

Tuning structure and magnetic order through Cr substitution in $\text{Co}_3\text{O}_2\text{BO}_3$ Ludwigite

D. L. Mariano^{*a}, D. R. Sanchez^b, D. C. Freitas^b, C. Salazar Mejia^c, S. N. Sofronova^d, M. A. Continentino^e, L. F. Cohen^f, L. Ghivelder^a

^a*Instituto de Física Universidade Federal do Rio de Janeiro (IF-UFRJ), Av. Athos da Silveira Ramos 149, Cidade Universitária 21941-909, Rio de Janeiro-RJ, Brasil*

^b*Instituto de Física Universidade Federal Fluminense (IF-UFF) s/nº, Gragoatá 24210-346, Niterói-RJ, Brasil*

^c*Dresden High Magnetic Field Laboratory (HLD-EMFL), Helmholtz-Zentrum Dresden-Rossendorf, 01328 Dresden, Germany*

^d*Kirensky Institute of Physics, Federal Research Center KSC SB RAS, 660036 Krasnoyarsk, Russia*

^e*Centro Brasileiro de Pesquisas Físicas (CBPF) 150, Urca 22290-180, Rio de Janeiro-RJ, Brasil*

^f*Blackett Laboratory, Imperial College, London SW7 2BZ, United Kingdom*

Abstract

In the $\text{Co}_3\text{O}_2\text{BO}_3$ Ludwigite, there are four crystallographic sites for the metal ion Co. Three sites are occupied by Co^{2+} in a high-spin state, and one site by Co^{3+} in low-spin state, resulting in a compound where the number of Co^{2+} ions is twice that of Co^{3+} ions. Given the particular distribution of magnetic and non-magnetic ions, the compound can be visualized as consisting of magnetic planes containing Co^{2+} ions, separated by non-magnetic planes formed by Co^{3+} ions. In this work, we studied the structural changes, especially magnetic ones, caused by the gradual substitution of low-spin Co^{3+} ($S=0$) by Cr^{3+} ions ($S=3/2$). We synthesized the $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ series, and X-ray experiments showed a gradual increase in unit cell volume with increasing Cr concentration. Magnetization measurements show that this type of substitution drastically increases the magnetic transition temperature, from 42 K for the undoped compound to 115 K for the compound with the highest Cr concentration. The latter is the highest long-range magnetic ordering temperature recorded so far for cobalt Ludwigites. The results from specific heat and magnetization measurements show that this substitution changes the ground-state magnetic structure of the compound, transitioning from a ferrimagnetic state (at low Cr concentrations) to an antiferromagnetic state (at high Cr concentrations), in agreement with the results of exchange integral calculations.

Keywords:

^{*}Corresponding author, Present address: UFRJ

Email address: davor@if.ufrj.br (D. L. Mariano^{*})

1. Introduction

Ludwigites are oxiborates members of the Pinakiolite group of minerals. This name was given in honor of professor Ernest Ludwig, the first to study this mineral family in 1873. Ludwigites have the general formula $\text{M}_2\text{M}'\text{O}_2\text{BO}_3$, where M ions are a bivalent metal, e.g. Co^{2+} , Fe^{2+} and Ni^{2+} , and a M' can be trivalent or tetravalent ions e.g. Co^{3+} [1], Fe^{3+} [1, 2], Al^{3+} [3], Ti^{4+} [4] and Sn^{4+} [5]. Ludwigites have attracted the attention of the scientific community due to a variety of physical properties, such as: low-dimensional magnetism [6], charge ordering [7], long-range magnetic order [7, 5], dimensional crossover [8], and magnetocaloric effect [3], among others. With regard to its potential for technological applications, some of them can be used, such as crystals for laser technology, luminescence, and nonlinear optics [9, 10, 11]. This mineral family also have some applications as low frequency oscillators[12], lithium-ion and sodium-ion batteries [13, 14, 15, 16], and present multiferroic properties [17, 18]. Many of the physical properties shown by Ludwigites have not yet been fully understood, and they are related to the particular crystal structure of these compounds.

The Ludwigite structure is formed by the junction of oxygen octahedron that contains a M or M' metal ion inside. Each oxygen octahedron consists of one crystallographic site, and in total there are four distinct crystallographic sites. Sites 3–1–3 are interconnected by the vertices of oxygen octahedrons, while sites 3–2–3 are interconnected by the edges. The structure formed by the junction of sites 1–2–3 forms magnetic planes, and these parallel planes are interconnected by site 4. This structure is shown in Fig. 1. Magnetic planes formed by the 1–2–3 sites provide the two-dimensional magnetic character of cobalt Ludwigite [8, 19].

Among several studied Ludwigites, one of the most outstanding is the Co homometallic Ludwigite, $\text{Co}_3\text{O}_2\text{BO}_3$. This Ludwigite displays a long-range ferrimagnetic order at 42 K [1, 19], and presents a low-spin state (LS) Co^{3+} ($S=0$) ion at site 4 which does not contribute to magnetic interactions. Very interesting features appear when Co Ludwigite is doped with non-magnetic Ga^{3+} [20], Al^{3+} [3], Sn^{4+} [5], Zr^{4+} and Hf^{4+} [21] or magnetic Fe^{3+} [1, 17], Mn^{3+} [22, 23] and Cr^{3+} [8] ions. In each case the magnetic properties of the compound are affected differently depending on the dopant ion. For example, when the Co Ludwigite is doped with non-magnetic Sn^{4+} ion, the Sn enter mostly at site 4 and favors the appearance of high-spin state (HS) Co^{2+} at this site. This substitution strengthens the magnitude of the magnetic interactions, resulting in an increase of ferrimagnetic interactions and increases the magnetic transition temperature from 42 to 82 K [5]. On the other hand, when the compound is doped with Ga^{3+} , the dopant ion does not enter into the structure systematically, weakening the magnetic interactions and the magnetic transition temperature

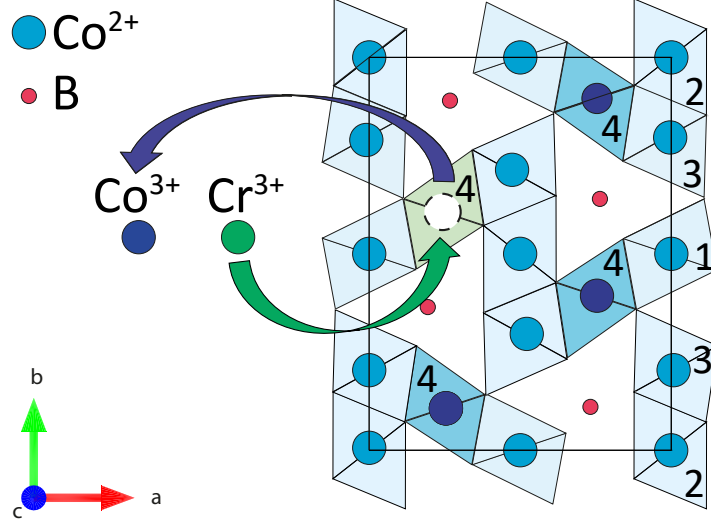


Figure 1: Crystallographic structure of $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigite. Oxygen atoms were omitted for best visualization of the structure. The numbers indicate the location of Ludwigite crystallographic sites.

decays to 37 K [20]. On the other hand, when Co Ludwigite is doped with magnetic ions the result is not always to strengthen the magnetic interactions. For example, when Co^{3+} is substituted by Fe^{3+} , these ions enter mostly at site 4 which causes the competition between double-exchange and super-exchange magnetic interactions and long range magnetic order is no longer seen at low-temperatures [24]. A similar behavior is observed when Co ions are replaced by Mn ions, where the Mn ions occupy the entire three-legged-ladder (3LL) 4–2–4 creating magnetic frustration due to the competition between exchange interactions, which yields a spin-glass state below at 50 K [22].

When Co^{3+} are replaced by magnetic ion Cr^{3+} , the magnetic properties are drastically affected. In this case, Cr ions systematically enter into the structure and occupy mostly site 4 of the compound [8]. Contrary to the cases mentioned above, the interaction between Co and Cr ions reinforces the ferrimagnetic interactions and raises magnetic ordering temperature of the compound from 42 to 78 K [8]. This is one of the few cases where doping the Co Ludwigite with a magnetic ion strengthens the magnetic interactions generating a long-range order and also a significant increase in the **magnetic transition temperature (T_M)**.

In this work, we study the structural and magnetic properties of the $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ series, where gradual substitution of Co^{3+} ions by Cr^{3+} ions is carried out in steps of $x = 0.1$. The substitution of Co by Cr progressively increases the lattice parameters, leading to an expansion of the structure, and

concurrently modifies the magnetic properties with increasing Cr content. The replacement of Co by Cr gradually modifies the magnetic properties of the compounds, changing from a ferrimagnetic system (FIM) of the pure Co compound, to an antiferromagnetic system (AFM) for the compound with the highest Cr content.

2. Experimental

2.1. Synthesis

To synthesize polycrystalline $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigites the well-known high temperature solid state reaction method was applied. In total, ten samples were prepared using analytical reagents in stoichiometric mixture of CoO, Cr_2O_3 , and H_3BO_3 , in the proportion of $3 - x : 0.5 x : 1$. Agate mortar was used to ground the reagents and then compacted into pellets of approximately 10 mm using a pressure of 8 tons. The pellets were then subjected to a heat treatment at 750°C for 12 h in air atmosphere, followed by cooling to room temperature under the natural cooling rate of the furnace. After this first stage, the pellets were grounded in an agate mortar to homogenize the product. It was pressed into tablets and taken to the oven for a second heat treatment in air atmosphere at 1050°C for 24 hours. The cooling process was done in the same way as in the first stage. As a result of the synthesis, a fine black powder was obtained for all samples.

Single crystals of $\text{Co}_{2.22}\text{Cr}_{0.78}\text{O}_2\text{BO}_3$ Ludwigite were synthesized with the sole purpose of obtaining more reliable structural parameters, in order to calculate the exchange integrals. The synthesis was carried out using the flux method, where a stoichiometric mixture of CoO, Cr_2O_3 , H_3BO_3 , and borax was ground in an agate mortar in a proportion of 2:0.5:1:5, respectively. The mixture was placed in a platinum crucible and heated in a furnace at approximately 1150°C for 24 hours, followed by slow cooling to 600°C over approximately 90 hours. The furnace was then turned off, allowing the mixture to cool to room temperature by the thermal inertia of the furnace. As a result of the synthesis, fine black needles approximately 0.5 mm in length were obtained.

2.2. X-Ray diffraction

Single-crystal X-ray diffraction measurement was performed using a D8 Venture Bruker diffractometer at room temperature, using an Incoatec Microfocus Source ($\text{I}\mu\text{S}$) X-ray, Mo- $\text{K}\alpha$ radiation. The crystal was mounted on a Kappa goniometer, and the data were collected with Photon II detector, using Bruker APEX3 software [25]. Multiscan correction using a multifaceted crystal model was applied. The fullmatrix least-squares refinements based on F2 with anisotropic thermal parameters were carried out using ShelXle [26] and WinGX [27] softwares. The structural refinement parameters are display in Tables 1 and 2 of the supplementary material.

