Synthesis and magnetic properties of $\text{ALnO}_2$ ($A = \text{Cu or Ag}; \text{Ln} = \text{Rare Earths}$) with the delafossite structure

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ABSTRACT

Synthesis, structures, and magnetic properties of ternary rare earth oxides ALnO$_2$ (A = Cu or Ag; Ln = rare earths) have been investigated. CuLnO$_2$ (Ln = La, Pr, Nd, Sm, Eu) were synthesized by the direct solid state reaction of Cu$_2$O and Ln$_2$O$_3$, and AgLnO$_2$ (Ln = Tm, Yb, Lu) were obtained by the cation-exchange reaction of NaLnO$_2$ and AgNO$_3$ in a KNO$_3$ flux. These compounds crystallized in the delafossite-type structure with the rhombohedral 3R type (space group: R-3m). Magnetic susceptibility measurements showed that these compounds are paramagnetic down to 1.8 K. Specific heat measurements down to 0.4 K indicated that CuNdO$_2$ ordered antiferromagnetically at 0.8 K.
1. Introduction

It is well known that oxides containing rare earth elements show a variety of magnetic properties due to the behavior of unpaired 4f electrons. When the rare earth ions are arrayed in a structurally characteristic manner, interesting magnetic behavior has been often found. Here, we focus our attention on compounds with the delafossite-type (CuFeO₂) structure.

The synthesis, crystal structure, and electric transport properties of delafossite-type compounds were reported by Shannon, Rogers and Prewitt [1-3] and reviewed by Cann et al. [4]. Compounds with this structure have been of immense interest due to the discovery of the p-type transparent conductivity for CuAlO₂ [5]. Recently, the optical and electrical properties of silver delafossites were reported [6].

Delafossite compounds belong to a family of ternary oxides with the general formula ABO₂. In this structure, the A cation is linearly coordinated to two oxygen ions and occupied by a noble metal cation in the +1 oxidation state. Typical A cations include Pd, Pt, Cu, or Ag. The B cation is located in distorted edge-shared BO₆ octahedra with a central metal cation having a +3 charge. The delafossite structure can be visualized as consisting of two alternating layers: a planar layer of A cations in a triangular pattern and a layer of edge-sharing BO₆ octahedra flattened with respect to the c-axis. Depending on the stacking of the double layers (close-packed A cations and BO₆ octahedra), the delafossite structure can form as one of two
polytypes, i.e., the hexagonal 2H type and the rhombohedral 3R type.

In this structure, the B cations adopt triangular geometric arrangements. If the magnetic ions are located in the B sites, and if there exists an antiferromagnetic interaction between the nearest-neighbor magnetic ions, they can show magnetic frustrations.

There are some reports on the delafossite-type compounds containing rare earths. Haas et al. reported the preparation of CuLnO$_2$ (Ln = La, Pr, Nd, Sm, and Eu) [7]. Oxygen excess in delafossite structures was reported in the CuLnO$_2$ family, where several researchers have demonstrated the possibility to insert oxygen atoms in the Cu layer, namely in the center of Cu triangles [8-10]. Very recently, the preparation of one silver delafossite-type compound AgYbO$_2$ was reported [11].

In this study, we tried to synthesize a series of ALnO$_2$ (A = Cu or Ag; Ln = rare earths) and determined their crystal structures through the Rietveld analysis for the powder X-ray diffraction data. In these compounds, paramagnetic Ln ions adopt the triangle-based array. Therefore, anomalous magnetic properties reflecting the geometric frustration may be observed. In order to elucidate basic magnetic properties of ALnO$_2$ compounds containing rare earths, their magnetic susceptibilities were measured in the temperature range between 1.8 and 400 K. In addition, specific heat measurements of CuNdO$_2$ were performed in the temperature range between 0.4 and 300 K.
2. Experimental

2.1. Sample preparation

The CuLnO$_2$ (Ln = La, Pr, Nd, Sm, Eu) were prepared by heating 1:1 mixtures of Cu$_2$O and Ln$_2$O$_3$ in a flowing atmosphere of Ar gas at 1123 K for a day. For La$_2$O$_3$ and Nd$_2$O$_3$, they absorb moisture in air and easily form lanthanide hydroxides Ln(OH)$_3$. Therefore, these compounds were preheated at 1073 K for a day.

