

# Magnetic Properties of $\text{Cu}_2(\text{OH})_3(\text{alkancarboxylate})$ Compounds: Drastic Modification with Extension of the Alkyl Chain

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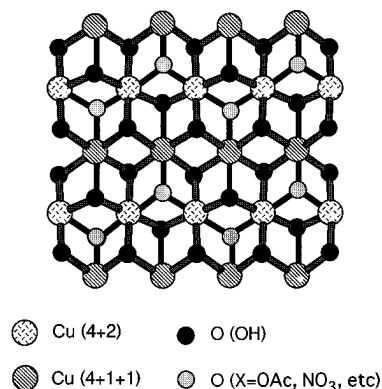
Magnetic properties of the layered materials  $\text{Cu}_2(\text{OH})_3(n\text{-C}_m\text{H}_{2m+1}\text{COO})$  ( $m = 0, 1, 7, 8,$  and  $9$ ) have been examined. X-ray powder diffraction patterns indicate that the interlayer distance increases in the order of  $m$ . The interlayer distances of the  $m = 0$  and  $1$  materials are shorter than the molecular heights of the intercalated carboxylates, respectively, while the distances of the  $m = 7\text{--}9$  materials are nearly double those of the molecular heights of the corresponding carboxylates, indicating a bilayer structure in them. The temperature dependence of the paramagnetic susceptibilities of the  $m = 0$  and  $1$  materials suggests an intralayer ferromagnetic interaction and an interlayer antiferromagnetic interaction. The metamagnetic behavior is supported by S-shape dependence of their magnetization curves. The temperature dependence of the paramagnetic susceptibilities of the  $m = 7\text{--}9$  materials indicates an intralayer antiferromagnetic interaction, in opposition to those in the former two. Further, they show a divergence of the ac magnetic susceptibility at 22 K, indicating a ferromagnetic order. The magnetization curve is characterized by an immediate increase at lower fields, succeeded by a gradual increase without saturation at higher fields. The magnetic properties of the  $m = 7\text{--}9$  materials are well understood in terms of the weak ferromagnetism. The change of the intralayer magnetic interaction could be caused by some structural change in the CuOH layer with the intercalation.

## Introduction

Layered metal hydroxides are of great interest to both science and technology, because of their utility as an ion-exchange material,<sup>1</sup> catalyst,<sup>2</sup> antacid,<sup>3</sup> and modified electrode.<sup>4</sup> They also attract interest as a two-dimensional magnetic material.<sup>5</sup> The copper hydroxy salts  $\text{Cu}_2(\text{OH})_3\text{X}$  ( $\text{X} =$  exchangeable anion OAc,  $\text{NO}_3$ , etc.) exhibit a botallackite-type structure, where two crystallographically distinct copper atoms lie in  $4 + 2$  (oxygen + X) and  $4 + 1 + 1$  (oxygen + oxygen + X) environments.<sup>6</sup> The structure of  $\text{Cu}_2(\text{OH})_3\text{X}$  is schematically shown in Figure 1. The anion is located in the interlayer, while the molecular end of it coordinates the copper ion. To see the effect of the molecular size of the intercalated anion on the magnetic behavior of the inorganic layer, we have carried out magnetic measurements on the  $\text{Cu}_2(\text{OH})_3(n\text{-C}_m\text{H}_{2m+1}\text{COO})$  series ( $m = 0, 1, 7, 8,$  and  $9$ ). In this report we describe two distinguished magnetic properties of the series, focusing on the magnetic data of  $\text{Cu}_2(\text{OH})_3(\text{HCOO})$  ( $m = 0$ ) and  $\text{Cu}_2(\text{OH})_3(\text{CH}_3(\text{CH}_2)_6\text{COO})$  ( $m = 7$ ).