Room temperature X-ray powder diffraction (XRD) experiments were performed on $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigites using a Bruker AXS D8 diffractometer

with Lynx-Eye detector, equipped with Co-K α source radiation to avoid fluorescence. The diffraction patterns were collected in a Bragg-Brentano configuration in 10-100°, 2θ range, with incremental steps of 0.02°. XRD data were refined using the Rietveld method, implemented in Fullprof software [28]. Rietveld analysis showed that in all samples, the majority phase corresponds to Ludwigite with space group *Pbam* n°55, with a small impurity phase ($\leq 5\%$ wt.) (see Tables 3 and 4 of suppl. mat.). The appearance of a certain type of impurity depends on the Cr content used in the synthesis. With lower Cr contents ($x \leq 0.5$) the Co₃O₄ [29] and CoO [30] phases are formed while for high concentrations ($x \geq 0.5$) CoCr₂O₄ [31, 32] phase appears (see Table 3 of suppl. mat.). However, these compounds already have well-known magnetic properties and these impurity phases will not hinder magnetic properties.

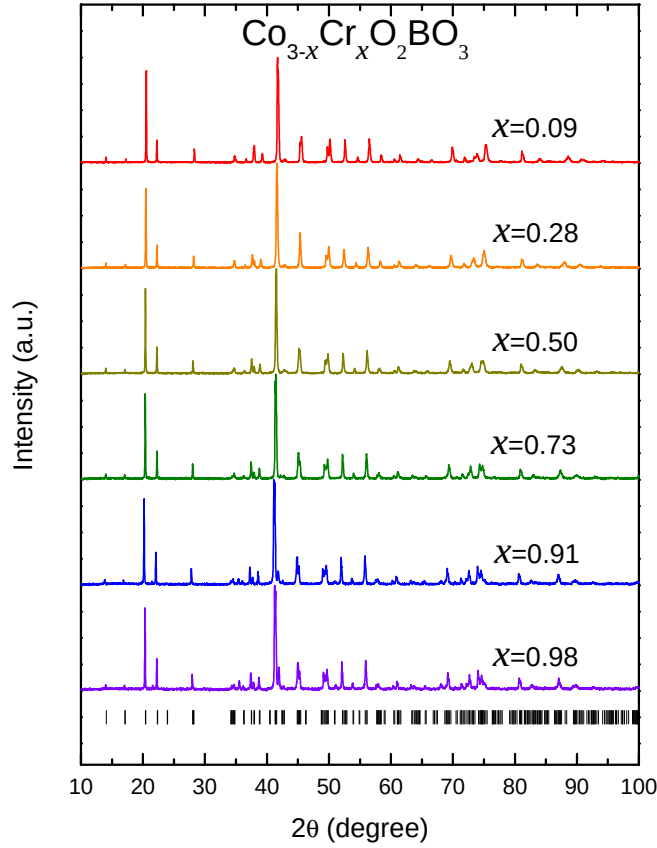


Figure 2: X-ray diffraction powder pattern of $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigites and black vertical traces represent the Bragg Ludwigite peaks. The x values indicates the actual Cr content.

The Rietveld analysis revealed that Cr^{3+} ions preferentially occupy the site 4 of the Ludwigite structure. For compounds with $x > 0.5$, a small fraction of Cr ions also occupy sites 2. Rietveld refinement also showed that the actual Cr

concentrations of the compounds are very close to the nominal values (Table 4 suppl. mat.).

Figures 3(a) to (d) show the lattice parameters and the unit cell volume as a function of actual Cr content for $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigites. The variation of the lattice parameters and unit cell volume with the Cr concentration makes it evident that Cr is replacing Co ions. This increase of unit cell volume is related to the difference in the sizes of the ionic radii of Cr^{3+} (0.615 Å) and LS Co^{3+} (0.545 Å) [33]. The Rietveld refinement of the XRD data shows that Cr^{3+} ions substitute exclusively Co^{3+} ions at sites 4.

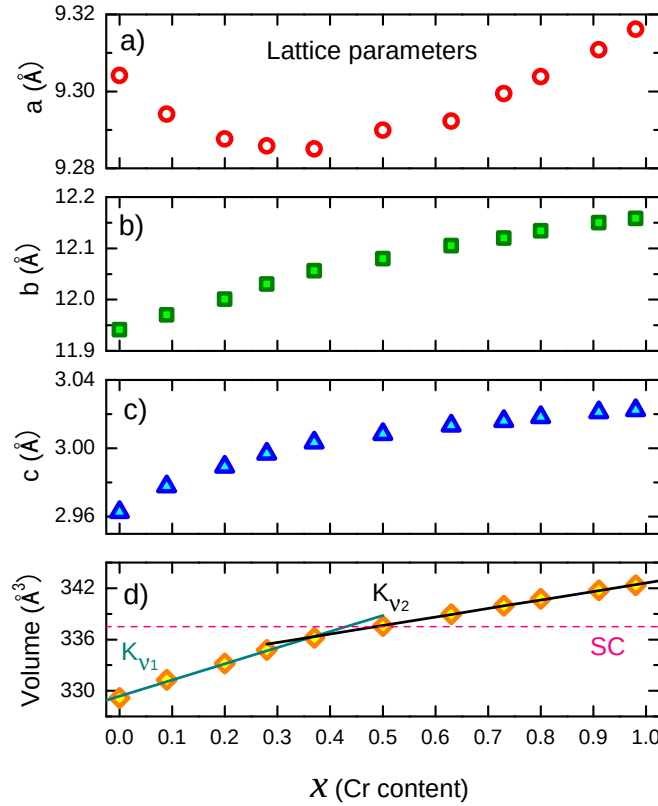


Figure 3: Panels a), b), c) presents a , b and c lattice parameters and panel d) shows the unit cell volume *vs.* Cr content. The parameters were obtained through the Rietveld refinement. The lines K_{v1} and K_{v2} represents the fits of unit cell volume as function of Cr content. The dotted line indicates the unit cell volume of spin crossover (SC) on $\text{Co}_3\text{O}_2\text{BO}_3$ [34]. For a comparison the pure compound [1] ($x = 0$) was added to the figure.

In Figure 3(d) we observe a monotonic increase in the unit cell volume with increasing Cr content. There is a linear relationship between these two parameters and above $x \sim 0.45$ there is a change in the slope and the increase of the volume becomes slower. Thus, we used Vegard's law [35, 36] to analyze

the data in two regions of chromium content. For $x \leq 0.45$ we obtained an expansion coefficient $K_{v1}=18.9 \text{ \AA}^3/x$ and for $x \geq 0.45$ the coefficient decreased to $K_{v2}=9.96 \text{ \AA}^3/x$. It is evident that in both regions the data follow Vergard's law. The variation of the slope at $x \sim 0.45$ may indicate a structural change occurring at this Cr concentration. Another more plausible scenario, compatible with the magnetic data (see section C) is as follows. Starting at low Cr contents the LS Co^{3+} ($r = 0.545 \text{ \AA}$) ions at site 4 are gradually substituted by larger Cr^{3+} ($r = 0.615 \text{ \AA}$) and a monotonic (linear) increase of the volume with the Cr concentration is observed. Above $x = 0.5$, where the volume is favorable for Co ions to adopt a HS state [8], the sites 4 contain basically HS Co^{3+} ($r = 0.61 \text{ \AA}$) and Cr^{3+} ($r = 0.615 \text{ \AA}$) with almost the same ionic radio. Therefore, if we continue to replace the HS Co ions with slightly larger Cr ions, the crystal volume would be expected to increase more slowly when compared to the variation for concentrations below $x = 0.5$. This scenario appropriately describes the magnetization results as will be discussed later.

Another parameter that gives us information about the position of the Cr ions within the structure is the ionic radius of the metal ions. The calculation of this parameter showed that the average radii of sites 1, 2, and 3 are hardly affected by the Cr concentration. However, there is a systematic increase of the average ionic radius of site 4 with the increasing in Cr concentration, as seen in Fig. 4. For a concentration of $x = 0.5$, the ionic radii value of site 4 is already comparable to Co^{3+} in a high-spin state. For higher concentrations, these values match and even exceed those corresponding to Cr^{3+} . This is further evidence that Cr occupies site 4 and that Co adopts a high-spin state for Cr concentrations greater than 0.5.

2.3. Magnetization

Magnetization measurements were performed on polycrystalline powder samples using a vibrating sample magnetometer on a commercial Quantum Design PPMS and SQUID. Figure 5 shows the temperature dependence of the magnetization measured with a field-cooled warming (FCW) protocol with an applied magnetic field of 100 Oe.

The magnetic transition temperatures were obtained from the inflection point of magnetization *vs.* temperature, increases almost linearly with increasing Cr content. Starting at 42 K for the undoped $\text{Co}_3\text{O}_2\text{BO}_3$, it reaches 115 K for the $\text{Co}_2\text{CrO}_2\text{BO}_3$ ($x = 1$) compound (see inset Fig. 5). This magnetic transition temperature is the highest for an cobalt Ludwigite.

As the temperature decreases, the magnetization curves for compounds with low Cr concentration gradually increase until almost reaching saturation close to 2 K, similar to the magnetization curve shown by the undoped compound with a ferrimagnetic structure below the magnetic transition temperature [19, 37]. Below the magnetic transition temperature, the magnetization for the samples with $x > 0.75$ increases rapidly when the temperature decreases. It reaches a maximum at approximately 50 K, and for lower temperatures the magnetization decreases, characteristic of compounds with an antiferromagnetic structure. Similar results were obtained for homometallic $\text{Fe}_3\text{O}_2\text{BO}_3$ Ludwigite

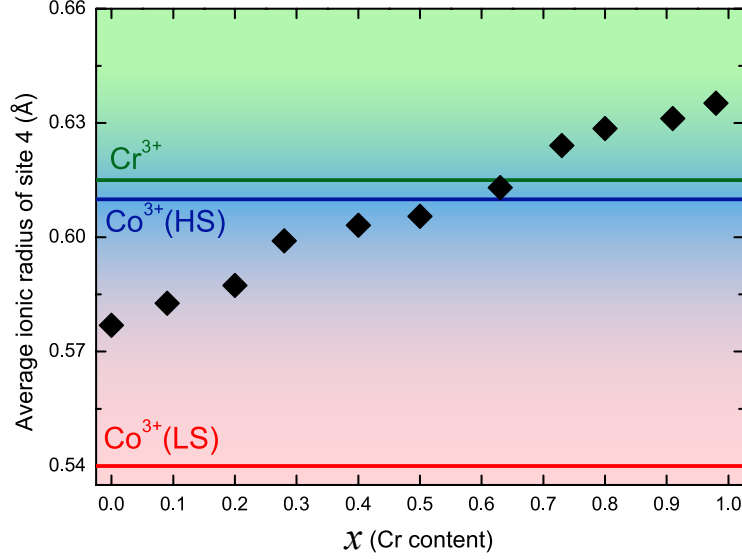


Figure 4: Average Ionic radii of site 4 *vs.* Cr content. The dot line represents a fit for the average ionic radius. Solid lines represent the theoretical value for average ionic radius of low-spin Co^{3+} (red), high-spin Co^{3+} (blue) and Cr^{3+} (dark green). For a comparison, the parameter of pure compound [1] ($x = 0$) was added.

with a ground-state antiferromagnetic structure [7, 37]. As we will see later, the low temperature AFM structure of compounds with $x > 0.75$ becomes evident in the hysteresis loops.