Silver delafossite compounds AgLnO$_2$ were prepared by the following cation-exchange reactions using NaLnO$_2$ as precursors;

\[ \text{NaLnO}_2 + \text{AgNO}_3 \rightarrow \text{AgLnO}_2 + \text{NaNO}_3 \]

The reactions were carried out in a flux of AgNO$_3$-KNO$_3$. The NaLnO$_2$ was prepared by the solid state reactions [12]. As starting materials, Ln$_2$O$_3$, Na$_2$CO$_3$, and NaNO$_3$ were used. These reagents were weighed in the Na/Ln = 1.2 metal ratios to prevent loss of sodium from evaporation, and ground in an agate mortar. The mixtures were pelletized and heated in air at 1173 K for 12-48 h with some addition of Na$_2$CO$_3$ or NaNO$_3$ and several regrindings. The obtained NaLnO$_2$ were mixed with AgNO$_3$ and KNO$_3$ in a dry process (mixing ratio: Na:Ag:K = 3:3:2). The molded samples were heated from 323 to 573 K. After heat treatments, the products were washed with distilled water, ethanol and finally with acetonitrile to eliminate the flux and byproducts.
2.2. X-ray diffraction analysis

Powder X-ray diffraction profiles were measured using a Rigaku Multi-Flex diffractometer with Cu-Kα radiation equipped with a curved graphite monochromator. The data were collected by step-scanning in the angle range of $10° \leq 2\theta \leq 120°$ at a $2\theta$ step-size of 0.02°. The X-ray diffraction data were analyzed by the Rietveld technique, using the programs RIETAN2000 [13].

2.3. Magnetic susceptibility measurements

The temperature-dependence of the magnetic susceptibility was measured in an applied field of 0.1 T over the temperature range of $1.8 \, \text{K} \leq T \leq 400 \, \text{K}$, using a SQUID magnetometer (Quantum Design, MPMS5S). The susceptibility measurements were performed under both zero-field-cooled (ZFC) and field-cooled (FC) conditions. The former was measured upon heating the sample to 400 K under the applied magnetic field of 0.1 T after zero-field cooling to 1.8 K. The latter was measured upon cooling the sample from 400 to 1.8 K at 0.1 T.

2.4. Specific heat measurements

The specific heat measurements were carried out using a relaxation technique supplied by the commercial heat capacity measurement system (Quantum Design, Model PPMS). The sample in the form of a pellet (~ 10 mg) was mounted on an alumina plate with apiezon for better thermal contact. The specific heat and magnetic susceptibility were measured in the
temperature range from 0.4 to 300 K.

3. Results and discussion

3.1. Preparation and crystal structure

For A = Cu, we could successfully prepare a series of CuLnO$_2$ compounds with Ln = La, Pr, Nd, Sm, Eu. A representative powder X-ray diffraction profile is shown in Fig. 1 for CuPrO$_2$. The observed diffraction peaks were indexed on a rhombohedral cell with the space group R-3m. The X-ray diffraction data for all the compounds prepared in this study were analyzed by the Rietveld method on the basis of the same space group. The refined structural parameters for CuPrO$_2$ are listed in Table 1. The lattice parameters and reliability factors for all CuLnO$_2$ compounds prepared in this study are summarized in Table 2.

Figure 2 (a) shows a schematic crystal structure of CuLnO$_2$ (Ln = La, Pr, Nd, Sm, Eu). The Ln ions are located in distorted edge-shared LnO$_6$ octahedra, forming Ln-O layers. The linear O-Cu-O coordination is parallel to the hexagonal c axis. If successive O layers are labeled O1, O2, and O3, the sequence of this structure is (O1 Ln O2)-Cu-(O2 Ln O3)-Cu-(O3 Ln O1)-Cu-O1. This yields a rhombohedral structure with a three-layer periodicity along c axis. The orientation of the LnO$_6$ octahedra is the same for all layers in this 3R form. This is in contrast with the case for the 2H form in which the orientation of the octahedra switches back
and forth [14]. Figure 2 (b) shows a partial projection of the CuLnO$_2$ structure into the hexagonal plane. One layer of LnO$_6$ octahedra is depicted. As seen from this figure, Ln ions adopt the triangle-based array. Above and below this layer, triangular Cu layers exist.