## Materials

The intercalation compounds were obtained according to the procedure in ref 7. The parent material,  $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$  ( $m = 1$ ), was prepared: slow titration of an aqueous solution of  $\text{Cu}(\text{OAc})_2$  (1 l, 0.1 M) with NaOH (0.1 M) to a  $\text{OH}^-:\text{Cu}^{2+}$  ratio of 1 gave a



**Figure 1.** Schematic view of the inorganic layer in  $\text{Cu}_2(\text{OH})_3\text{X}$  (from ref 6).

precipitate of bluish-green crystals. Anal. Calcd (found) for  $\text{C}_2\text{H}_8\text{O}_6\text{-Cu}_2$ : C, 9.42 (9.32); H, 3.13 (3.02). The  $m = 0$  and  $7\text{--}9$  materials were obtained by anion exchanges: 200 mg of the parent material and 0.1 mol of the corresponding sodium alkanecarboxylate were dispersed in 0.1 l of water. The mixture was stirred for a day at room temperature, and the obtained material was filtrated, washed with water, and dried under vacuum. Anal. Calcd (found) for the  $m = 0$  material ( $\text{CH}_4\text{O}_5\text{-Cu}_2$ ): C, 5.38 (5.47); H, 1.75 (1.79). Anal. Calcd (found) for the  $m = 7$  material ( $\text{C}_8\text{H}_{18}\text{O}_5\text{Cu}_2$ ): C, 29.90 (28.97); H, 5.61 (5.31). Anal. Calcd (found) for the  $m = 8$  material ( $\text{C}_9\text{H}_{20}\text{O}_5\text{Cu}_2$ ): C, 32.94 (34.08); H, 6.10 (6.01). Anal. Calcd (found) for the  $m = 9$  material ( $\text{C}_{10}\text{H}_{22}\text{O}_5\text{-Cu}_2$ ): C, 34.40 (34.41); H, 6.30 (6.31). These results indicate completeness of the ion exchanges. However, the exchanges for the  $m = 2\text{--}6$  materials were not successful, because of decomposition ( $m = 2\text{--}4$ ) and of a too slow exchange rate ( $m = 5, 6$ ), in contrast to the stableness and immediate exchange for the  $m = 0$  and  $7\text{--}9$  materials.

The X-ray powder diffraction patterns of the parent and the exchanged materials showed intense (00l) reflections, indicating the layered structure in them.<sup>8</sup> The interlayer distance was estimated by subtracting the thickness of the inorganic host layer from the distance between two neighboring planes of class (00l). Figure 2 shows the dependence of the interlayer distance on  $m$ , namely, the number of the

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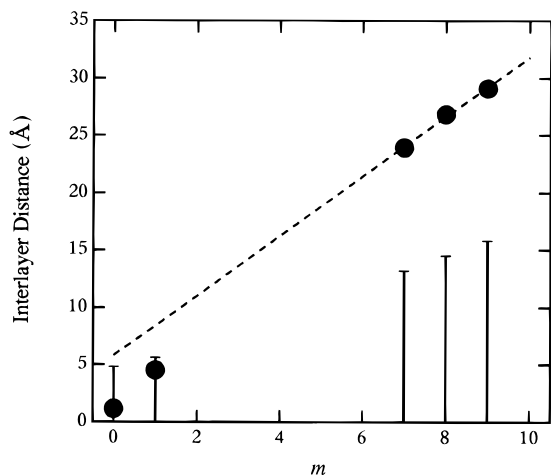


Figure 2. Interlayer distances of the  $\text{Cu}_2(\text{OH})_3(n\text{-C}_m\text{H}_{2m+1}\text{COO})$  series.

carbon in the alkyl chain. The distance increases in the order of  $m$ . The bars in this figure show calculated molecular heights of the carboxylates. The interlayer distances of the  $m = 0$  and 1 materials are shorter than the molecular heights of the intercalated carboxylates, respectively, presumably because of the coordination of the carboxylates to the intralayer copper ion. The distances of the  $m = 7-9$  materials are nearly double those of the molecular heights of the corresponding carboxylates, indicating a bilayer structure in them. The structural difference of the organic layer is also suggested by the fact that the plots for the  $m = 0$  and 1 materials appear to deviate from the fitted line to the plots for the  $m = 7-9$  materials.

### Magnetic Properties

The ac and dc magnetic susceptibilities and magnetization of the intercalation compounds were investigated. The ac susceptibility,  $\chi_{ac}$ , was measured in the field of 5 Oe (375 Hz) among 5–30 K on an ac magnetosusceptometer (Lake Shore ACS 7221). The dc susceptibility and magnetization were measured with a Faraday balance.<sup>9</sup> Temperature dependence of the dc susceptibility was examined in the range 3–280 K under the field of 1 T. The paramagnetic susceptibility,  $\chi_p$ , was obtained from the dc susceptibility, subtracting the diamagnetic susceptibility evaluated by assuming that  $\chi_p$  follows the Curie law at high temperatures. We did not compensate the effect of nonlinear relation between the magnetization and the applied field, observed at low temperatures, in the calculation of the dc susceptibility.

