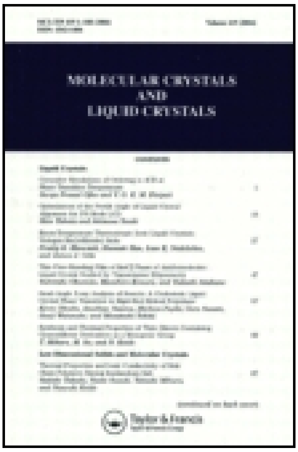

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006.

To cite this article: Wasuke Mori & Kizashi Yamaguchi (1995): Spin Glass Behavior of Synthetic Atacamite, $Cu_2Cl(OH)_3$, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 274:1, 113-118

To link to this article: http://dx.doi.org/10.1080/10587259508031871

Mol. Cryst. Liq. Cryst., 1995, Vol. 274, pp. 113–118
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SPIN GLASS BEHAVIOR OF SYNTHETIC ATACAMITE, $Cu_2Cl(OH)_3$

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Abstract It has been found that the magnetic susceptibility of synthetic atacamite, $Cu_2Cl(OH)_3$, reveals existence of a relaxation phenomenon similar to that in the spin glass. The magnetic susceptibility shows an unusual behavior below 8K; there is a sharp peak in the magnetic susceptibility at about 5.3K when the crystal is cooled in zero magnetic field and the magnetization is a very slow process following a logarithmic law. On the other hand, the susceptibility decreases monotonously as the temperature is raised. The AC magnetic susceptibility x' shows a sharp peak at 5.8K, which shifts to higher temperature with increasing AC field frequency.

INTRODUCTION

The spin glass is usually observed in random systems such as dilute metallic alloys.[1)] However, it was found that synthetic atacamite, which is regular system, behaves like a spin glass, although mineral atacamite does not show such behavior. The present investigation has been undertaken in order to make clear the unusual magnetic behavior.

EXPERIMENTAL

The dark green powder crystals of $Cu_2Cl(OH)_3$ are obtained by heating mixed aqueous solution (50ml) of $Cu(HCOO)_2 \cdot 4H_2O$ (10g) and KCl (4g) at 70-80°C for several hours. Anal. Calcd. for $Cu_2Cl(OH)_3$: Cu, 59.5; Cl, 16.6; H, 1.42%. Found: Cu, 58.7; Cu, 16.5 ; H, 1.60%.

The powdered sample thus obtained was identified as an atacamite by powder X-ray diffraction as shown in Fig. 1.

The DC magnetic susceptibility was determined by the Faraday method with a magnetic balance (cahn1000 electric balance, Nippon Komitu electromagnet) in the temperature range 4.2-300 K. The AC magnetic susceptibility was measured by SQUID magnetometer (QUANTUM Design, MPMS-5S) in the temperature range 4.5-8 K.

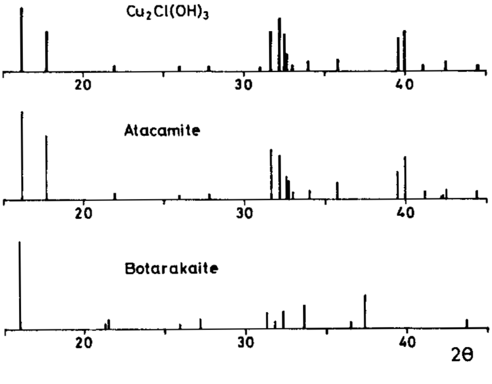

Fig.1 Powder X-ray diffraction of $Cu_2Cl(OH)_3$ (a), atacamite (b) and botarakite (isomer of atacamite) (c).

RESULT

Synthetic $Cu_2Cl(OH)_3$ exhibited the temperature dependence of magnetic susceptibility as Fig. 2, which shows the reciprocal molar magnetic susceptibility corresponding to chemical formula $CuCl_{1/2}(OH)_{3/2}$.