For $A = \text{Ag}$, a single-phase compound AgLnO$_2$ was prepared for Ln = Tm, Yb, and Lu by the cation-exchange reaction using NaLnO$_2$. The precursors NaLnO$_2$ (Ln = Tm-Lu) adopt the $\alpha$-NaFeO$_2$ structure (space group: R-3m), and the Ln ion is octahedrally coordinated by six oxygen ions. The crystal structure of AgLnO$_2$ is the same with that of CuLnO$_2$ (Ln = La, Pr, Nd, Sm, Eu). That is, the replacement of sodium by silver in the hexagonal framework brings an important change of the coordination of the interlayer cation. The coordination number decreases from 6 in NaLnO$_2$ to 2 in AgLnO$_2$. The refined positional parameters of AgLuO$_2$ are listed in Table 1, and the lattice parameters for AgLnO$_2$ (Ln = Tm, Yb, Lu) are also summarized in Table 2.

Some bond lengths (A-O, Ln-O) and the bond valence sums (BVSs) [15, 16] for Ln and Cu(Ag) ions were calculated using the refined structural parameters, and they are listed in Table 3. The BVS values for the Ln ion are almost constant (~3.0) and they are reasonable for trivalent ions. However, the BVS values of the Ln ions in CuLnO$_2$ are actually increasing with decreasing the ionic radius of Ln$^{3+}$. It is estimated that for smaller size of Ln ions (Ln = Gd-Lu), the BVS values should be calculated to be much larger than 3. This accounts for the difficulty in
preparing the delafossite-type CuLnO$_2$ compounds with the smaller size of Ln ions. Those for the Cu and Ag ions are close to 1.0 for all of the ALnO$_2$ compounds except CuLaO$_2$. The Cu-O bond length of CuLaO$_2$ is a little shorter than the value expected for Cu$^{+}$-O$^{2-}$ and the BVS value for the Cu$^{+}$ is calculated to be 1.33, which indicates some oxidation of Cu$^{+}$ ions. This will be discussed later.

Figure 3 shows the variation of lattice parameters with the ionic radius of Ln$^{3+}$ for CuLnO$_2$ and AgLnO$_2$. The value of $a$ is strongly influenced by the ionic radii of the Ln ion, while the $c$ value is fixed largely by the O-Cu-O or O-Ag-O bond length. This trend is directly reflected by the structure. Due to the repulsive nature of the Ln$^{3+}$ ions along the shared octahedral edges, a distortion occurs, resulting in a shortened interatomic distance between the oxygen ions. As the Ln ionic radius increases, the Ln-O distance increases while the O-O contact distance remains relatively unchanged. Therefore, an increase in the Ln ionic size has little impact on the $c$ lattice parameter.

We tried to prepare CuLnO$_2$ type compounds for Ln = Ce or Gd-Lu. However, starting materials did not react even at higher temperatures than 1200 K. For cerium compounds, this is due to the fact that the Ce$^{4+}$ ion is more stable than Ce$^{3+}$. For the case of Ln = Gd-Lu, the atomic distance between Cu should become too smaller, because the a-axis lattice parameter decreases with decreasing Ln$^{3+}$ ionic size. The strong electric repulsion between Cu$^{+}$ will make difficult to
form CuLnO$_2$ compounds.

3.3. Magnetic properties

The results of the magnetic susceptibility measurements on CuLnO$_2$ (Ln = La, Pr, Nd, Sm, Eu) and AgLnO$_2$ (Ln = Tm, Yb, Lu) are summarized in Table 4. Compounds CuLnO$_2$ (Ln = Pr, Nd, Sm, Eu) and AgLnO$_2$ (Ln = Tm, Yb) are paramagnetic in the temperature range between 1.8 and 400 K. Even a lanthanum-containing compound CuLaO$_2$ shows paramagnetic behavior. Magnetic properties of each compound will hereinafter be described.

