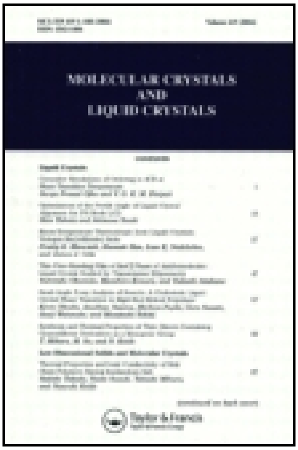

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Magnetic Properties of Layered Copper Hydroxides under High Pressure

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The effects of high pressure up to 1 GPa were investigated on a layered copper hydroxides, $Cu_2(OH)_3(n\text{-}C_7H_{15}CO_2)$, which exhibits weak ferromagnetism of T_N=22 K at the ambient pressure. With an increase in pressure, the magnetization gradually decreases especially in the temperature range 20–30 K. The high pressure effect can be explained in terms of a weakening of the exchange interaction in the Cu-O-Cu superexchange pathway.

Keywords: layered copper hydroxides; intercalation; phase transition; magnetic properties

INTRODUCTION

Physical and chemical properties of nanostructured organic-inorganic materials have attracted recent interest.[1] In such structures, the organic molecules have exhibited selective and reversible reactions, and packing transformations between various orientations, while the inorganic layers including transition metals have done electrical and magnetic properties. This suggests the possibility of a controllable and/or switchable magnetic material, in which the inorganic layer carries magnetic moments and the organic layer controls the magnetic properties of the inorganic layer.

Layered copper hydroxides, $Cu_2(OH)_3X$ (X = inorganic anion, carboxylate and so on), are known as a two-dimensional magnetic material.[2,3] Figure 1 shows the crystal structure of copper hydroxy nitrate (X=NO_3).[4] The structure of the copper hydroxy layer is similar to that of $Cd(OH)_2$; the structure of the former can be obtained by periodically replacing one fourth of the OH^- ions in $Cd(OH)_2$ with the guest anions X. The anions X, located between the inorganic layers, are exchangeable, so that various organic-inorganic nanocomposite hybrids can be easily produced.[5] The copper

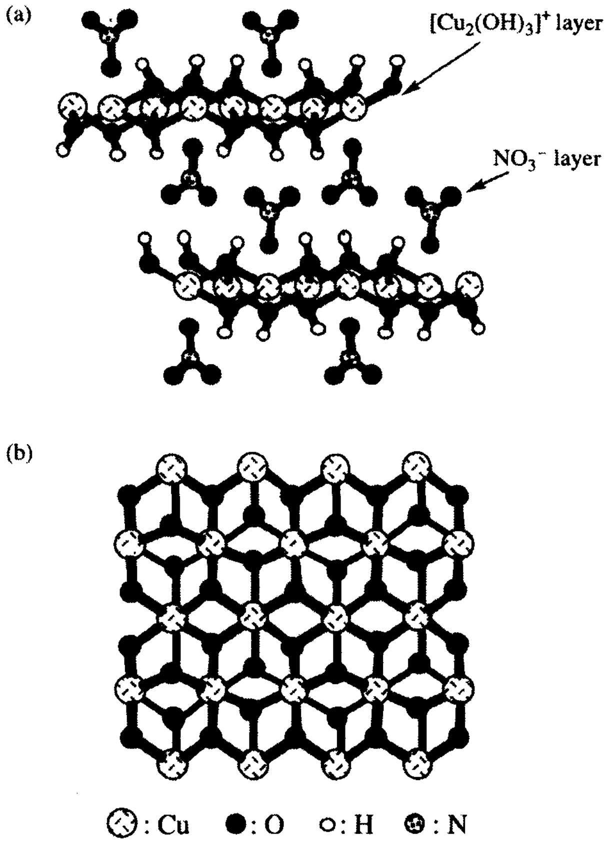

Figure 1. The crystal structure of $Cu_2(OH)_3NO_3$; (a) side view; (b) top view.

hydroxy layer shows a magnetic variety which depends drastically on the molecular shape and orientation of X.[6-8] It is believed that the magnetic variety is due to the sensitivity of the nearest-neighbor Cu-Cu magnetic interaction to the Cu-O-Cu bridging angle in the $[Cu_2(OH)_3]^+$ network.[9] It is well known that the Cu-OH-Cu exchange coupling in the OH-bridged Cu(II) di-nuclei complexes seriously depends on the bridging angle; the correlation is expressed as

$$J\,(\mathrm{cm}^{-1}) = -74\alpha\,(^{\circ}) + 7270.^{10} \qquad (1)$$

In this study, we investigated the magnetic properties of the layered copper hydroxides, $Cu_2(OH)_3(n\text{-}C_7H_{15}CO_2)$ (**1**) under high pressure, to elucidate how the pressure brings about structural and magnetic modifications.