Above the magnetic transition temperature, in the paramagnetic region, the magnetization decreases asymptotically with increasing temperature, following the Curie-Weiss law [38, 39]. Using the Curie-Weiss law, we estimated the experimental effective moments (p_{eff}^{exp}) through the high-temperature linear fit of inverse dc-susceptibility *vs.* temperature. For comparison, the effective magnetic moment was calculated as a function of the Cr content. The following scenario was proposed for the calculation: for Cr concentrations of $x < 0.4$, Co^{3+} adopts a low-spin state, while for Cr concentrations of $x > 0.5$, it adopts a high-spin state. To estimate the P_{eff}^{cal} values, the following formula was used: $\sqrt{p_1^2 + p_2^2 + p_3^2 + \dots}$ [40], where the magnetic contribution of the ions is given by: $m_{eff}^{\text{Co}^{2+}} = 4.8 \mu_B$, $p_{eff}^{HSCo^{3+}} = 5.4 \mu_B$, $p_{eff}^{LSCo^{3+}} = 0$ and $p_{eff}^{Cr^{3+}} = 3.8 \mu_B$ [38]. The results are shown in Fig. 6. The experimental and calculated p_{eff} values exhibit the same trends. The p_{eff} increases gradually with the increase in Cr content, which is expected if we consider that LS Co^{3+} ions are being gradually replaced by Cr^{3+} ions. At $x = 0.5$, there is a sudden increase in the p_{eff} values, reaching a maximum, which is consistent with a transition to HS state for all Co^{3+} ions. For concentrations greater than $x = 0.5$, p_{eff} gradually decreases with increasing Cr content. This decrease in p_{eff} for

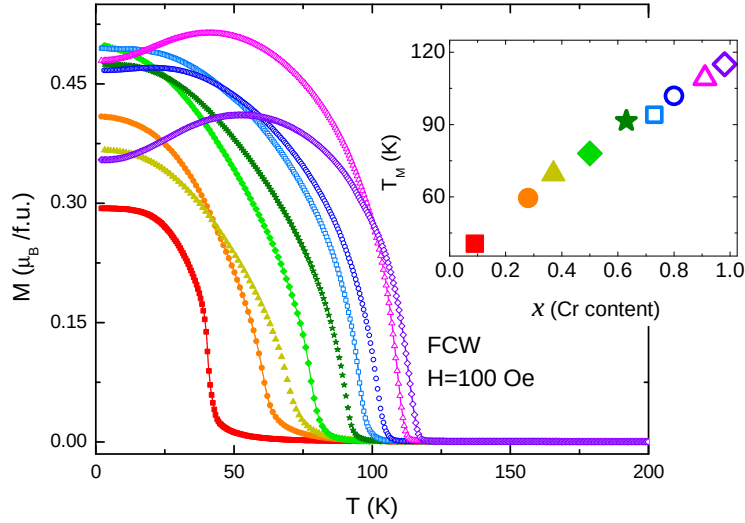


Figure 5: M vs. T measurements for $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigites under an applied field of 100 Oe. Insert graphic presents T_M vs. Cr concentration.

$x > 0.5$ can be explained by considering that high-spin Co^{3+} ions are being replaced by Cr^{3+} ions, which have a lower magnetic moment.

The arguments used to explain the increase and subsequent decrease in the effective moment as the Cr content increases are based on X-ray diffraction results, which show that Cr ions occupy site 4. This occupancy causes the remaining Co^{3+} ions in this site to adopt an ionic radius compatible with a high-spin state. As a result, at lower Cr concentrations, the effective moment increases due to the gradual transition of Co^{3+} from a LS state to a HS state. At $x = 0.5$, all remaining Co^{3+} ions in site 4 are in a high-spin state. However, as more Cr ions occupy site 4, replacement of high-spin Co^{3+} ions by Cr^{3+} ions with a lower magnetic moment leads to a gradual decrease in the effective moment.

In Fig. 6, we observe that, for the Cr concentration $x \leq 0.4$, the experimental p_{eff} values are slightly higher than the calculated ones. However, for concentrations $x \geq 0.5$, there is a closer match between the experimental and calculated values. The calculated p_{eff} for $x \leq 0.4$ content can be adjusted to match the experimental value if we consider that, in this Cr concentration range, a fraction of the Co^{3+} ions in site 4 adopt a high-spin state. It was estimated that, to make this adjustment, approximately 10% of the remaining Co^{3+} ions in this site would need to be in a high-spin state. A second interpretation to justify the difference observed in the p_{eff} may be the fact that a portion of the Co^{3+} ions may be in the intermediate spin state ($S=1$) [41]. However, further studies are necessary to address this issue. For example, combined X-ray absorption spectroscopy (XAS) and X-ray magnetic circular dichroism (XMCD) or even resonant inelastic X-ray scattering (RIXS) could provide a more accurate in-

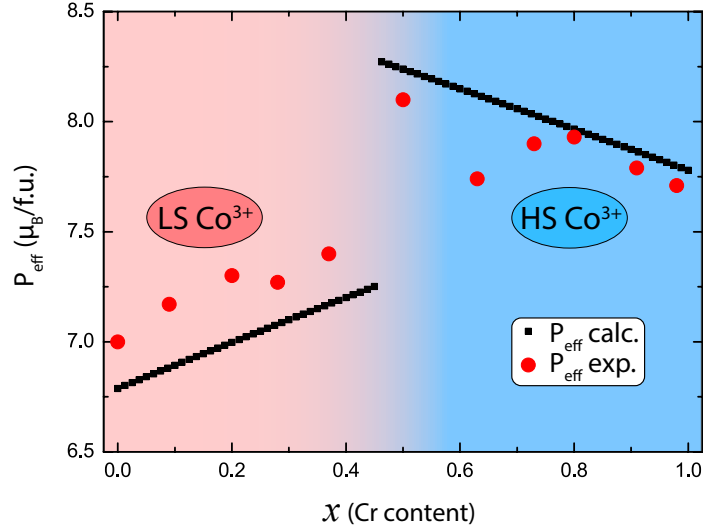


Figure 6: Effective magnetic moment *vs.* Cr content for $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigites. The data were obtained from the inverse of magnetic susceptibility (χ_{dc}^{-1}) from FCW curves under applied magnetic field of 1 kOe. For a comparison, the p_{eff}^{exp} of pure compound [1] ($x = 0$) was added to the figure.

formation about the spin state of the Co^{3+} ions. The analysis of the inverse dc-susceptibility at high temperatures yield negative Curie-Weiss temperatures θ_{CW} , indicating that antiferromagnetic interactions are dominant, as occurs in cobalt Ludwigites [1, 3, 5, 8, 21]. The presence of different ions with different magnetic moments leads to a competition between different types of exchange interactions. **Despite this, the compounds with lower Cr concentrations present ferrimagnetic type ordering, while higher concentrations are antiferromagnetic.**

The hysteresis loops, *M vs. H*, obtained with applied magnetic fields up to 7 T, are shown in Figs. 7(a) to (d). Figure 7(a) displays the *M vs. H* results at 2 K. In the compound with the lowest Cr concentration ($x = 0.1$), the hysteresis loop produces a coercive field (H_c) of approximately 1.6 T. As the Cr concentration increases, the hysteresis loops widen and the coercive field increases, reaching a maximum value of 4.8 T for compound $x = 0.5$. **At 2 K, the hysteresis loops for compounds with $x \leq 0.5$ show a steep increase, which is related to the metamagnetic transitions typical of ferrimagnetic systems [42, 43]. This characteristic was also observed in other Ludwigites [4, 5, 44], may be related to a rearrangement of the magnetic configuration due to the competition between the Zeeman energy and the magnetic anisotropy present in this material [5]. In this concentration range, an increase in the coercive field is also observed with increase in Cr concentration, indicating that the presence of Cr leads to an enhancement of the ferromagnetic interactions between the spins. As the temperature begins to rise, the hysteresis loops gradually narrow (Fig. 7(b)-7(d))**

until they eventually become linear above the magnetic transition temperature (Fig. 7(d)), indicating a transition to a paramagnetic state. For $x \leq 0.5$, the compounds exhibit a ferrimagnetic behavior, while for $x \geq 0.6$, the behavior is very close to that of an antiferromagnetic material.

The spurious phases identified in the XRD measurements may have a magnetic contribution to the M vs. H measurements. However, the compounds that exhibit the greatest broadening in the hysteresis loops are those with concentrations $x \leq 0.6$. Based on Table 3 of the suppl. mat., the spurious phases present at these concentrations are Co_3O_4 , with $T_N=40$ K [29], and CoO , with $T_N=287$ K [30]. At low temperatures, these phases are already antiferromagnetically aligned and will contribute nothing or very little to the broadening of the hysteresis curves. On the other hand, the spurious phase present in compounds with concentrations $x \geq 0.7$, CoCr_2O_4 , has a ferrimagnetic ordering $T_c=93$ K [31, 32]. The hysteresis curves for these compounds are practically closed and no ferrimagnetic contribution is observed. Therefore, the presence of these small amounts of impurity phases does not affect the interpretation given to the magnetization results.

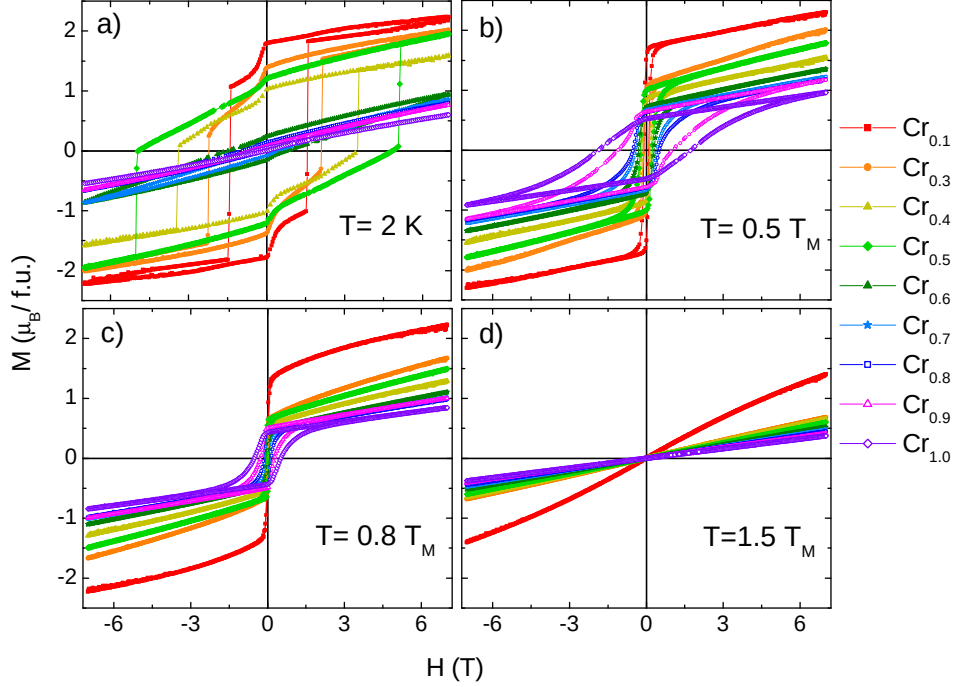


Figure 7: M vs. H measurements performed on the powder of $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigites at different temperatures.

Figure 8 displays the remanent magnetization (right axis) and coercive field (left axis) as a function of Cr content. The values were obtained from M vs. H measurements at 2 K. Coercive field is around 1.5 T for lower content, and

increases with doping, reaching a maximum for $x = 0.5$. At higher concentrations, the coercive field drops, reaching values close to zero for the highest Cr content. On the other hand, the remanent magnetization gradually decreases with increasing Cr substitution, reaching a value close to zero for the highest Cr concentration. This fact also shows that increasing the amount of Cr strengthens antiferromagnetic interactions.