3.3.1. CuLnO$_2$ (Ln = La, Pr, Nd, Sm, Eu)

Figure 4 shows the magnetic susceptibility – temperature curve of CuLaO$_2$. This temperature dependence of the susceptibility indicates the existence of paramagnetic substance in the CuLaO$_2$ compound. If the oxygen-stoichiometric compounds were formed, there should exist no magnetic ions. Experimental results indicate that some Cu$^+$ ions are oxidized to the divalent state due to the existence of excess oxygen ions. It is known that excess oxygen in the delafossite structure was reported in the CuLnO$_2$ compounds [8-10], where several researchers demonstrated the possibility to insert oxygen atoms in the Cu layers [10].

The temperature dependence of the magnetic susceptibility of CuLaO$_2$ prepared in this study (actually CuLaO$_{2+\delta}$) can be fitted by the Curie law including the temperature independent term,
\[ \chi = \frac{C}{T} + \chi_{\text{tip}}, \]

and the effective magnetic moment is obtained to be \( \mu_{\text{eff}} = 0.264 \mu_B \) per CuLaO\(_{2.5}\). Since the effective magnetic moment of Cu\(^{2+}\) with [Ar]3d\(^9\) electronic configuration is 1.73 \( \mu_B \), the ratio of the Cu\(^{2+}\)/Cu is estimated to be \((0.264/1.73)^2 = 0.024\). Therefore, the oxygen-nonstoichiometry of CuLaO\(_{2.5}\) is \( \delta = 0.012 \). This value is very close to that for the CuLaO\(_{2.01}\) sample prepared under the same conditions [9].

Figures 5 and 6 show the temperature dependences of the magnetic susceptibility of CuPrO\(_2\) and CuNdO\(_2\), respectively. Both of them indicate no magnetic transition in the temperature range between 1.8 and 400 K, and the susceptibilities follow the Curie-Weiss law. The obtained effective magnetic moment and the Weiss constant are listed in Table 4. The effective magnetic moments of these compounds are almost equal to those of the free ion value of Ln\(^{3+}\). However, the effective magnetic moment of CuPrO\(_2\) is actually a bit of larger than the moment of Pr\(^{3+}\) ion. This is due to the existence of some Cu\(^{2+}\) ions in CuPrO\(_2\). The Pr\(^{3+}\) ion is located in a distorted LnO\(_6\) octahedron. The ground state \( ^3H_4 \) of the Pr\(^{3+}\) ion is split into one singlet (\( \Gamma_1 \)), one doublet (\( \Gamma_3 \)), and two triplets (\( \Gamma_4 \) and \( \Gamma_5 \)) in the octahedral symmetry [17]. We expect that the ground state and the first excited state are \( \Gamma_1 \) and \( \Gamma_4 \), respectively, and that the upper excited states are \( \Gamma_3 \) and \( \Gamma_5 \). In that case, the magnetic susceptibility of the Pr\(^{3+}\) ion should be temperature-independent at low temperatures (for example, in the temperature region below
The rapid increase of the magnetic susceptibility of CuPrO₂ with decreasing temperature also shows the existence of Cu²⁺ ions in CuPrO₂. The large deviation of the magnetic susceptibility from the Curie-Weiss law around 50 K is ascribed to the paramagnetic behavior of Cu²⁺ ions. The negative Weiss constants suggest the existence of antiferromagnetic interaction at lower temperatures. However, the Weiss constants obtained from high temperature (50-400 K) data are obviously overestimated due to the crystal field splitting of the ground state of Ln³⁺ ions. In order to assess them, the Weiss constant at low temperature (θ_LT) was also calculated from the data between 1.8 and 15 K for CuNdO₂. The negative value of θ_LT (-3.79 K) indicates that if we perform magnetic susceptibility measurements at furthermore lower temperatures, the antiferromagnetic interaction should be observed. Specific heat measurements for CuNdO₂ down to 0.4 K showed the antiferromagnetic interaction between Nd³⁺ ions, which will be described later section.

Magnetic susceptibilities of CuSmO₂ and CuEuO₂ are plotted as a function of temperature in Fig. 7. No magnetic transition was observed down to 1.8 K. Both the magnetic susceptibilities do not obey the Curie-Weiss law. For the Sm³⁺ and Eu³⁺ ions, the multiplet levels are not large compared to k_BT (kB : Boltzmann constant), so the excited state should contribute to the magnetic susceptibility. A susceptibility plateau of CuEuO₂ is observed below 50 K, which is attributed to the temperature-independent term of the Van Vleck formula.
Since the ground state of Eu$^{3+}$ ion is $^7F_0$, i.e., nonmagnetic, the Eu$^{3+}$ ion does not contribute to the temperature dependence of the magnetic susceptibility at low temperatures ($T < 50$ K).

