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INTERCALATION OF FUNCTIONAL ORGANIC MOLECULES INTO COPPER(II) MAGNETIC MATERIALS

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Abstract (i) The magnetic properties of the series of a layered material, $Cu_2(OH)_3(n\text{-}C_mH_{2m+1}COO)$, are found to show an anomalous change, depending on the alkyl-chain length: the m=0 and 1 materials are metamagnetic while the m=7-9 materials become weak ferromagnets below 22 K. Further, 4-phenylazobenzoate and 2-anthracene carboxylate, which are derivatives of well-known photo-functional molecules, are intercalated into the copper hydroxides. The obtained materials are both antiferromagnetic in the whole temperature range of 3-280 K. However, the photochemical reactions do not take place by irradiation with a xenon lump. (ii) The magnetic properties of the layered perovskite ferromagnets $(p\text{-cyanoanilinium}^+)_2CuCl_4^{2-}$ and $(p\text{-chloroanilinium}^+)_2CuBr_4^{2-}$ are studied under hydrostatic high pressure of 1.0 GPa. Above T_c, they show an increase of the magnetization, which would due to enhancement of the ferromagnetic coupling, but, below T_c, they show different magnetic response to the pressure.

INTRODUCTION

Organic/inorganic hybrid nanocomposites attract much interest for creating new functionality which is superior to those of the components. For instance, intercalation of an organic molecule which is sensitive to a perturbation, such as irradiation, pressure, electric field or etc., into an inorganic magnetic material, may lead to a functional magnetic system which can be controlled by the perturbation. In this report we describe the magnetic properties of two different Cu(II) layered materials intercalated with organic molecules.

INTERCALATION OF FUNCTIONAL ORGANIC MOLECULES INTO LAYERED COPPER(II) HYDROXIDES

The copper hydroxy salts, $Cu_2(OH)_3X$ (X=exchangeable anion OAc, NO_3 etc.), exhibit a botallackite-type structure, which is schematically shown in Figure 1. In the structure

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two-crystallographically distinct copper atoms lie in 4+2 (oxygen+X) and 4+1+1 (oxygen+oxygen+X) environments.[1] The anion is located in the interlayer, while the molecular end of it coordinates the copper ion. In this section we describe the magnetic behavior of the $Cu_2(OH)_3(n\text{-}C_mH_{2m+1}COO)$ series and intercalation of photo-functional organic molecules.

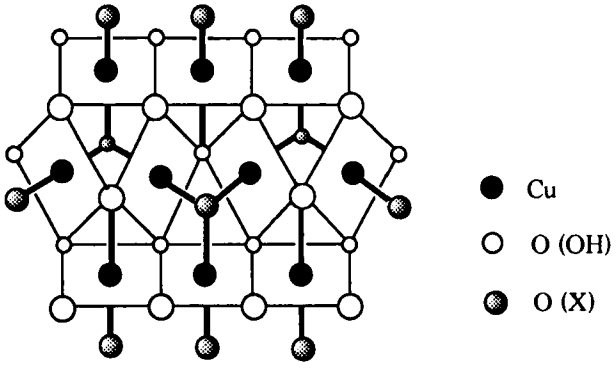

FIGURE 1 Schematic view of the botallackite-type structure.

Magnetic Properties of the $Cu_2(OH)_3(n\text{-}C_mH_{2m+1}COO)$ series [2]

To see the effects of the size of the intercalated molecule on the magnetic behavior of the $[Cu_2(OH)_3]^-$ layer, we have examined the magnetic properties of the $Cu_2(OH)_3(n\text{-}C_mH_{2m+1}COO)$ (m=0, 1, 7, 8 and 9) series. The m=1 material was prepared by the reaction between $Cu(CH_3COO)_2$ and NaOH.[3] The others were obtained by means of the anion exchange of the m=1 material.[3] Figure 2 shows the X-ray powder diffraction pattern of the parent m=1 material. One can see intense (00l) reflections because of the layered structure. The other materials also show similar diffraction patterns.

The open circles in Figure 3 show the temperature dependence of the paramagnetic susceptibilities χ_p of the m=0 material, $Cu_2(OH)_3(HCOO)$. In this figure χ_pT is plotted as a function of temperature and half of $Cu_2(OH)_3X$ is adopted as the molar unit. The value of χ_pT 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 would be ferromagnetic. However χ_pT decreases suddenly below 4 K, suggesting an interlayer antiferromagnetic coupling. The observed behavior is quite similar to those of the transition metal hydroxides, $M(OH)_2$ with M=Fe, Co and Ni, whose structure can be understood as that of $M_2(OH)_3X$ with X=OH, and which are well characterized as metamagnets.[4-6] 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 also shows metamagnetic behavior (see Figure 5).