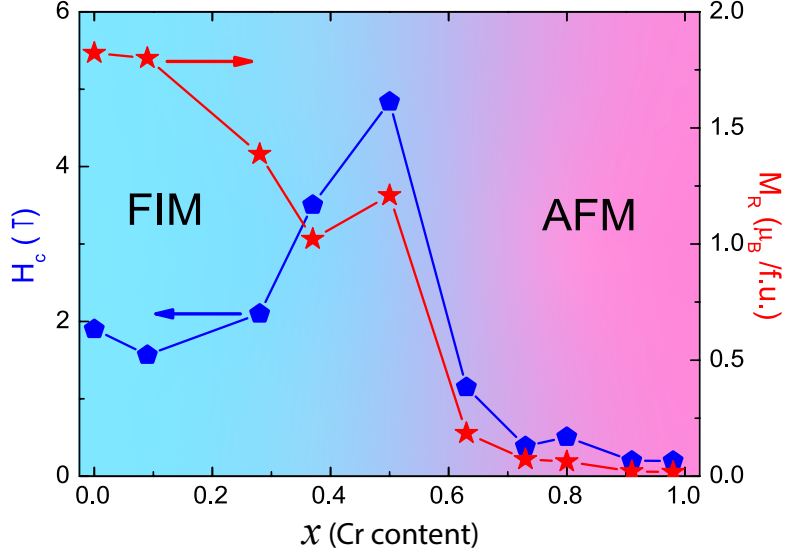


Figure 8: Coercive field (H_C) and Remanent magnetization (M_R) *vs.* Cr content for $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigites. The data were obtained from the M *vs.* H measurements at 2 K. For a comparison the pure compound [1] ($x = 0$) data was added to the figure.

M *vs.* H measurements under high applied magnetic fields were carried out to investigate whether the applied field induces a spin state transition in Co^{3+} , similar to what occurs in some Perovskites [45, 46, 47, 48]. The measurements were conducted using high pulsed magnetic fields at the Hochfeld-Magnetlabor Dresden (HLD) laboratory. Magnetization measurements were performed at a temperature of 4.2 K, with magnetic fields up to 60 T. The results are shown in Fig. 9. The magnetization increases almost linearly with the applied field. However, none of the compounds exhibit jumps or abrupt changes in the magnetization which would indicate a possible change in the spin state of the Co^{3+} ions. It is likely that 60 T field is still insufficient to induce the Co^{3+} spin state transition.

Figure 10 displays the real and imaginary parts of AC magnetic susceptibility as a function of temperature for $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ series. The χ_{ac} measurements display a pronounced peak, whose position coincides with the sudden increase in magnetization and with the position of the peak of the specific heat data (see below) evidencing the long-range magnetic ordering temperature of these compounds. The compound with highest Cr-content has the susceptibility peak

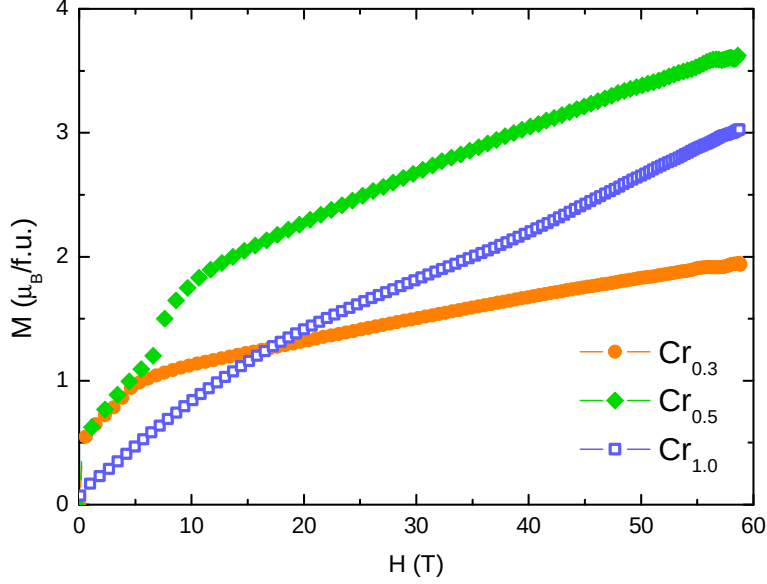


Figure 9: M vs. H measurements for $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigites. The measurements were performed at 4.2 K.

at 110 K, and that with the lowest content has the peak at 38 K. T_M increases ~ 10 K per $x = 0.1$ of Cr-content. It is also possible to observe a decrease in the AC susceptibility peak as Cr content increases, this happens for both the real χ'_{ac} and for imaginary χ''_{ac} parts. The decrease in χ_{ac} peak is related to the magnetic changes induced by the increase in the amount of Cr in the Ludwigites structure.

For $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigites series, the transition temperature varies little as a function of frequency, about 0.1 K per order of magnitude in frequency. In order to verify if some of these compounds present a spin-glass like behavior, we assume the opposite that the magnetic transition peaks change their position with frequency, and analyze the results using power law [49, 50], $\tau = \tau_0 \left(\frac{T}{T_{SG}} - 1 \right)^{-z\nu}$, where $z\nu$ is a critical exponent, τ is given by $1/2\pi f$, τ_0 is the relaxation time, and T_{SG} is the freezing temperature, obtained through the plot of $T_{peak} \times \log(\text{freq})$ when the frequency tends to zero. The fits using this power law provided $z\nu$ values in the range of a classical spin-glass compounds (5 to 11) [49]. **Nonetheless, the values obtained for τ_0 are in the range of 3.3×10^{-15} to 1.0×10^{-90} s. These values have no physical meaning. A standard spin-glass presents values of τ_0 in the range of 10^{-10} to 10^{-13} s, and cluster-glass compounds have relaxation times of the order of 10^{-10} to 10^{-7} s [50, 51].** This results confirms that none of the analyzed compounds exhibit classical a spin-glass behavior. The small variation of the position of the peak with frequency probably has its origin in the dynamics of the spins in domain walls [52] or is

due to the presence of clusters of a ferromagnetic phase, which coexists with the majority magnetic ordered phase [53]. According to χ_{ac} and specific heat results, there is no evidence for a spin-glass state in any of these compounds.

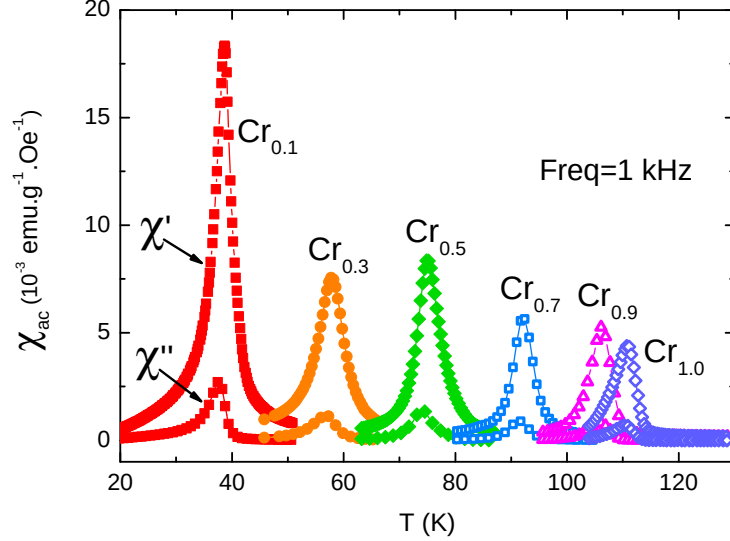


Figure 10: AC magnetic susceptibility *vs.* temperature for $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigites. The frequency of measurements is 1 kHz and the amplitude of oscillating magnetic field is 10 Oe.

2.4. Specific heat

Specific heat measurements as a function of temperature were performed with a commercial Quantum Design PPMS system. To improve thermal contact, the powder samples were compressed into pellets. Figures 11(a) to 11(f) show the temperature dependencies of C/T for $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigites with different applied magnetic fields. All curves show a peak at the temperature where the magnetic transition occurs. The transition temperatures match (within experimental error) those obtained through magnetization and AC susceptibility. When an external magnetic field is applied, the specific heat curves change their shape, and the peaks shift differently depending on the chromium concentration. In Figs. 11(a) through 11(c), we can observe that for $x \leq 0.5$, the magnetic transition peaks become broader and shift to higher temperatures as the applied magnetic field increases, consistent with ferrimagnetic system [38, 39]. On the other hand, for chromium concentrations $x \geq 0.7$, the peaks only broaden, decreasing in intensity without shifting their position as the magnetic field increases (Figs. 11(d) to 11(f)). For an antiferromagnetic system, the position of the specific heat peak should shift to lower temperatures as the applied magnetic field increases [39, 38]. However, this is not the response that we observe for compounds with $x > 0.7$. These results indicate that compounds with high Cr concentrations are not conventional antiferromagnets. In fact,

particularly for compound $x = 1.0$, we observe the appearance of a hysteresis loop just below the magnetic transition temperature. As the temperature decreases further, the hysteresis loops become wider up to 50 K. Decreasing the temperature even more, the hysteresis loops begin to narrow until they practically disappear at 10 K. These results are similar to those reported for $\text{Fe}_3\text{O}_2\text{BO}_3$ Ludwigite [54]. This latter compound exhibits weak ferromagnetism below 70 K, confirmed by the $M(H)$ isotherms and the opening of the hysteresis loops. Below 40 K, the hysteresis loops become linear, showing that the compound transitions to an antiferromagnetic state. $\text{Co}_2\text{CrO}_2\text{BO}_3$ Ludwigite also appears to exhibit a weak ferromagnetic state below $T_M=115$ K and tends toward a purely antiferromagnetic state at very low temperatures, as suggested by exchange integrals calculations. These results further corroborate the findings from magnetization, AC susceptibility, and exchange interaction calculations, which demonstrate that the system crossover from a ferrimagnetic state to an antiferromagnetic state as the Cr concentration increases.

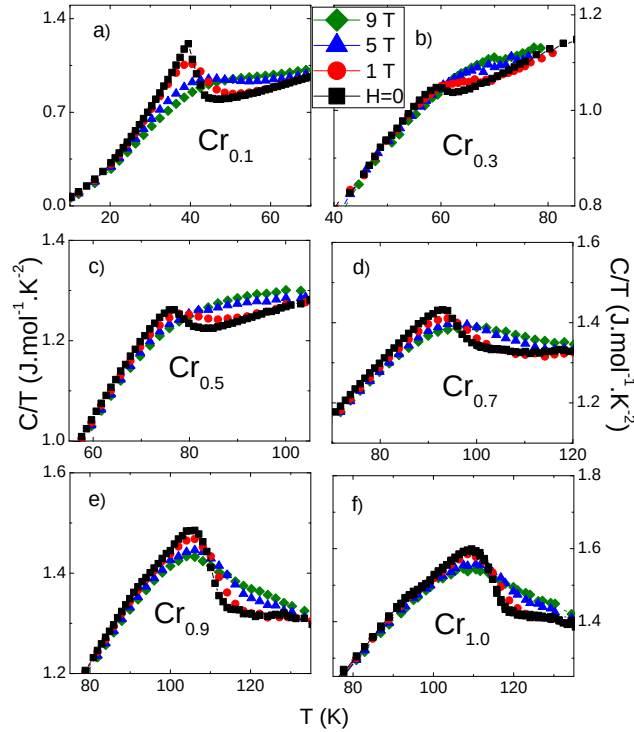


Figure 11: Heat capacity *vs.* temperature plotted as C/T *vs.* T . Panels *a* to *f* displays the specific heat peaks of magnetic transition for $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigites.