The increase of the magnetic susceptibility below 20 K is due to the presence of some Cu$^{2+}$ ions in this EuCuO$_2$ as in the case of LaCuO$_2$. The effective magnetic moments ($\mu_{eff}$) of CuSmO$_2$ and CuEuO$_2$ are estimated from the data only at room temperature. The $\mu_{eff}$ values are very close to the moments calculated for free Ln$^{3+}$ ions (see Table 4).

3.3.2. AgLnO$_2$ (Ln = Tm, Yb)

Figure 8 shows the temperature dependence of the magnetic susceptibility of AgTmO$_2$ in the temperature range between 1.8 and 300 K. No magnetic anomaly was observed down to 1.8 K and this compound shows paramagnetic behavior in this temperature range. The inset of Fig. 8 depicts the reciprocal susceptibility against temperature. The Curie-Weiss fitting in the temperature range between 100 and 300 K gives the effective magnetic moment of 7.52 $\mu_B$. This value is almost consistent with the theoretical moment for Tm$^{3+}$ (7.55 $\mu_B$), indicating that the thulium ion is in the trivalent state.

Similar magnetic results have been observed for the magnetic susceptibility of AgYbO$_2$. Figure 9 depicts its magnetic susceptibility vs. temperature curve and the inset shows the temperature dependence of the reciprocal susceptibility. This compound also shows paramagnetic behavior in the temperature range between 1.8 and 400 K. The Curie-Weiss fitting
in the temperature range between 100 and 400 K gives the effective magnetic moment of 4.46 μB. This value is close to the theoretical moment for Yb^{3+} (4.54 μB), indicating that the ytterbium ion is in the trivalent state. The negative Weiss constant θ = -66 K suggests the existence of antiferromagnetic interaction. The Weiss constant in a low-temperature region from 1.8 to 20 K (θ_{LT}) was also calculated to prevent its overestimation by the convexity of the reciprocal susceptibility vs. temperature curve due to the crystal field effect. It is θ_{LT} = -2.98 K, indicating that the antiferromagnetic interaction should be observed at furthermore lower temperatures.

3.3.3. Specific heat results for CuNdO₂

For CuNdO₂, specific heat measurements were performed in the temperature range between 0.4 and 300 K. Figure 10 (a) shows the temperature dependence of the specific heat C_p for CuNdO₂ between 0.4 and 15 K. The specific heat data show a λ-type anomaly at 0.8 K, indicating the existence of the long-range magnetic ordering. To calculate the magnetic contribution to the specific heat, we have to subtract the contribution of lattice specific heat from the total specific heat. They were estimated by using a polynomial function of the temperature, \( f(T) = aT^3 + bT^5 + cT^7 \) [20], in which the constants \( a, b \) and \( c \) were determined by fitting this function to the observed specific heat data above 10 K. Figure 10 (b) shows the temperature dependence of the magnetic specific heat divided by temperature (C_{mag}/T). From the temperature dependence of the magnetic specific heat, the magnetic entropy change of
CuNdO$_2$ is calculated by the relation $S_{\text{mag}} = \int \left( C_{\text{mag}} / T \right) dT$. It is also shown in Fig. 10 (b). The magnetic entropy change due to the antiferromagnetic ordering is determined to be 5.8 J mol$^{-1}$ K$^{-1}$.

In an octahedral crystal field environment, the ground state of the Nd$^{3+}$ ion (the electronic configuration: [Xe]4f$^3$, the state $^4$I$_{9/2}$) is the ten-fold degenerate state. The magnetic entropy change of Nd$^{3+}$ is calculated to be $R \ln (2J+1) = R \ln 10 = 19.14$ J mol$^{-1}$ K$^{-1}$, where $R$ and $J$ are the molar gas constant and the total quantum number, respectively. In the case of lower symmetry, this state splits into five Kramers doublet states. For such a case, the magnetic entropy change is expected to be $R \ln 2 = 5.76$ J mol$^{-1}$ K$^{-1}$; the experimental value is close to this value. The result of the magnetic entropy change indicates that the degeneracy of the ground state for the Nd$^{3+}$ ion in CuNdO$_2$ should be doublet; the observed magnetic entropy of $R \ln 2$ indicates that the ground doublet is selectively populated at low temperatures and this state causes the antiferromagnetic transition.