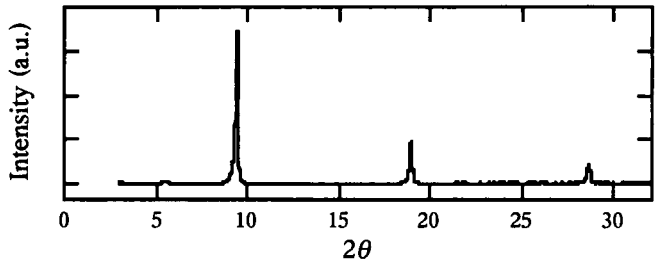

FIGURE 2 X-ray diffraction pattern of $Cu_2(OH)_3(CH_3COO)\cdot H_2O$.

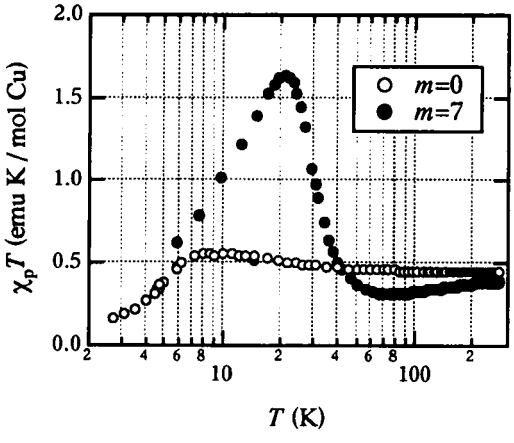

FIGURE 3 Temperature dependence of χ_pT of $Cu_2(OH)_3(HCOO)$ (m=0) and $Cu_2(OH)_3(CH_3(CH_2)_6COO)$ (m=7).

The closed circles in Figure 3 show χ_pT of the m=7 material, $Cu_2(OH)_3(CH_3(CH_2)_6COO)$. χ_pT 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 χ_pT increases suddenly below 60 K. The temperature dependence of the ac susceptibilities χ_{ac} of the m=7 material makes an anomalous peak around 22 K whose maximum value is 14.9 emu mol^{-1} (not shown). The behavior can be interpreted in terms of weak ferromagnetism. The m=8 and 9 materials also show divergence of χ_{ac}

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at the same temperature, and are also indicated to be weak ferromagnets with a transition temperature of T_c=22 K.

The m=0 and 1 materials show metamagnetic behavior, while the m=7-9 materials become weak ferromagnets below 22 K. The intralayer magnetic interaction is thought to be ferromagnetic in the former ones, while antiferromagnetic in the latter ones. The change of the intralayer magnetic interaction would be due to some structural change in the CuOH layer. 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 complex, $[Cu(EAEP)OH]_2(ClO_4)_2$, with the angle of 99° shows an antiferromagnetic coupling of $2J$=-130 cm^{-1}, while $[Cu(bipy)OH]_2SO_4 \cdot 5H_2O$ with 97° does a ferromagnetic interaction of 48 cm^{-1}.[7] It may be 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.

Intercalation of Photo-Functional Organic Molecules

Since the $[Cu_2(OH)_3]^-$ layer was found to show a drastic change of the magnetic properties, depending on the size of the intercalated organic molecule, and to be a good candidate for a controllable magnet, we carried out intercalation of 4-phenylazobenzoate (1) and 2-anthracene carboxylate (2), by the anion exchange method. Their parent materials, azobenzene and anthracene, are well known to show the following photochemical reactions, (a) and (b), respectively.

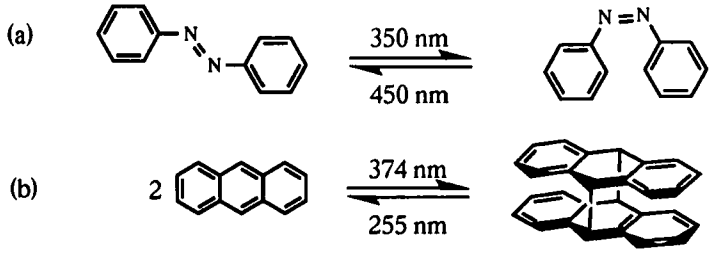

Figure 4 shows the X-ray diffraction patterns of the obtained materials, $Cu_2(OH)_3$(1) and $Cu_2(OH)_3$(2). There is no peak assignable to that of the parent material in their patterns, indicating that the exchange reactions take place. However the diffraction intensities are weaker than that of the parent material shown in Figure 2, presumably because of inhomogeneity and/or poor crystallinity. The basal spacing are estimated to be 9.7 Å for $Cu_2(OH)_3$(1) and 12 Å for $Cu_2(OH)_3$(2).