2.5. Exchange Integrals Calculations

Based on the crystallographic structure of the $\text{Co}_{2.22}\text{Cr}_{0.78}\text{O}_2\text{BO}_3$ Ludwigite obtained from the X-ray diffraction data (Table 1. Suppl. mat), the calcula-

tion of exchange integrals was performed. To assess the exchange interaction, we used the model of indirect interaction developed earlier [55, 56, 57]. The nearest-neighbor approach is used in the framework of the given model, i.e. the interaction of two $3d$ -actions through an intermediate ligand M-O-M (superexchange, SE). The strength and sign of pair spin interactions depend on the atomic arrangement of magnetic ions and they are qualitatively predicted by the Goodenough-Kanamori-Anderson rule [58, 59, 60]. The next-nearest neighbor interactions M-O-B-O-M and M-O-M-O-M (super-superexchange, SSE) are not considered.

The model uses, the parameters for electron transfer along the σ and π bonds, represented by b and c , respectively, intra-atomic exchange integrals J (Hund energy) and cation-ligand excitation energies. All five $3d$ orbitals of the neighboring cations (α , β) and three $2p$ orbitals of the intermediate ligand (γ) are considered. The sum of the individual orbital exchange integrals constitutes the total integral of the cation-cation exchange interactions in this model of the cation-ligand-cation complex.

According to the structural data, sites 1 and 3 are fully occupied by Co^{2+} ions. Site 2 is occupied by Co^{2+} (79%) and Cr^{3+} (21%). Based on the condition of electroneutrality, we suggest that three types of ions occupy site 4: Co^{2+} (10,5%), Co^{3+} (22,5%) and Cr^{3+} (67%) (Table 2 Suppl. mat). The expressions for calculating the superexchange integrals were obtained for the interacting pair of each type, depending on the occupation of sites. The contribution to the total value J_λ from each interacting pair depends on the concentration of ions at the site. The expressions and weights for each type of the interacting pair are shown in Table S2 (Suppl. mat). For calculations were used the following parameters of b , c , J and Δpd : $b = 0.02$, $c = 0.01$, $\Delta pd(\text{Co}^{2+}) = 3.3$ eV, $\Delta pd(\text{Co}^{3+}) = 3.9$ eV, $\Delta pd(\text{Cr}^{3+}) = 4.5$ eV, $J(\text{Co}^{2+}) = 1.83$ eV, $J(\text{Co}^{3+}) = 3.07$ eV, and $J(\text{Cr}^{3+}) = 1.49$ eV [57].

The calculated superexchange integrals are shown in Table 5 of Supl. mat.. All superexchange integrals of Cr-Cr pairs are antiferromagnetic, and most superexchange integrals of Co - Cr pairs are also antiferromagnetic and strong. Thus, the replacement of cobalt ions by chromium ions leads to a change in the sign of exchange interactions or to an increase in the value of antiferromagnetic interactions. Using the suggestion that magnetic moments should be collinear and the calculated values of exchange interactions, we estimate the exchange part of energy for different magnetic configurations: $E = -1/2 \sum J_\lambda s_i s_j$.

The structure with the lowest energy is antiferromagnetic. In triads 3-1-3 the magnetic moments of sites 3 and 1 are oriented antiferromagnetically. Triads 4-2-4 are divided into two almost independent elements: the first element is a ferromagnetically ordered dimer 4-2, and the second element is a magnetic moment at position 4. Magnetic ordering in subsystem 4-2-4 is similar to ordering of this subsystem in $\text{Fe}_3\text{O}_2\text{BO}_3$ [61]. Ordering of magnetic moments along the c -axis is ferromagnetic for sites 1, 2 and 3, but for site 4 the magnetic ordering along the c -axis is antiferromagnetic. The two different triads of each type (3-1-3 and 4-2-4) in the unit cell are oriented antiferromagnetically to each other.

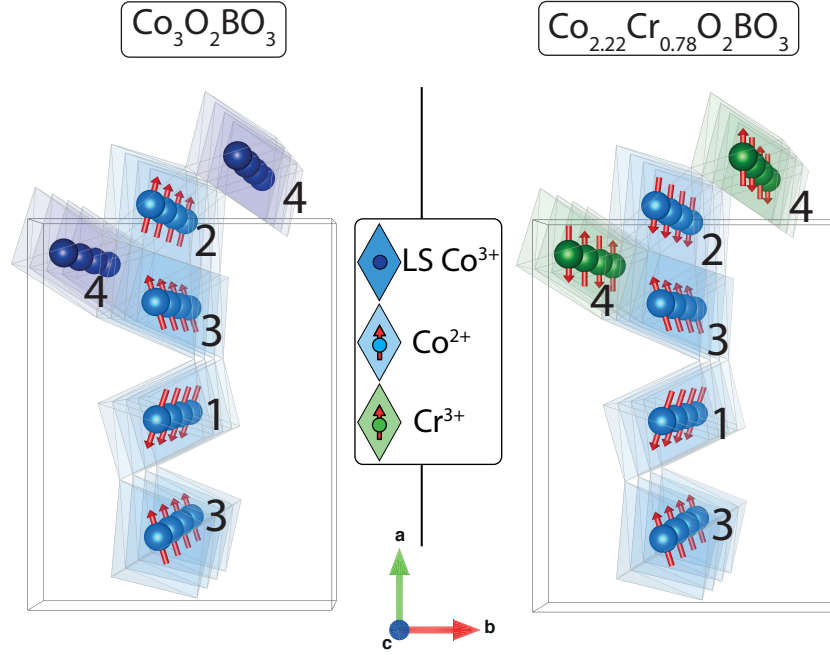


Figure 12: Magnetic arrangement obtained determined through calculations of exchange integrals for $\text{Co}_{2.22}\text{Cr}_{0.78}\text{O}_2\text{BO}_3$ Ludwigite.

3. Discussion

X-ray diffraction shows that Cr^{3+} ions substitute Co^{3+} ions at site 4. As expected, the substitution of the LS Co^{3+} ions by Cr^{3+} ions leads to an expansion of the lattice due to the Cr greater ionic radius ($r_{\text{Cr}^{3+}} - r_{\text{Co}_{LS}^{3+}} = 0.07 \text{ \AA}$). For $x \leq 0.5$ the volume of the lattice is such that the oxygen octahedra size of the site 4 becomes favorable for the establishment of a high-spin state for Co^{3+} [34]. Calculations to estimate the ionic radius of the different ions show that the ionic radius of sites 1, 2 and 3, which contain Co^{2+} in HS, are almost not affected by the Cr concentration. However, the ionic radius of site 4 increases linearly with Cr content. For $x \leq 0.5$ the average ionic radii are compatible with the presence of Co^{3+} in HS. Thus, the presence of HS Co^{3+} ions at sites 4 explains why the increase in volume with higher Cr concentration is less pronounced for $x \leq 0.5$. For this range of Cr content, the involved ions (HS Co^{3+} and Cr^{3+}) have similar ionic radii ($\Delta r = 0.005 \text{ \AA}$). The establishment of a high-spin state for Co^{3+} at site 4 for $x \geq 0.5$ is compatible with the magnetization results.

With the information about the arrangement of the ions in the structure we will now discuss the magnetization results. Measurements of magnetization, AC susceptibility and specific heat as a function of temperature show long-range magnetic ordering, below a magnetic transition temperature, for all compounds.

Table 1: Exchange Integrals calculations for $\text{Co}_{2.22}\text{Cr}_{0.78}\text{O}_2\text{BO}_3$ Ludwigite. The Exchange Integrals values of $\text{Co}_3\text{O}_2\text{BO}_3$ Ludwigite [37] was added for comparison.

J_λ	Site interaction	$\text{Co}_3\text{O}_2\text{BO}_3$ [37] J (Kelvin)	$\text{Co}_{2.22}\text{Cr}_{0.78}\text{O}_2\text{BO}_3$ J (Kelvin)
J_1	1-1	+3.50	+3.0
J_2	1-3	-2.89	-1.2
J_3	1-4	-	-5.4
J_4	2-2	+3.50	-0.5
J_5	2-3	+1.88	-4.8
J_6	2-4	-	-4.8
J_7	3-3	+3.50	+3.0
J_8	3-4	-	-0.1
J_9	3-4	-	-5.4
J_{10}	2-4	-	-1.0
J_{11}	4-4	-	-2.7

The analysis of the magnetization yield a value for the frustration parameter $f = \theta_{CW}/T_M \approx 1$, for all compounds. Although the analysis of the susceptibility data using a power law gives a value for the critical exponent $z\nu$ that falls within the values of a spin-glass system, the relaxation time τ_0 obtained has no physical meaning. These results show that magnetic frustration or spin-glass states are ruled out in these compounds in agreement with magnetization and specific heat results that show long-range magnetic ordering below the magnetic transition temperature. The T_M increases monotonically with increasing Cr concentration. Starting at 42 K for pure Co compound, reaching 120 K for Ludwigite with $x = 1.0$ (Fig. 5). The latter is the highest magnetic transition temperature achieved in Co Ludwigite doped with magnetic ions. Up to $x = 0.5$ the temperature dependence of the magnetization curves is typical for ferrimagnetic systems (see Fig. 5). Above this Cr concentration, the curves undergo an inflection at low temperatures indicating the emergence of an antiferromagnetic state. The negative values of θ_{CW} found for all compounds indicate a predominance of AFM interactions that, depending on the concentration of LS Co^{3+} , HS Co^{3+} and Cr^{3+} at sites 4, can lead to a ferri- or antiferromagnetic type spin structure. Magnetization results for the compound with the highest Cr concentration are compatible with a weak ferromagnetic state below the T_M . This weak ferromagnetic state may be the result of canting of antiferromagnetically aligned spins, which gives rise to a small net magnetization, as occurs in the $\text{Fe}_3\text{O}_2\text{BO}_3$ Ludwigite and Hematite [54, 62]. Like these latter two compounds, at much lower temperatures, $\text{Co}_2\text{CrO}_2\text{BO}_3$ also moves towards a purely antiferromagnetic state.

Information about the spin state of the Co ions at site 4 can be obtained through the calculation of the effective magnetic moment per formula unit p_{eff} . Figure 6 shows the p_{eff} values as a function of Cr concentration. For $x \leq 0.4$

there is a gradual increase in p_{eff} values, consistent with the substitution of LS Co^{3+} ions ($S=0$) by Cr^{3+} ions ($S=3/2$). For $x \geq 0.5$ there is a significant increase in p_{eff} , consistent with a change in the spin state of Co^{3+} ions, adopting now a high-spin state with $S = 2$. This change in the spin state of Co ions at site 4 is in full agreement with the ionic ratio values obtained by XRD experiments. For concentrations greater than $x = 0.5$, the p_{eff} values gradually decrease until the maximum Cr concentration is reached. This is consistent with the fact that HS Co^{3+} ($S=2$) ions are progressively being replaced by Cr^{3+} ($S=3/2$) ions. The p_{eff} values obtained from the analysis of the magnetization curves are consistent with a scenario where for low Cr contents ($x < 0.5$) the Co^{3+} ions at sites 4 are in a LS state while for $x \geq 0.5$ they adopt a HS state.

The magnetization curves, below the magnetic transition, indicate a change in the spin structure of the compounds as the Cr concentration increases. This change in spin arrangements type is clearly seen in the magnetic hysteresis loops (see Fig. 7). For low Cr content *Mvs.H* curves show a coercive field around 1.7 T at 2 K (Fig. 8), typical of ferrimagnetic systems. The coercive field increases with the increase of Cr content, reaching a maximum of 4.5 T at 2 K for $x = 0.5$, compatible with the ferrimagnetic character of these compounds for this range of Cr concentration. Analyzing the hysteresis curves at 2 K, the coercive field decreases drastically with values close to zero for compounds with high Cr content, $x = 0.9$ and 1.0, showing that for high Cr concentrations the compounds become antiferromagnetic.