The CuLnO$_2$ compounds have a triangle-based array of Ln$^{3+}$ ions and are expected to behave as frustrated magnets. Geometrically frustrated materials often show a large ratio $\theta/T_m$ for the Weiss constant ($\theta$) and the magnetic ordering temperature ($T_m$), since such a frustration suppresses the long-range magnetic ordering [21]. In the case of CuNdO$_2$, the $\theta_{LT}/T_m$ value is 5. This result indicates that the magnetic ordering is highly suppressed by the magnetic frustration,
that is, the magnetic interaction between Ln ions in the Ln-O layers should be frustrated. Further studies such as neutron diffraction measurements will elucidate whether the magnetic frustration due to the triangular lattice is operative in the whole temperature range.

ACKNOWLEDGEMENTS

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REFERENCES


FIGURE CAPTIONS

Fig.1  Powder x-ray diffraction profiles of CuPrO$_2$. The calculated and observed profiles are shown on the top solid line and cross markers, respectively. The vertical marks in the middle show positions calculated for Bragg reflections. The lower trace is a plot of the difference between calculated and observed intensities.

Fig.2  (a) The schematic crystal structure of CuLnO$_2$. (b) Structure of CuLnO$_2$ viewed from the c-axis. Only one layer of LnO$_6$ octahedra is shown. The Ln ions form triangular array perpendicular to the c-axis (see text).

Fig.3  Variation of lattice parameters for CuLnO$_2$ and AgLnO$_2$ with the ionic radius of Ln$^{3+}$.

Fig.4  Temperature dependence of the magnetic susceptibility of CuLaO$_2$. The inset shows the reciprocal susceptibility vs. temperature curve.

Fig.5  Temperature dependence of the magnetic susceptibility of CuPrO$_2$. The inset shows the reciprocal susceptibility vs. temperature curve. The solid line is the Curie-Weiss fitting.

Fig.6  Temperature dependence of the magnetic susceptibility of CuNdO$_2$. The inset shows the reciprocal susceptibility vs. temperature curve. The solid line is the Curie-Weiss fitting.

Fig.7  Temperature dependence of the magnetic susceptibility of CuSmO$_2$ and CuEuO$_2$.

Fig.8  Temperature dependence of the magnetic susceptibility of AgTmO$_2$. The inset shows the reciprocal susceptibility vs. temperature curve. The solid line is the Curie-Weiss fitting.
Fig. 9  Temperature dependence of the magnetic susceptibility of AgYbO$_2$. The inset shows the reciprocal susceptibility vs. temperature curve. The solid line is the Curie-Weiss fitting.

Fig. 10  (a) Temperature dependence of the specific heat $C_p$ for CuNdO$_2$ below 15 K. The dotted line is the calculation results for the lattice specific heat (see text).

(b) Temperature dependences of the magnetic specific heat divided by temperature $C_{\text{mag}}/T$ and the magnetic entropy change $S_{\text{mag}}$ for CuNdO$_2$ below 8 K.
Fig. 1
Fig. 2(a)
Fig. 2(b)
Fig. 3

Ionic radius of Ln$^{3+} / \text{Å}$

<table>
<thead>
<tr>
<th>Ln</th>
<th>Ionic radius of Ln$^{3+} / \text{Å}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yb</td>
<td>3.4</td>
</tr>
<tr>
<td>Tm</td>
<td>3.6</td>
</tr>
<tr>
<td>Lu</td>
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<tr>
<td>Eu</td>
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<td>Sm</td>
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<td>Pr</td>
<td>4.2</td>
</tr>
<tr>
<td>La</td>
<td>4.3</td>
</tr>
</tbody>
</table>