The open circles in Figure 3 show the temperature dependence of the product  $\chi_p T$  of the  $m = 0$  material,  $\text{Cu}_2(\text{OH})_3(\text{HCOO})$ , where the  $x$  axis is in a log scale. We adopt half of  $\text{Cu}_2(\text{OH})_3\text{X}$  as the molar unit. The value of  $\chi_p T$  increases with decreasing temperature down to *ca.* 10 K, indicating dominance of a ferromagnetic interaction. The Weiss constant evaluated, using the data  $T > 100$  K is 4 K. The intralayer interaction between the copper ions is ferromagnetic. However,  $\chi_p T$  decreases suddenly below it, suggesting an interlayer antiferromagnetic coupling. The open circles and squares in Figure 4 show the real ( $\chi'$ ) and imaginary ( $\chi''$ ) parts of the ac susceptibilities of the  $m = 0$  material, respectively.  $\chi'$  increases with decreasing temperature down to 5.8 K, and after making a rather sharp maximum, it decreases slightly, while  $\chi''$  depends little on temperature in the range. The open circles in Figure 5 show the magnetization curve at 3.0 K, the lowest temperature attainable in our apparatus. One can see S-shape dependence on the field. This is consistent with the coexistence of the ferromagnetic and antiferromagnetic interactions. The observed

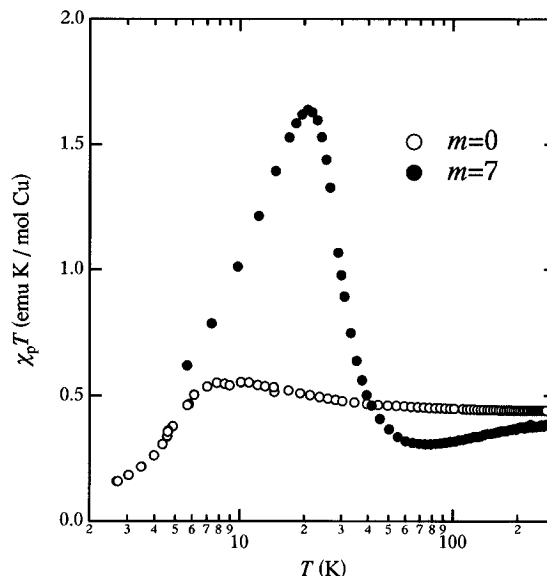


Figure 3. Temperature dependence of the paramagnetic susceptibilities  $\chi_p$  of  $\text{Cu}_2(\text{OH})_3(\text{HCOO})$  ( $m = 0$ ) and  $\text{Cu}_2(\text{OH})_3(\text{CH}_3(\text{CH}_2)_6\text{COO})$  ( $m = 7$ ).  $\chi_p T$  is plotted as a function of temperature.

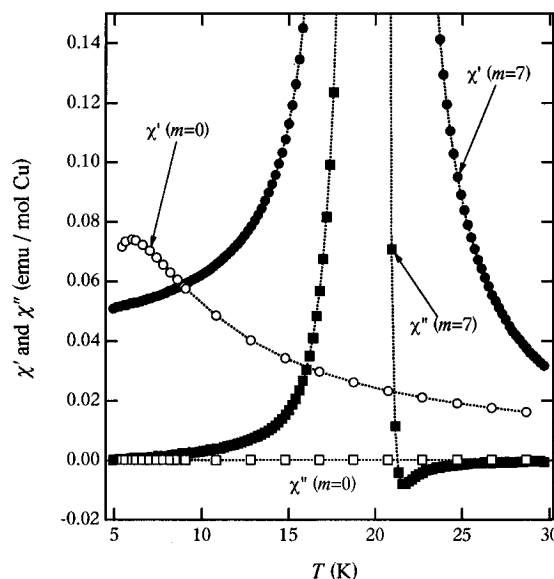


Figure 4. Temperature dependence of the ac susceptibilities of  $\text{Cu}_2(\text{OH})_3(\text{HCOO})$  ( $m = 0$ ) and  $\text{Cu}_2(\text{OH})_3(\text{CH}_3(\text{CH}_2)_6\text{COO})$  ( $m = 7$ ).

