFord and O. W. Johnson, *J. Appl. Phys.* **44**, 3001 (1973).
 - ⁸O. W. Johnson and J. W. DeFord, *Bull. Am. Phys. Soc.* **17**, 618 (1972).
 - ⁹O. W. Johnson, S. H. Paek, and J. W. DeFord, *J. Appl. Phys.* **46**, 1026 (1975).
 - ¹⁰S. Klauer and M. Wöhlecke, *Europhys. Lett.* **20**, 439 (1992).
 - ¹¹S. Klauer and M. Wöhlecke, *Phys. Rev. B* **49**, 158 (1994).
 - ¹²A. von Hippel, J. Kalnajas, and W. B. Westphal, *J. Phys. Chem. Solids* **23**, 779 (1962).
 - ¹³P. O. Andersson, E. L. Kollberg, and A. Jelenski, *Phys. Rev. B* **8**, 4956 (1973).
 - ¹⁴R. J. Swope, J. R. Smyth and A. C. Larson, *Am. Mineral.* **80**, 448 (1995).
 - ¹⁵G. C. Pimentel and A. L. McClellan, *The Hydrogen Bond* (Freeman, San Francisco, 1960), Chap. 3.
 - ¹⁶J. B. Bates and R. A. Perkins, *Phys. Rev. B* **16**, 3713 (1977).
 - ¹⁷K. Nakamoto, M. Marghoshes, and R. E. Rundle, *J. Am. Chem. Soc.* **77**, 6480 (1955).
 - ¹⁸M. C. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, *Rev. Mod. Phys.* **64**, 1045 (1992).
 - ¹⁹CASTEP 3.9 Academic version, licensed under the UKCP-MSI agreement, 1999.
 - ²⁰J. P. Perdew, in *Electronic Structure of Solids 91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991), p. 11.
 - ²¹D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
 - ²²J. K. Burdet, T. Hughbanks, G. J. Miller, J. W. Richardson, and J. V. Smith, *J. Am. Chem. Soc.* **109**, 3639 (1987).
 - ²³M. V. Koudriachova, N. M. Harrison, and S. W. de Leeuw, *Phys. Rev. B* **65**, 235423 (2002).
 - ²⁴C. Lee, P. Ghosez, and X. Gonze, *Phys. Rev. B* **50**, 13 379 (1994).
 - ²⁵B. Montanari and N. M. Harrison, *Chem. Phys. Lett.* **364**, 528 (2002).
 - ²⁶E. van der Krol (private communication).
 - ²⁷L. A. Bursill and M. G. Blanchin, *J. Solid State Chem.* **51**, 321 (1984).
 - ²⁸U. Gesenhues and T. Rentschler, *J. Solid State Chem.* **143**, 210 (1999).