$Ln$ refers to lanthanides in the periodic table.
Fig. 4

The figure shows the magnetic susceptibility ($\chi_M$) normalized to the molar volume ($\chi_M / \text{em} \cdot \text{mol}^{-1}$) as a function of temperature ($T$ in K) for CuLaO$_2$. The data is presented for two different conditions: zero-field cooled (ZFC) and field cooled (FC). The inset graph provides a zoomed-in view of the susceptibility data at lower temperatures. The magnetic susceptibility is given in units of $10^3 \text{emu} \cdot \text{mol}^{-1}$. The CuLaO$_2$ sample is characterized by a decrease in susceptibility with increasing temperature, indicating antiferromagnetic behavior. The ZFC data points are represented by filled circles, while the FC data points are represented by open circles.
Fig. 5
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig7.png}
\caption{Magnetic susceptibility ($\chi_{M}$) vs. temperature ($T$) for CuEuO$_2$ and CuSmO$_2$.}
\end{figure}

\textbf{CuEuO$_2$}:
- ZFC (filled circle)
- FC (empty circle)

\textbf{CuSmO$_2$}:
- ZFC (filled square)
- FC (empty square)
Fig. 8
Fig. 9
Fig. 10

(a) CuND02

$C_p \cdot T^{-1}$ / J mol$^{-1} \cdot K^{-2}$

$T / K$

(b) CuND02

$C_{mag} \cdot T^{-1}$ / J mol$^{-1} \cdot K^{-2}$

$S_{mag}$ / J mol$^{-1} \cdot K^{-1}$

$T / K$
Table 1. Structural parameters for CuPrO$_2$ and AgLuO$_2$.

### CuPrO$_2$

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<thead>
<tr>
<th>Atom</th>
<th>Site</th>
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<th>y</th>
<th>z</th>
<th>B / Å$^2$</th>
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<td>Cu</td>
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<td>0</td>
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<tr>
<td>Pr</td>
<td>3$b$</td>
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<td>0</td>
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<td>O</td>
<td>6$c$</td>
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<td>0</td>
<td>0.1047(5)</td>
<td>1.2(2)</td>
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</table>

**Note.** Space group $R$-3$m$, $a = 3.7518(2)$ Å, $c = 17.086(2)$ Å, $R_{wp} = 8.46$ %, $R_1 = 8.80$ %, and $R_e = 5.69$ %.

Definition of reliability factors $R_{wp}$, $R_1$ and $R_e$ are given as follows:

$$R_{wp} = \left[ \sum w(F(o)|-|F(c)|)^2 / \sum w|F(o)|^2 \right]^{1/2},$$

$$R_1 = \frac{\sum |I_k(o) - I_k(c)|}{\sum I_k(o)},$$

$$R_e = \left[ \frac{(N-p)\sum w_i y_i^2}{\sum w_i} \right]^{1/2}.$$

### AgLuO$_2$

<table>
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<tr>
<th>Atom</th>
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<th>z</th>
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<td>0</td>
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<td>1.2(2)</td>
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</table>