The squares in Figure 5 show the temperature dependence of $\chi_p T$ of the parent compound, $Cu_2(OH)_3(CH_3COO) \cdot H_2O$ (m=1). As mentioned before, it exhibits

metamagnetic behavior. The open and closed circles in this figure are $\chi_p T$ of $Cu_2(OH)_3$(1) and $Cu_2(OH)_3$(2), respectively. They show weak antiferromagnetic behavior in the whole temperature range of 3-280 K. The magnetic interactions in them are similar to those in the m=7-9 materials, but they do not show spin canting.

We irradiated the absorption bands of the organic molecules which are intercalated into the interlayer of $[Cu_2(OH)_3]^-$, but there was no indication of the photochemical reactions. The interlayer space seems to be too rigid for the reactions.

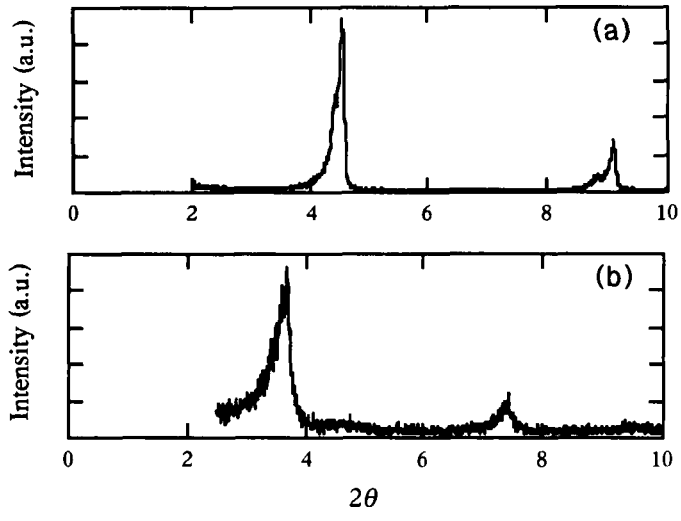

FIGURE 4 X-ray powder diffraction patterns of $Cu_2(OH)_3$(1) (a) and $Cu_2(OH)_3$(2) (b).

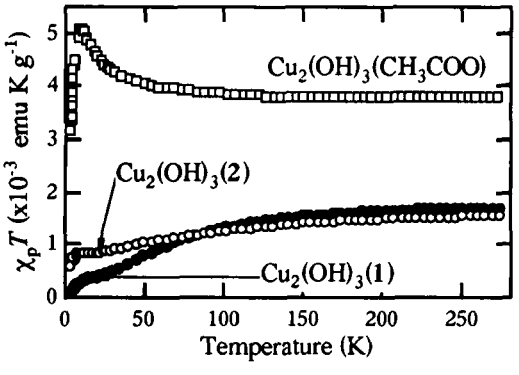

FIGURE 5 Temperature dependence of $\chi_p T$ of $Cu_2(OH)_3(CH_3COO)\cdot H_2O$, $Cu_2(OH)_3$(1) and $Cu_2(OH)_3$(2).

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HIGH-PRESSURE EFFECTS ON THE MAGNETIC PROPERTIES OF COPPER(II) LAYERED PEROVSKITE FERROMAGNETS

Compounds of the type $(RNH_3^+)_2CuX_4^{2-}$, where R is an *n*-alkyl chain or an aromatic group and X=Cl or Br, have been known to be two-dimensional ferromagnets.[8] They crystallize in a layered perovskite structure, consisting of isolated layers of corner-sharing CuX_6 octahedra, sandwiched by the organic cations.[9,10] Figure 6 schematically shows the structure of the CuX_4^{2-} layer, which governed by the cooperative Jahn-Teller effect; the prolonged Jahn-Teller *z* axis of the CuX_6 octahedra lies in the CuCl plane with nearly-orthogonal relations between those of the neighbors. The intralayer magnetic interaction is ferromagnetic, because of the nearly-orthogonal relation between the magnetic $d_{x^2-y^2}$ orbitals.[11] Recently, Moritomo and Tokura carried out optical measurements on $(C_2H_5NH_3^+)_2CuCl_4^{2-}$ under high pressure and found an unusual phase transition at 4 GPa.[12] They concluded that rearrangement of the Jahn-Teller distortion takes place at the phase transition and the prolonged *z* axes are aligned to be normal to the Cu-Cl plane after it. They also speculated that the magnetic interaction between the neighboring Cu^{2+} ions turns over from ferromagnetic to antiferromagnetic, because of overlaps between the magnetic $d_{x^2-y^2}$ orbitals. These compounds can be regarded as a candidate for a switchable or controllable magnet by pressure.