These magnetic structures as revealed by magnetization data are in agreement with super-exchange interaction calculations. According to these results, the most significant difference between $\text{Co}_3\text{O}_2\text{BO}_3$ and $\text{Co}_{2.22}\text{Cr}_{0.78}\text{O}_2\text{BO}_3$ resides in the interaction between the Co^{2+} ions at sites 2 and 3 (J_{2-3}), while in the former this interaction is ferromagnetic, in the latter it is antiferromagnetic. Another remarkable thing about these calculations is that the lowest energy for $\text{Co}_{2.22}\text{Cr}_{0.78}\text{O}_2\text{BO}_3$ is achieved for an AFM coupling between Cr ions at sites 4 along the *c*-axis (in this compound sites 4 are almost completely occupied by Cr ions, see section 2.5).

Analyzing the magnetic contribution of the ions to the total magnetization, we must consider that for each Co^{2+} ion in sites 1 there are two Co^{2+} ions at sites 3. In the same way, for each Co^{2+} ion in sites 2 there are two Co^{3+} (Cr^{3+}) at sites 4. Super-exchange calculations show that in the undoped $\text{Co}_3\text{O}_2\text{BO}_3$ compound, all ions at the same site are ferromagnetically coupled along the *c*-axis (positive values of J_{1-1} , J_{2-2} and J_{3-3} [37]). The AFM coupling among ions at sites 1 and 3 (J_{1-3}) and FM among 2 and 3 (J_{2-3}) (see Fig. 12) gives rise to a ferrimagnetic structure, as confirmed by neutron diffraction studies [19].

For the Cr-substitution compound, the number of interactions between ions at different sites increases significantly since now sites 4 are occupied by magnetic ions (Cr^{3+} , HS Co^{3+}). In $\text{Co}_{2.22}\text{Cr}_{0.78}\text{O}_2\text{BO}_3$, sites 4 are occupied almost completely by Cr^{3+} ions ($S=1$), considerably reducing the number of magnetic interactions and consequently the magnetic disorder. The interaction between the Co ions at sites 1 and 3 (J_{1-3}) remains AFM, same as in the undoped $\text{Co}_3\text{O}_2\text{BO}_3$ Ludwigite. However, the substantial change, in relation to undoped

$\text{Co}_3\text{O}_2\text{BO}_3$, lies in the fact that now the interaction between Co ions at sites 2 and 3 is AFM (J_{2-3}). The interaction between Cr ions at sites 4, along the c -axis, is antiferromagnetic (J_{4-4}) resulting in a null contribution by these ions to total magnetization. Thus, including the magnetic contribution from the Cr ions, the system remains with an antiferromagnetic structure (see Fig. 12) (which has the lowest energy) in agreement with the experimental results.

The analysis of specific heat measurements confirms this change in magnetic structure with the Cr content. For Cr concentrations $x \leq 0.5$, the peak observed in the specific heat curve, corresponding to the magnetic transition, is shifted to higher temperatures as the applied magnetic field increases, typical of ferrimagnetic systems [38]. For Cr contents $x \geq 0.7$, the peak remains in the same position, independent of the applied field. If the compound was a conventional AFM the peak of the magnetic transition should move to lower temperatures as the applied magnetic field increases. Since this does not occur, it shows that the compounds with $x \geq 0.7$ are likely an unconventional AFM. Hence, the ferrimagnetic and antiferromagnetic character of the $\text{Co}_3\text{O}_2\text{BO}_3$ and $\text{Co}_{2.22}\text{Cr}_{0.78}\text{O}_2\text{BO}_3$ respectively, is evidenced by both, experimental data and super-exchange interactions calculations. **These results are in agreement with the findings from magnetization, specific heat, and exchange integrals results, where an increase in Cr concentration drives the system from a ferrimagnetic state to a complex antiferromagnetic state.**

Materials that exhibit spin transitions hold great potential in fields such as spintronics, geological sensors, catalysts, and energy [63]. A notable example is the family of LaCoO_3 Perovskites. In these materials, the spin state of Co^{3+} can be manipulated by temperature, chemical doping, or pressure [41, 63, 64, 65, 66]. These compounds combine the robustness of oxides with the versatility of spin transitions, paving the way for new technologies. $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigite also exhibits interesting magnetic properties relevant for technological applications, since it is a ferrimagnetic insulator and presents controllable spin transitions of Co^{3+} . It is possible to access the different spin states of Co^{3+} through the contraction and expansion of the crystal lattice. In this study, it was observed that the Co^{3+} ion in $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigite can alternate between low-spin and high-spin states through chemical substitution. This enables a dynamic control of the magnetic and electronic properties and the miniaturization of these systems making this material a promising candidate for applications in spintronics, **Resistive Random Access Memory (ReRAM)** storage, and magnetic logic devices requiring binary states.

4. Conclusion

X-ray diffraction, magnetization, specific heat measurements, and exchange integral calculations show that in Cr-substitution $\text{Co}_3\text{O}_2\text{BO}_3$ Ludwigite, Cr ions preferentially occupies site 4, leading the system to adopt different types of magnetic structures depending on the amount of Cr in the compound. The presence of Cr in site 4 causes the remaining Co^{3+} ions in this site, which are in a low-spin state in the undoped compound, to adopt a high-spin state.

Consequently, all the ions in sites 4 (Co and Cr), now possessing a magnetic moment, couple the magnetic b - c planes formed by the Co^{2+} ions in sites 1, 2, and 3, strengthening the magnetic interactions and enhancing the magnetic transition temperature from 42 K (in the undoped compound) to 118 K in the compound with $x = 1.0$. The presence of high-spin Cr^{3+} and Co^{3+} in site 4 does not affect the ferromagnetic interactions of the Co^{2+} ions in the same sites (1, 2, and 3) along the c -axis, nor the type of interaction between Co^{2+} ions in two different sites. In this way, all changes in the magnetic structure of the system are essentially due to the interactions of the magnetic ions (Co^{3+} and Cr^{3+}) in site 4 along the c -axis, transitioning the system from a ferrimagnetic state (in the undoped compound) to an antiferromagnetic state in $\text{Co}_2\text{CrO}_2\text{BO}_3$ compound. In the antiferromagnetic state, with all sites 4 positions occupied by magnetic Cr^{3+} , these ions couple antiferromagnetically along the c -axis. **However, neutron diffraction measurements are needed to fully consolidate the actual magnetic order of the compounds.**

5. Acknowledgement

DLM was supported by a post doctoral fellowship from Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ), project number E-26/204.184/2021. DCF was supported by FAPERJ, projects 260003/011355/2021 and 260003//005772/2024. LG was also supported by FAPERJ, projects E-26/211.270/2021 and E-26/200.964/2022. The authors acknowledge the funding from HLD at HZDR, a member of the European Magnetic Field Laboratory (EMFL), and from the EU Horizon 2020 project ISABEL (Grant Agreement No. 871106).

References

- [1] D. C. Freitas, M. A. Continentino, R. B. Guimarães, J. C. Fernandes, J. Ellena, L. Ghivelder, Structure and magnetism of homometallic ludwigites $\text{Co}_3\text{O}_2\text{BO}_3$ versus $\text{Fe}_3\text{O}_2\text{BO}_3$, Phys. Rev. B 77 (2008) 184422. doi:10.1103/PhysRevB.77.184422. URL <https://link.aps.org/doi/10.1103/PhysRevB.77.184422>
- [2] M. Mir, R. B. Guimarães, J. C. Fernandes, M. A. Continentino, A. C. Doriguetto, Y. P. Mascarenhas, J. Ellena, E. E. Castellano, R. S. Freitas, L. Ghivelder, Structural transition and pair formation in $\text{Fe}_3\text{O}_2\text{BO}_3$, Phys. Rev. Lett. 87 (2001) 147201. doi:10.1103/PhysRevLett.87.147201. URL <https://link.aps.org/doi/10.1103/PhysRevLett.87.147201>
- [3] C. P. C. Medrano, D. C. Freitas, E. C. Passamani, C. B. Pinheiro, E. Baggio-Saitovitch, M. A. Continentino, D. R. Sanchez, Field-induced metamagnetic transitions and two-dimensional excitations in ludwigite $\text{Co}_{4.76}\text{Al}_{1.24}(\text{O}_2\text{BO}_3)_2$, Phys. Rev. B 95 (2017) 214419. doi:10.1103/PhysRevB.95.214419. URL <https://link.aps.org/doi/10.1103/PhysRevB.95.214419>

- [4] D. C. Freitas, R. B. Guimaraes, D. R. Sanchez, J. C. Fernandes, M. A. Continentino, J. Ellena, A. Kitada, H. Kageyama, A. Matsuo, K. Kindo, G. G. Eslava, L. Ghivelder, Structural and magnetic properties of the oxyborate $\text{Co}_5\text{TiO}_2(\text{BO}_3)_2$, Phys. Rev. B 81 (2010) 024432. doi:10.1103/PhysRevB.81.024432.
URL <https://link.aps.org/doi/10.1103/PhysRevB.81.024432>
- [5] C. P. C. Medrano, D. C. Freitas, D. R. Sanchez, C. B. Pinheiro, G. G. Eslava, L. Ghivelder, M. A. Continentino, Nonmagnetic ions enhance magnetic order in the ludwigite $\text{Co}_5\text{Sn}(\text{O}_2\text{BO}_3)_2$, Phys. Rev. B 91 (2015) 054402. doi:10.1103/PhysRevB.91.054402.
URL <https://link.aps.org/doi/10.1103/PhysRevB.91.054402>
- [6] S. Sofronova, L. Bezmaternykh, E. Eremin, I. Nazarenko, N. Volkov, A. Kartashev, E. Moshkina, The superexchange interactions and magnetic ordering in low-dimensional ludwigite $\text{Ni}_5\text{GeB}_2\text{O}_{10}$, Journal of Magnetism and Magnetic Materials 401 (2016) 217–222. doi:<https://doi.org/10.1016/j.jmmm.2015.10.024>.
URL <https://www.sciencedirect.com/science/article/pii/S0304885315306594>
- [7] P. Bordet, E. Suard, Magnetic structure and charge ordering in Fe_3BO_5 : A single-crystal x-ray and neutron powder diffraction study, Phys. Rev. B 79 (2009) 144408. doi:10.1103/PhysRevB.79.144408.
URL <https://link.aps.org/doi/10.1103/PhysRevB.79.144408>
- [8] D. L. Mariano, M. A. V. Heringer, D. C. Freitas, E. Baggio-Saitovitch, M. A. Continentino, E. C. Passamani, D. R. Sanchez, Dimensional crossover in Cr-doped Co_3BO_5 , Phys. Rev. B 102 (2020) 064424. doi:10.1103/PhysRevB.102.064424.
URL <https://link.aps.org/doi/10.1103/PhysRevB.102.064424>
- [9] N. Leonyuk, Structural aspects in crystal growth of anhydrous borates, Journal of Crystal Growth 174 (1) (1997) 301–307, american Crystal Growth 1996 and Vapor Growth and Epitaxy 1996. doi:[https://doi.org/10.1016/S0022-0248\(96\)01164-5](https://doi.org/10.1016/S0022-0248(96)01164-5).
URL <https://www.sciencedirect.com/science/article/pii/S0022024896011645>
- [10] Q. Wei, L. Sun, J. Zhang, G.-Y. Yang, Two deep-ultraviolet nonlinear optical alkaline-earth metal borates based on different types of oxoboron clusters, Dalton Trans. 46 (2017) 7911–7916. doi:10.1039/C7DT01677H.
URL <http://dx.doi.org/10.1039/C7DT01677H>
- [11] Z.-G. Hu, T. Higashiyama, M. Yoshimura, Y. K. Yap, Y. Mori, T. Sasaki, A new nonlinear optical borate crystal $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$ (KAB), Japanese Journal of Applied Physics 37 (Part 2, No. 10A) (1998) L1093–L1094. doi:10.1143/jjap.37.11093.
URL <https://doi.org/10.1143/jjap.37.11093>