EXPERIMENTAL

The compound **1** was obtained by a modification of the literature methods.[5] Hydrostatic pressure was applied to about 10 mg of the sample with the pressure fluid, Lipolube 40 oil (Lion, Tokyo) and was maintained by using a miniature Be-Cu pressure clamp cell.[11] The temperature dependence of the magnetization of the Be-Cu cell that contained the sample, was measured with a Faraday susceptometer[11] on 1 T at ambient and high pressures under the same conditions. The pressure-induced difference between the magnetization at ambient pressure and high pressure, ΔM, includes the pressure dependence of the magnetizations of both the pressure cell and the pressure liquid, which have been confirmed to be negligibly smaller than the observed ΔM. The magnetization at ambient pressure $M(0)$ was separately measured by using a standard quartz cell and the high-pressure magnetization $M(P)$ was calculated from the equation, $M(P) = M(0) + \Delta M$.

RESULTS AND DISCUSSION

The open circles in Fig. 2 show the temperature dependence of the paramagnetic susceptibilities of **1** at ambient pressure, where the bottom axis is in a log scale. The Curie and Weiss constants are obtained to be 0.429 emu K mol^{-1} and -30 K, respectively, using the data T>100 K. This negative Weiss constant indicates dominance of an antiferromagnetic interaction. However, the magnetization increases suddenly below 40 K. The low-field magnetic susceptibilities and magnetization curve measurements indicate weak ferromagnetism with T_N=22 K (not shown).[12] Figure 3 shows the difference, ΔM, between the magnetization at high pressure and at ambient pressure. The magnetizations at high pressures, $M(P)$, calculated according to the procedure described in the experimental section, are shown in Fig. 2. With an increase in the pressure, the magnetization exhibits a decrease in magnitude, especially in the temperature range 20-30 K. The abrupt increase of the magnetization caused by the ferromagnetic ordering shifts toward lower temperatures, suggesting that the pressure decreases T_N. Further the decrease of the

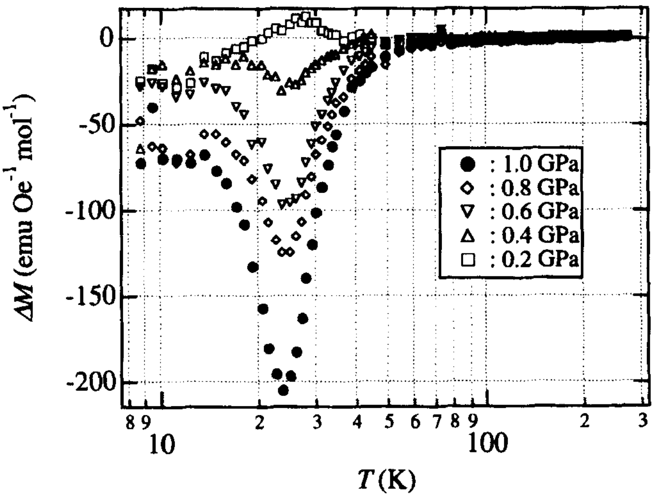

Figure 2. Temperature dependence of the difference between the magnetizations of **1** at five different pressures on 1 T.

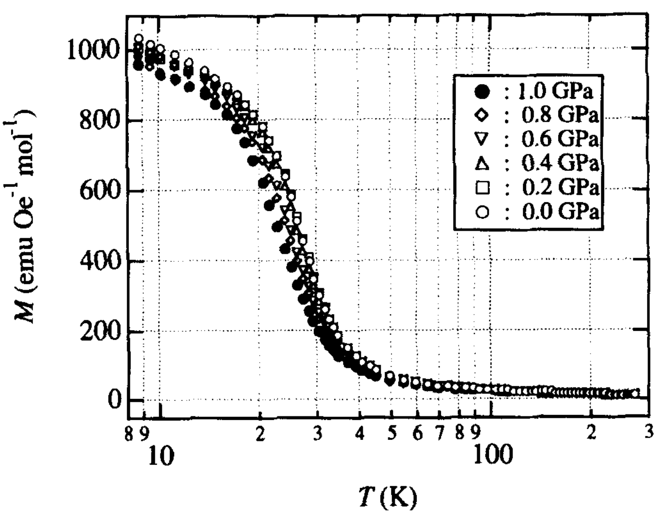

Figure 3. Temperature dependence of the magnetization of **1** at high pressure and ambient pressure.

magnetization below 10 K induced by pressurre is presumably explained by an increase of the canting angle.

The magnetic measurements indicated a pressure-induced decrease in T_N. This could be caused by a suppression of the antiferromagnetic coupling between the copper ions. High pressure leads to compression of the crystalline lattice and possibly induces a decrease in the Cu-OH-Cu bridging angle in the $[Cu_2(OH)_3]^+$ network. As shown in eq. (1), a decrease in the angle results in a weakening of the antiferromagnetic coupling. This also can explain the decrease of the magnetization in the ordered state, in terms of a weakening of the Dzyaloshinsky-Moriya interaction, which causes the spin canting.[12]

CONCLUSION

We have applied hydrostatic high pressure up to 1 GPa to $Cu_2(OH)_3(n\text{-}C_7H_{15}CO_2)$, which is a weak ferromagnet below 22 K. It is found that the pressure significantly decreases the magnetization. It is speculated that the pressure effects are caused by a small change in the Cu-O-Cu bridges which weakens the antiferromagnetic exchange interaction.

Acknowledgments
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