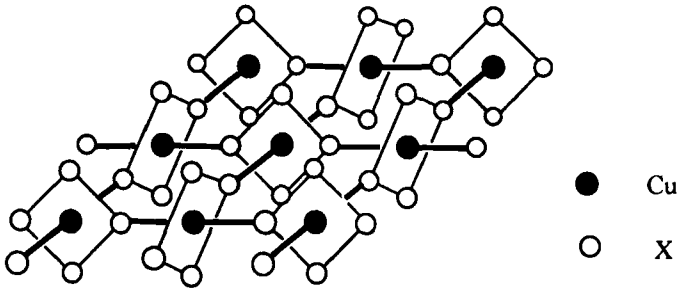

FIGURE 6 Schematic view of the structure of the CuX_4^{2-} layer. The bold lines indicate the prolonged Jahn-Teller *z* axes.

We have examined high pressure effects on the magnetic properties of $(p$-cyanoanilinium$^+)_2CuCl_4^{2-}$ (**3**) and $(p$-chloroanilinium$^+)_2CuBr_4^{2-}$ (**4**) on a Faraday balance.[13] Their ferromagnetic transition temperatures were determined to be $T_c = 9.5$ K for **3**[14] and 15 K for **4** by ac susceptibility measurements. The results on **3** are shown in Figure 7, where ΔM is the difference between the magnetizations at high pressures and at

the ambient pressure, namely $\Delta M=M(P)-M(0)$. The pressure is found to increase the magnetization of **3** in the whole temperature range, making a maximum of ΔM at *ca.* 18 K. The observed effects indicate that the applied pressure increases both T_C and in-plane ferromagnetic exchange J.[14]

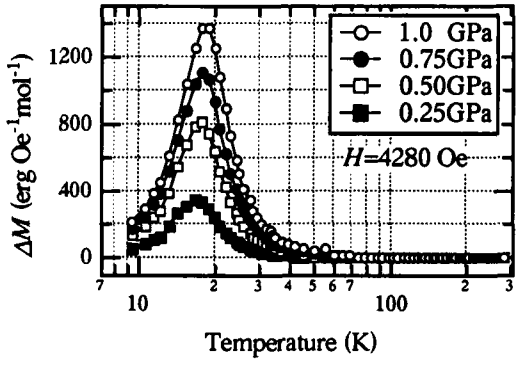

FIGURE 7 High-pressure effects on the temperature dependence of the magnetization of **3**. The difference between the magnetizations at high pressures and at the ambient pressure.

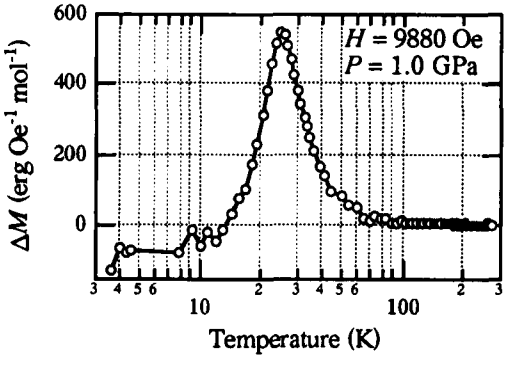

FIGURE 8 High-pressure effects on the temperature dependence of the magnetization of **4**.

Figure 8 shows the results on **4**, where the difference between the magnetizations at 1.0 GPa and at the ambient pressure is plotted as a function of temperature. Above T_C the applied pressure increases the magnetization, such as found for **3**. However, below T_C, the pressure slightly decreases the magnetization. This may suggest an intrinsic

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difference in the magnetic ordered state between **3** and **4**. Detail examinations are now in progress.

We have studied high-pressure effects on **3** and **4**. Above T_c, we found pressure-induced enhancement of the ferromagnetic interaction in the CuCl layer for both **3** and **4**, but, below T_c, characteristic difference between them was discovered. Since the maximum pressure in this study was much smaller than that for the phase transition discovered by Moritomo and Tokura,[12] we could not confirm the transition from the magnetic measurements. However, the conclusion in this magnetic study, namely enhancement of the ferromagnetic interaction in the CuCl layer in the low pressure phase, was consistent with their optical results.[12]

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