behavior is quite similar to those of the transition metal hydroxides,  $\text{M}(\text{OH})_2$  with  $\text{M} = \text{Fe}, \text{Co},$  and  $\text{Ni}$ , whose structure can be understood as that of  $\text{M}_2(\text{OH})_3\text{X}$  with  $\text{X} = \text{OH}$ , and which are well-characterized as metamagnets.<sup>10-12</sup> The  $m = 0$  material is expected to be a metamagnet at a lower temperature which consists of an intralayer ferromagnetic interaction and an interlayer antiferromagnetic interaction. The  $m = 1$  material,  $\text{Cu}_2(\text{OH})_3(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$ , also shows metamagnetic behavior (not shown).

The closed circles in Figure 3 show  $\chi_p T$  of the  $m = 7$  material,  $\text{Cu}_2(\text{OH})_3(\text{CH}_3(\text{CH}_2)_6\text{COO})$ .  $\chi_p T$  decreases with decreasing temperature down to 60 K, indicating an intralayer antiferromagnetic interaction, in opposition to the ferromagnetic ones in the  $m = 0$  and 1 materials. The Weiss constant is obtained to be  $-30$  K with the data  $T > 100$  K. However,  $\chi_p T$  increases

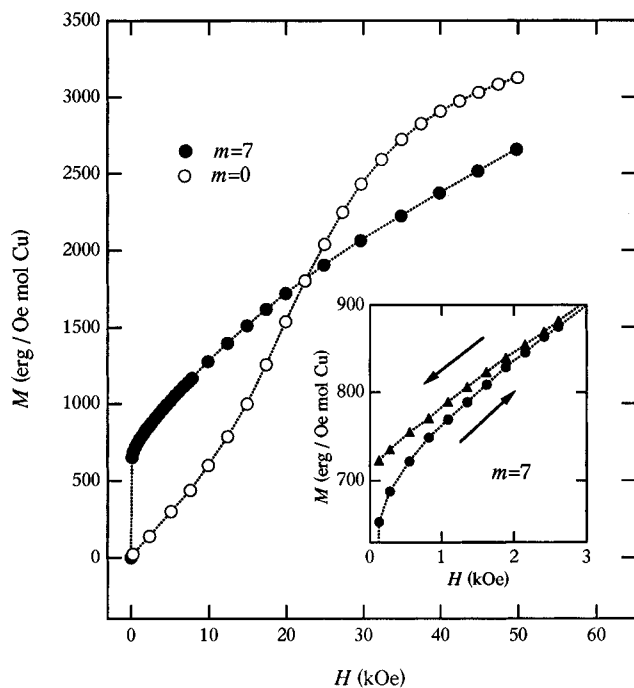
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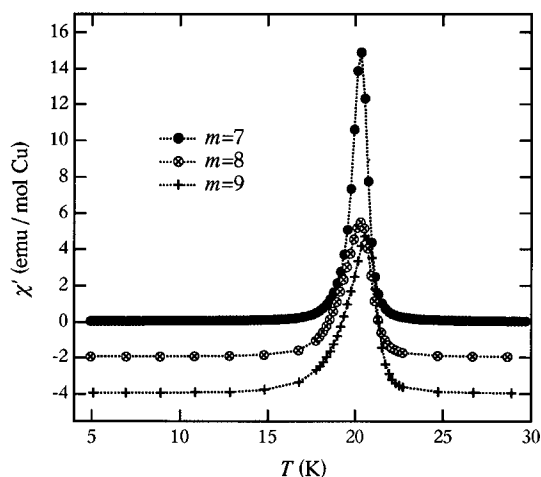
**Figure 5.** Field dependence of the magnetizations of  $\text{Cu}_2(\text{OH})_3(\text{HCOO})$  ( $m = 0$ ) at 4.2 K and  $\text{Cu}_2(\text{OH})_3(\text{CH}_3(\text{CH}_2)_6\text{COO})$  ( $m = 7$ ) at 3.0 K. The inset shows the hysteresis of the magnetization of the  $m = 7$  material at 3.0 K.