**Note.** Space group $R$-3$m$, $a = 3.4086(9)$ Å, $c = 18.588(8)$ Å, $R_{wp} = 14.13$ %, $R_1 = 3.17$ %, and $R_e = 4.87$ %.
Table 2. Lattice parameters and reliability factors for CuLnO$_2$ and AgLnO$_2$.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$a$ / Å</th>
<th>$c$ / Å</th>
<th>$R_{wp}$ / %</th>
<th>$R_l$ / %</th>
<th>$R_e$ / %</th>
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<tr>
<td>CuPrO$_2$</td>
<td>3.7518(2)</td>
<td>17.086(2)</td>
<td>8.46</td>
<td>8.80</td>
<td>5.69</td>
</tr>
<tr>
<td>CuNdO$_2$</td>
<td>3.7119(2)</td>
<td>17.085(2)</td>
<td>7.63</td>
<td>9.27</td>
<td>4.36</td>
</tr>
<tr>
<td>CuSmO$_2$</td>
<td>3.6628(1)</td>
<td>17.078(2)</td>
<td>9.38</td>
<td>3.51</td>
<td>6.63</td>
</tr>
<tr>
<td>CuEuO$_2$</td>
<td>3.6316(2)</td>
<td>17.074(4)</td>
<td>12.65</td>
<td>8.03</td>
<td>6.18</td>
</tr>
<tr>
<td>AgTmO$_2$</td>
<td>3.4670(9)</td>
<td>18.588(12)</td>
<td>14.85</td>
<td>5.02</td>
<td>4.45</td>
</tr>
<tr>
<td>AgYbO$_2$</td>
<td>3.4404(11)</td>
<td>18.587(13)</td>
<td>15.68</td>
<td>5.21</td>
<td>4.79</td>
</tr>
<tr>
<td>AgLuO$_2$</td>
<td>3.4086(9)</td>
<td>18.588(8)</td>
<td>14.13</td>
<td>3.17</td>
<td>4.87</td>
</tr>
</tbody>
</table>
Table 3. Bond lengths and BVSs for ALnO$_2$ (A = Cu, Ag).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$d$(A–O) / Å</th>
<th>BVS</th>
<th>$d$(Ln–O) / Å</th>
<th>BVS</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuLaO$_2$</td>
<td>1.760(9) × 2</td>
<td>1.33</td>
<td>2.466(4) × 6</td>
<td>2.71</td>
</tr>
<tr>
<td>CuPrO$_2$</td>
<td>1.789(8) × 2</td>
<td>1.23</td>
<td>2.411(4) × 6</td>
<td>2.85</td>
</tr>
<tr>
<td>CuNdO$_2$</td>
<td>1.836(7) × 2</td>
<td>1.09</td>
<td>2.370(3) × 6</td>
<td>3.03</td>
</tr>
<tr>
<td>CuSmO$_2$</td>
<td>1.880(8) × 2</td>
<td>0.96</td>
<td>2.325(3) × 6</td>
<td>3.16</td>
</tr>
<tr>
<td>CuEuO$_2$</td>
<td>1.895(9) × 2</td>
<td>0.93</td>
<td>2.302(5) × 6</td>
<td>3.26</td>
</tr>
<tr>
<td>AgTmO$_2$</td>
<td>2.017(11) × 2</td>
<td>1.13</td>
<td>2.275(8) × 6</td>
<td>2.85</td>
</tr>
<tr>
<td>AgYbO$_2$</td>
<td>2.034(12) × 2</td>
<td>1.08</td>
<td>2.253(7) × 6</td>
<td>2.78</td>
</tr>
<tr>
<td>AgLuO$_2$</td>
<td>1.996(9) × 2</td>
<td>1.19</td>
<td>2.256(3) × 6</td>
<td>2.91</td>
</tr>
</tbody>
</table>
Table 4. Effective magnetic moments ($\mu_{\text{eff}}$: experimental, $\mu_{\text{Ln}^3+}$: calculated) and Weiss constants for CuLnO$_2$ and AgLnO$_2$.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\mu_{\text{eff}} / \mu_B$</th>
<th>$\mu_{\text{Ln}^3+} / \mu_B$</th>
<th>$\theta / \text{K}$</th>
<th>$\theta_{LT}$*** / K</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuLaO$_2$</td>
<td>0.26(1)</td>
<td>–</td>
<td>–</td>
<td>para. (&gt;1.8 K)</td>
</tr>
<tr>
<td>CuPrO$_2$</td>
<td>3.75(6)</td>
<td>3.58</td>
<td>–113(6)</td>
<td>para. (&gt;1.8 K)</td>
</tr>
<tr>
<td>CuNdO$_2$</td>
<td>3.55(1)</td>
<td>3.62</td>
<td>–50(1)</td>
<td>–3.79(6) AF ($T_N = 0.8$ K)</td>
</tr>
<tr>
<td>CuSmO$_2$</td>
<td>1.66(1)*</td>
<td>1.55**</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>CuEuO$_2$</td>
<td>3.53(1)*</td>
<td>3.40**</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>AgTmO$_2$</td>
<td>7.52(1)</td>
<td>7.55</td>
<td>–34(1)</td>
<td>para. (&gt;1.8 K)</td>
</tr>
<tr>
<td>AgYbO$_2$</td>
<td>4.46(1)</td>
<td>4.54</td>
<td>–66(2)</td>
<td>–2.98(2) para. (&gt;1.8 K)</td>
</tr>
<tr>
<td>AgLuO$_2$</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Note. para. : paramagnetic, AF : antiferromagnetic, dia : diamagnetic.

*Observed values at room temperature. **Calculated values by van Vleck [19].
***Weiss constants obtained from low temperature data (<10 K).