- [12] E. dos Santos, D. Freitas, I. Fier, J. Fernandes, M. Continentino, A. de Oliveira, L. Walmsley, Current controlled negative differential resistance behavior in $\text{Co}_2\text{FeO}_2\text{BO}_3$ and $\text{Fe}_3\text{O}_2\text{BO}_3$ single crystals, *Journal of Physics and Chemistry of Solids* 90 (2016) 65 – 68. doi:<https://doi.org/10.1016/j.jpcs.2015.11.015>.
URL <http://www.sciencedirect.com/science/article/pii/S0022369715301049>
- [13] B. Xu, Y. Liu, J. Tian, X. Ma, Q. Ping, B. Wang, Y. Xia, $\text{Ni}_3(\text{BO}_3)_2$ as anode material with high capacity and excellent rate performance for sodium-ion batteries, *Chemical Engineering Journal* 363 (2019) 285–291. doi:<https://doi.org/10.1016/j.cej.2019.01.089>.
URL <https://www.sciencedirect.com/science/article/pii/S1385894719300877>
- [14] V. Pralong, B. Le Roux, S. Malo, A. Guesdon, F. Lainé, J. Colin, C. Martin, Electrochemical activity in oxyborates toward lithium, *Journal of Solid State Chemistry* 255 (2017) 167–171. doi:<https://doi.org/10.1016/j.jssc.2017.08.010>.
URL <https://www.sciencedirect.com/science/article/pii/S0022459617303171>
- [15] M. Dong, Q. Kuang, X. Zeng, L. Chen, J. Zhu, Q. Fan, Y. Dong, Y. Zhao, Mixed-metal borate fevbo4 of tunnel structure: Synthesis and electrochemical properties in lithium and sodium ion batteries, *Journal of Alloys and Compounds* 812 (2020) 152165. doi:<https://doi.org/10.1016/j.jallcom.2019.152165>.
URL <https://www.sciencedirect.com/science/article/pii/S0925838819334115>
- [16] Q. Ping, B. Xu, X. Ma, J. Tian, B. Wang, An iron oxyborate Fe_3BO_5 material as a high-performance anode for lithium-ion and sodium-ion batteries, *Dalton Trans.* 48 (2019) 5741–5748. doi:10.1039/C9DT00010K.
URL <http://dx.doi.org/10.1039/C9DT00010K>
- [17] A. Maignan, F. Lainé, A. Guesdon, S. Malo, F. Damay, C. Martin, Charge ordering and multiferroicity in Fe_3BO_5 and Fe_2MnBO_5 oxyborates, *Journal of Solid State Chemistry* 246 (2017) 209–213. doi:<https://doi.org/10.1016/j.jssc.2016.11.034>.
URL <https://www.sciencedirect.com/science/article/pii/S0022459616304728>
- [18] A. G. Gamzatov, Y. S. Koshkidko, D. C. Freitas, E. Moshkina, L. Bezmaternykh, A. M. Aliev, S. C. Yu, M. H. Phan, Anisotropic magnetocaloric properties of the ludwigite single crystal Cu_2MnBO_5 , *Applied Physics Letters* 116 (23) (2020) 232403. arXiv:<https://doi.org/10.1063/5.0012490>, doi:10.1063/5.0012490.
URL <https://doi.org/10.1063/5.0012490>

- [19] D. C. Freitas, C. P. C. Medrano, D. R. Sanchez, M. N. n. Regueiro, J. A. Rodríguez-Velamazán, M. A. Continentino, Magnetism and charge order in the ladder compound $\text{Co}_3\text{O}_2\text{BO}_3$, *Phys. Rev. B* 94 (2016) 174409. doi:10.1103/PhysRevB.94.174409.
URL <https://link.aps.org/doi/10.1103/PhysRevB.94.174409>
- [20] N. B. Ivanova, M. S. Platunov, Y. V. Knyazev, N. V. Kazak, L. N. Bezmaternykh, A. D. Vasiliev, S. G. Ovchinnikov, V. I. Nizhankovskii, Effect of the diamagnetic dilution on the magnetic ordering and electrical conductivity in the $\text{Co}_3\text{O}_2\text{BO}_3$: Ga ludwigite, *Physics of the Solid State* 54 (11) (2012) 2212–2221. doi:10.1134/S1063783412110133.
URL <https://doi.org/10.1134/S1063783412110133>
- [21] D. Mariano, M. Heringer, D. Freitas, V. Andrade, E. Saitovitch, M. Continentino, L. Ghivelder, E. Passamani, D. Sánchez, Metamagnetic transitions induced by doping with non-magnetic 4+ ions in ludwigites $\text{Co}_5\text{A}(\text{O}_2\text{BO}_3)_2$ (A=Zr and Hf), *Journal of Alloys and Compounds* 890 (2022) 161717. doi:<https://doi.org/10.1016/j.jallcom.2021.161717>.
URL <https://www.sciencedirect.com/science/article/pii/S0925838821031261>
- [22] M. A. V. Heringer, D. L. Mariano, D. C. Freitas, E. Baggio-Saitovitch, M. A. Continentino, D. R. Sanchez, Spin-glass behavior in $\text{Co}_3\text{Mn}_3(\text{O}_2\text{BO}_3)_2$ ludwigite with weak disorder, *Phys. Rev. Materials* 4 (2020) 064412. doi:10.1103/PhysRevMaterials.4.064412.
URL <https://link.aps.org/doi/10.1103/PhysRevMaterials.4.064412>
- [23] Y. Knyazev, N. Ivanova, N. Kazak, M. Platunov, L. Bezmaternykh, D. Velikanov, Crystal structure and magnetic properties of mn substituted ludwigite $\text{Co}_3\text{O}_2\text{BO}_3$, *Journal of Magnetism and Magnetic Materials* 324 (6) (2012) 923–927. doi:<https://doi.org/10.1016/j.jmmm.2011.07.044>.
URL <https://www.sciencedirect.com/science/article/pii/S0304885311005208>
- [24] D. C. Freitas, M. A. Continentino, R. B. Guimarães, J. C. Fernandes, E. P. Oliveira, R. E. Santelli, J. Ellena, G. G. Eslava, L. Ghivelder, Partial magnetic ordering and crystal structure of the ludwigites $\text{Co}_2\text{FeO}_2\text{BO}_3$ and $\text{Ni}_2\text{FeO}_2\text{BO}_3$, *Phys. Rev. B* 79 (2009) 134437. doi:10.1103/PhysRevB.79.134437.
URL <https://link.aps.org/doi/10.1103/PhysRevB.79.134437>
- [25] APEX3, version 2017.3-0, Bruker AXS Inc. Wisconsin (USA (2017)) (Madison) 837–838.
- [26] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *ShelXle*: a Qt graphical user interface for *SHELXL*, *Journal of Applied Crystallography* 44 (6) (2011) 1281–1284. doi:10.1107/S0021889811043202.
URL <https://doi.org/10.1107/S0021889811043202>

- [27] L. J. Farrugia, *WinGX* suite for small-molecule single-crystal crystallography, *Journal of Applied Crystallography* 32 (4) (1999) 837–838. doi:
10.1107/S0021889899006020.
URL <https://doi.org/10.1107/S0021889899006020>
- [28] J. Rodríguez-Carvajal, Recent advances in magnetic structure determination by neutron powder diffraction, *Physica B: Condensed Matter* 192 (1) (1993) 55–69. doi:[https://doi.org/10.1016/0921-4526\(93\)90108-I](https://doi.org/10.1016/0921-4526(93)90108-I).
URL <https://www.sciencedirect.com/science/article/pii/092145269390108I>
- [29] W. Roth, The magnetic structure of Co_3O_4 , *Journal of Physics and Chemistry of Solids* 25 (1) (1964) 1–10. doi:[https://doi.org/10.1016/0022-3697\(64\)90156-8](https://doi.org/10.1016/0022-3697(64)90156-8).
URL <https://www.sciencedirect.com/science/article/pii/0022369764901568>
- [30] K. Tomiyasu, T. Inami, N. Ikeda, Magnetic structure of CoO studied by neutron and synchrotron x-ray diffraction, *Phys. Rev. B* 70 (2004) 184411. doi:10.1103/PhysRevB.70.184411.
URL <https://link.aps.org/doi/10.1103/PhysRevB.70.184411>
- [31] K. Tomiyasu, J. Fukunaga, H. Suzuki, Magnetic short-range order and reentrant-spin-glass-like behavior in CoCr_2O_4 and MnCr_2O_4 by means of neutron scattering and magnetization measurements, *Phys. Rev. B* 70 (2004) 214434. doi:10.1103/PhysRevB.70.214434.
URL <https://link.aps.org/doi/10.1103/PhysRevB.70.214434>
- [32] K. Singh, A. Maignan, C. Simon, C. Martin, FeCr_2O_4 and CoCr_2O_4 spinels: Multiferroicity in the collinear magnetic state?, *Applied Physics Letters* 99 (17) (2011) 172903. arXiv:https://pubs.aip.org/aip/apl/article-pdf/doi/10.1063/1.3656711/13145285/172903_1_online.pdf, doi:10.1063/1.3656711.
URL <https://doi.org/10.1063/1.3656711>
- [33] R. D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallographica Section A* 32 (5) (1976) 751–767. doi:10.1107/S0567739476001551.
URL <https://doi.org/10.1107/S0567739476001551>
- [34] C. W. Galdino, D. C. Freitas, C. P. C. Medrano, R. Tartaglia, D. Rigitano, J. F. Oliveira, A. A. Mendonça, L. Ghivelder, M. A. Continentino, D. R. Sanchez, E. Granado, Magnetic, electronic, structural, and thermal properties of the $\text{Co}_3\text{O}_2\text{BO}_3$ ludwigite in the paramagnetic state, *Phys. Rev. B* 100 (2019) 165138. doi:10.1103/PhysRevB.100.165138.
URL <https://link.aps.org/doi/10.1103/PhysRevB.100.165138>
- [35] E.-a. Zen, Validity of “vegard’s law”, *American Mineralogist* 41 (5-6) (1956) 523–524. arXiv:<https://pubs.geoscienceworld.org/msa/ammin/article-pdf/41/5-6/523/4246776/am-1956-523.pdf>.