suddenly below 60 K. The closed circles and squares in Figure 4 show  $\chi'$  and  $\chi''$  of the  $m = 7$  material, respectively. The plots of  $\chi'$  make an anomalous peak around 22 K whose maximum value is  $14.9 \text{ emu mol}^{-1}$ .  $\chi''$  also shows an anomaly at 22 K, although it is constantly zero above it. The ac susceptibilities indicate a ferromagnetic order with  $T_c = 22 \text{ K}$ , in spite of the intralayer antiferromagnetic interaction. The closed circles in Figure 5 show the magnetization curve measured with increasing field at  $T = 4.2 \text{ K}$ . The magnetization shows an abrupt increase at the lower fields, but it gradually increases without showing saturation at the higher fields. This is typical of a weak ferromagnet. The closed triangles in the inset of Figure 5 show the magnetizations measured with decreasing field. A small hysteresis is seen below 3 kOe, which supports the ferromagnetic order. The residual magnetization is  $710 \text{ erg Oe}^{-1} \text{ mol}^{-1}$  which corresponds to a canting angle of  $7.0^\circ$  between two antiferromagnetic moments. We speculate that the spin canting takes place between the two copper ion sites in the  $4 + 2$  and  $4 + 1 + 1$  environments (see Introduction). It is worth mentioning the significant decrease in  $\chi'$  in the ordered state below 22 K. Similar temperature dependence of  $\chi'$  is reported for the layered complexes,  $\text{A}_2\text{MX}_4$  (A = alkylammonium, etc.; M = Fe, Mn; and X = Cl, Br), which are characterized as a weak ferromagnet.<sup>13–15</sup> The phenomenon is explained in terms of the domain size effect on the ac magnetic susceptibility.<sup>16</sup>

The temperature dependence of  $\chi'$  of the  $m = 7, 8,$  and  $9$  materials are compared in Figure 6. These three show divergence of  $\chi'$  at the same temperature. The  $m = 8$  and  $9$  materials are also indicated to be weak ferromagnets with the transition temperature of  $T_c = 22 \text{ K}$ .

## Discussion

The intercalation compounds,  $\text{Cu}_2(\text{OH})_3(n\text{-C}_m\text{H}_{2m+1}\text{COO})$ , show the interesting variety of magnetism. The  $m = 0$  and  $1$



**Figure 6.** Temperature dependence of the real-part ac susceptibilities of  $\text{Cu}_2(\text{OH})_3(n\text{-C}_m\text{H}_{2m+1}\text{COO})$  ( $m = 7, 8,$  and  $9$ ).

materials show the metamagnetic behavior, while the  $m = 7–9$  materials become the weak ferromagnets below 22 K. The intralayer magnetic interaction is ferromagnetic in the former ones, while antiferromagnetic in the latter ones. The change of the intralayer magnetic interaction could be caused by some structural change in the CuOH layer with the intercalation. This could be related to the fact that the Cu–OH–Cu exchange interaction is known to be quite sensitive to the Cu–OH–Cu angle: a di-nuclei's complex,  $[\text{Cu}(\text{EAP})\text{OH}]_2(\text{ClO}_4)_2$ , with the angle of  $99^\circ$  shows an antiferromagnetic coupling of  $2J = -130 \text{ cm}^{-1}$ , while  $[\text{Cu}(\text{bpy})\text{OH}]_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$  (bpy = 2,2'-bipyridine) with  $97^\circ$  does a ferromagnetic interaction of  $48 \text{ cm}^{-1}$ .<sup>17</sup> It is possible that the drastic magnetic change can be explained by a small structural change in the CuOH layer caused by the difference in the intercalated organic molecules.

It is notable that the  $m = 7–9$  materials in which the interlayer distances are more than  $20 \text{ \AA}$  have the magnetic ordered states with rather high  $T_c$ , although there are precedents for the magnetic order in two-dimensional magnetic materials.<sup>18</sup> The interlayer weak exchange interaction and the intralayer anisotropic exchange interaction are theoretically expected to be responsible for the three dimensional order.<sup>19</sup> It is clear that the  $m = 7–9$  materials involve an intralayer anisotropic exchange which results in the weak ferromagnetism. This could be the point for the realization of the ordered states in them.

The magnetic variety in the CuOH layer may lead to a functional magnetic material in the future: if an organic molecule which plays a role of sensor, namely, which changes the structure by small perturbation, such as irradiation, pressure, electric field, and so on, can be inserted in the interlayer, the magnetic variety may give rise to a "conditional" magnet which drastically changes the magnetic properties by the perturbation to the organic molecule. We are working on the other salts in the series. EXAFS studies are also now in progress.

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