- [36] K. T. Jacob, S. Raj, L. Rannesh, Vegard's law: a fundamental relation or an approximation?, *International Journal of Materials Research* 98 (9) (2007) 776–779 [cited 2024-07-23]. doi:doi:10.3139/146.101545.
URL <https://doi.org/10.3139/146.101545>
- [37] Y. Knyazev, N. Kazak, I. Nazarenko, S. Sofronova, N. Rostovtsev, J. Bartolome, A. Arauzo, S. Ovchinnikov, Effect of magnetic frustrations on magnetism of the Fe_3BO_5 and Co_3BO_5 ludwigites, *Journal of Magnetism and Magnetic Materials* 474 (2019) 493–500. doi:https://doi.org/10.1016/j.jmmm.2018.10.126.
URL <https://www.sciencedirect.com/science/article/pii/S0304885318320274>
- [38] J. Coey, *Magnetism and Magnetic Materials*, Knovel Library, Cambridge University Press, 2010.
URL <https://books.google.com.br/books?id=Ie72CFd-eSEC>
- [39] H. P. Wijn, *Ferromagnetism/Ferromagnetismus*, Vol. 4, Springer Science & Business Media, 2012.
- [40] L. T. Coutrim, E. M. Bittar, F. Stavale, F. Garcia, E. Baggio-Saitovitch, M. Abbate, R. J. O. Mossaneke, H. P. Martins, D. Tobia, P. G. Pagliuso, L. Bufaical, Compensation temperatures and exchange bias in $\text{La}_{1.5}\text{Ca}_{0.5}\text{CoIrO}_6$, *Phys. Rev. B* 93 (2016) 174406. doi:10.1103/PhysRevB.93.174406.
URL <https://link.aps.org/doi/10.1103/PhysRevB.93.174406>
- [41] S. Li, J. Wang, Q. Zhang, M. A. Roldan, L. Shan, Q. Jin, S. Chen, Z. Wu, C. Wang, C. Ge, M. He, H. Guo, L. Gu, K.-j. Jin, E.-J. Guo, Maximization of ferromagnetism in LaCoO_3 films by competing symmetry, *Phys. Rev. Mater.* 3 (2019) 114409. doi:10.1103/PhysRevMaterials.3.114409.
URL <https://link.aps.org/doi/10.1103/PhysRevMaterials.3.114409>
- [42] J. K. Murthy, K. D. Chandrasekhar, H. C. Wu, H. D. Yang, J. Y. Lin, A. Venimadhav, Metamagnetic behaviour and effect of field cooling on sharp magnetization jumps in multiferroic Y_2CoMnO_6 , *Europhysics Letters* 108 (2) (2014) 27013. doi:10.1209/0295-5075/108/27013.
URL <https://dx.doi.org/10.1209/0295-5075/108/27013>
- [43] L. Ghivelder, G. Eslava, R. Freitas, G. Leyva, F. Parisi, Avalanche-like metamagnetic transition in $(\text{LaNd})\text{CaMnO}$ manganites, *Journal of Alloys and Compounds* 680 (2016) 494–499. doi:https://doi.org/10.1016/j.jallcom.2016.04.152.
URL <https://www.sciencedirect.com/science/article/pii/S0925838816311318>

- [44] D. L. Mariano, D. R. S. Candela, A. Z. Freitas, Daniele C. and Trujillo, E. C. Passamani, M. A. Continentino, L. Ghivelder, Increasing the magnetic order temperature in $\text{Co}_3\text{O}_2\text{BO}_3$:In ludwigite, *Inorganic Chemistry* 62 (Nov 2023).
- [45] S. Asai, R. Okazaki, I. Terasaki, Y. Yasui, W. Kobayashi, A. Nakao, K. Kobayashi, R. Kumai, H. Nakao, Y. Murakami, N. Igawa, A. Hoshikawa, T. Ishigaki, O. Parkkima, M. Karppinen, H. Yamauchi, Spin state of Co^{3+} in $\text{LaCo}_{1-x}\text{Rh}_x\text{O}_3$ investigated by structural phenomena, *Journal of the Physical Society of Japan* 82 (11) (2013) 114606. [arXiv:https://doi.org/10.7566/JPSJ.82.114606](https://doi.org/10.7566/JPSJ.82.114606), doi:10.7566/JPSJ.82.114606. URL <https://doi.org/10.7566/JPSJ.82.114606>
- [46] M. M. Altarawneh, G.-W. Chern, N. Harrison, C. D. Batista, A. Uchida, M. Jaime, D. G. Rickel, S. A. Crooker, C. H. Mielke, J. B. Betts, J. F. Mitchell, M. J. R. Hoch, Cascade of magnetic field induced spin transitions in LaCoO_3 , *Phys. Rev. Lett.* 109 (2012) 037201. doi:10.1103/PhysRevLett.109.037201. URL <https://link.aps.org/doi/10.1103/PhysRevLett.109.037201>
- [47] A. Kirste, M. Goiran, M. Respaud, J. Vanaken, J. M. Broto, H. Rakoto, M. von Ortenberg, C. Frontera, J. L. García-Muñoz, High magnetic field study of charge melting in $\text{Bi}_{1/2}\text{Sr}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$ perovskites: Unconventional behavior of bismuth charge ordered compounds, *Phys. Rev. B* 67 (2003) 134413. doi:10.1103/PhysRevB.67.134413. URL <https://link.aps.org/doi/10.1103/PhysRevB.67.134413>
- [48] M. Respaud, A. Llobet, C. Frontera, C. Ritter, J. M. Broto, H. Rakoto, M. Goiran, J. L. García-Muñoz, High magnetic field study of lattice and magnetic effects on the charge-melting transition in $\text{La}_{1/2}\text{Ca}_{1/2}\text{MnO}_3$ perovskites, *Phys. Rev. B* 61 (2000) 9014–9018. doi:10.1103/PhysRevB.61.9014. URL <https://link.aps.org/doi/10.1103/PhysRevB.61.9014>
- [49] T. Lookman, X. Ren, *Frustrated Materials and Ferroic Glasses*, Springer Series in Materials Science, Springer International Publishing, 2018. URL <https://books.google.com.br/books?id=le11DwAAQBAJ>
- [50] P. Bag, K. Somesh, R. Nath, A study of cluster spin-glass behaviour at the critical composition $\text{Mn}_{0.73}\text{Fe}_{0.27}\text{NiGe}$, *Journal of Magnetism and Magnetic Materials* 497 (2020) 165977. doi:<https://doi.org/10.1016/j.jmmm.2019.165977>. URL <https://www.sciencedirect.com/science/article/pii/S0304885319313617>
- [51] I. N. Bhatti, I. N. Bhatti, Spin glass behavior and critical analysis across the magnetic phase transition in $\text{Gd}_2\text{CoMnO}_6$: dc magnetization and ac susceptibility study, *Current Applied Physics* 39 (2022) 97–106.

doi:<https://doi.org/10.1016/j.cap.2022.04.007>.
URL <https://www.sciencedirect.com/science/article/pii/S1567173922000955>

- [52] A. H. Morrish, The physical principles of magnetism, Wiley, 2001.
- [53] I. G. Deac, J. F. Mitchell, P. Schiffer, Phase separation and low-field bulk magnetic properties of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, Phys. Rev. B 63 (2001) 172408. doi:[10.1103/PhysRevB.63.172408](https://doi.org/10.1103/PhysRevB.63.172408).
URL <https://link.aps.org/doi/10.1103/PhysRevB.63.172408>
- [54] R. B. Guimarães, M. Mir, J. C. Fernandes, M. A. Continentino, H. A. Borges, G. Cernicchiaro, M. B. Fontes, D. R. S. Candela, E. Baggio-Saitovitch, Cation-mediated interaction and weak ferromagnetism in $\text{Fe}_3\text{O}_2\text{BO}_3$, Phys. Rev. B 60 (1999) 6617–6622. doi:[10.1103/PhysRevB.60.6617](https://doi.org/10.1103/PhysRevB.60.6617).
URL <https://link.aps.org/doi/10.1103/PhysRevB.60.6617>
- [55] P. W. Anderson, New approach to the theory of superexchange interactions, Physical Review 115 (1) (1959) 2.
- [56] G. Sawatzky, W. Geertsma, C. Haas, Magnetic interactions and covalency effects in mainly ionic compounds, Journal of Magnetism and Magnetic Materials 3 (1) (1976) 37–45. doi:[https://doi.org/10.1016/0304-8853\(76\)90008-1](https://doi.org/10.1016/0304-8853(76)90008-1).
URL <https://www.sciencedirect.com/science/article/pii/0304885376900081>
- [57] O. A. Bayukov, A. F. Savitskii, The prognostication possibility of some magnetic properties for dielectrics on the basis of covalency parameters of ligand-cation bonds, physica status solidi (b) 155 (1) 249–255. doi:<https://doi.org/10.1002/pssb.2221550125>.
URL <https://onlinelibrary.wiley.com/doi/abs/10.1002/pssb.2221550125>
- [58] J. B. Goodenough, Theory of the role of covalence in the perovskite-type manganites $[\text{La}, m(\text{II})]\text{MnO}_3$, Phys. Rev. 100 (1955) 564–573. doi:[10.1103/PhysRev.100.564](https://doi.org/10.1103/PhysRev.100.564).
URL <https://link.aps.org/doi/10.1103/PhysRev.100.564>
- [59] J. Kanamori, Superexchange interaction and symmetry properties of electron orbitals, Journal of Physics and Chemistry of Solids 10 (2) (1959) 87 – 98. doi:[https://doi.org/10.1016/0022-3697\(59\)90061-7](https://doi.org/10.1016/0022-3697(59)90061-7).
URL <http://www.sciencedirect.com/science/article/pii/0022369759900617>
- [60] P. W. Anderson, Antiferromagnetism. theory of superexchange interaction, Phys. Rev. 79 (1950) 350–356. doi:[10.1103/PhysRev.79.350](https://doi.org/10.1103/PhysRev.79.350).
URL <https://link.aps.org/doi/10.1103/PhysRev.79.350>

- [61] E. Vallejo, M. Avignon, Spin ordering in three-leg ladders in ludwigite systems, *Journal of Magnetism and Magnetic Materials* 310 (2, Part 2) (2007) 1130–1132, proceedings of the 17th International Conference on Magnetism. doi:<https://doi.org/10.1016/j.jmmm.2006.10.314>.
URL <https://www.sciencedirect.com/science/article/pii/S0304885306015101>
- [62] S. T. Lin, Magnetic properties of hematite single crystals. i. magnetization isotherms, antiferromagnetic susceptibility, and weak ferromagnetism of a natural crystal, *Phys. Rev.* 116 (1959) 1447–1452. doi:10.1103/PhysRev.116.1447.
URL <https://link.aps.org/doi/10.1103/PhysRev.116.1447>
- [63] M. A. Halcrow, *Spin-crossover materials: properties and applications*, John Wiley & Sons, 2013.
- [64] K. Knížek, J. Hejtmánek, M. Maryško, Z. Jiráček, J. Buršík, Stabilization of the high-spin state of Co^{3+} in $\text{LaCo}_{(1-x)}\text{Rh}_x\text{O}_3$, *Phys. Rev. B* 85 (2012) 134401. doi:10.1103/PhysRevB.85.134401.
URL <https://link.aps.org/doi/10.1103/PhysRevB.85.134401>
- [65] L. Guo, Y. Bai, C. Huang, W. Ma, Revisiting La_2MMnO_6 ($\text{M} = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) perovskites in view of 3d-electron configuration, *Journal of Applied Physics* 124 (6) (2018) 065103. doi:10.1063/1.5021975.
URL <https://doi.org/10.1063/1.5021975>
- [66] R. Sharma, N. Hooda, A. Hooda, S. Khasa, Improved magnetic properties of Fe substituted $\text{La}_2\text{CoMnO}_6$ for spintronic applications, *Journal of Magnetism and Magnetic Materials* 587 (2023) 171347. doi:<https://doi.org/10.1016/j.jmmm.2023.171347>.
URL <https://www.sciencedirect.com/science/article/pii/S0304885323009976>