The observed susceptibilities obey Curie-Weiss law $1/x=C/(T-\theta)$ in the two temperature

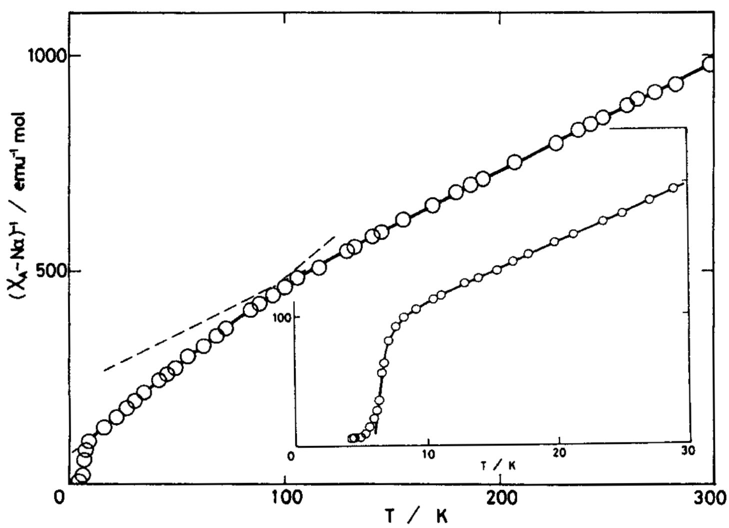

Fig. 2 Reciprocal magnetic susceptibility of $Cu_2Cl(OH)_3$. The solid line shows the susceptibility calculated curve for Heisenberg linear chain model [5](for Cu_{II}) and Curie-weiss model(for Cu_I). The solid line in the inset is theoretical curve for ferrrimagnetic transition.

ranges T ≧ 140K and 15-70K: the Curie-Weiss constant were determined as C_h=0.400 emu K mol^{-1} and θ_h=-93 K for the high temperature range, and C_l=0.24 0 emu K mol^{-1} and θ_l=-18.4 K for the low temperature range. At the temperature range 6-9 K, reciprocal magnetic susceptibilities decrease rapidly.

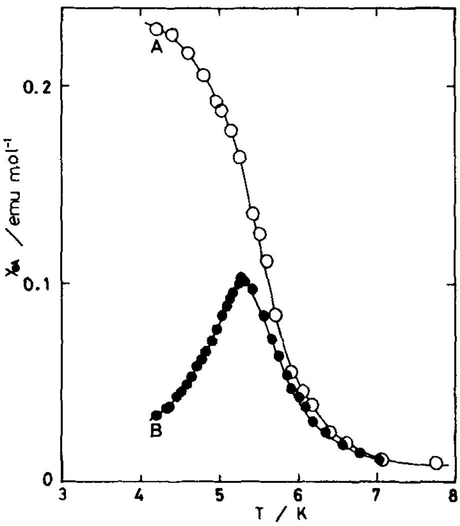

Fig.3 DC magnetic susceptibility. Zero-field-cooled(H=0.4G) susceptibility(●) and field-cooled (H= 20 G) susceptibility(○).

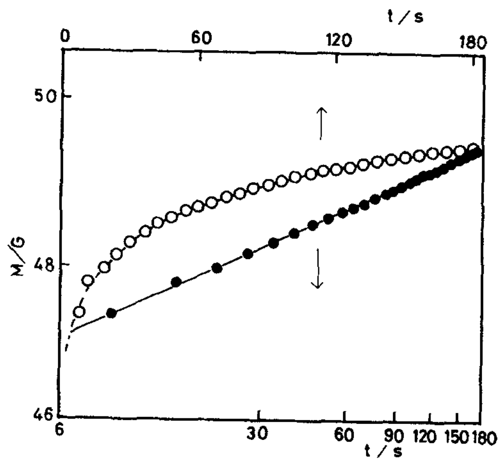

Fig.4The time dependent magnetization of zero-field-cooled sample(at 4.2). ○ : M-t curve, ●: M- ln t curve

Fig. 3 shows the field-cooled (FC) and the zero-field-cooled (ZFC) magnetic susceptibility measured at a DC field of 16 G. The ZFC-magnetic susceptibilities exhibit a sharp peak at 5.3 K, closely similar to that observed for spin glass.

The time dependent magnetization (ΔM), which follows equation 1, is observed at

$$\Delta M/M = C + S \log t \text{ ; } C, S = \text{constant} \qquad (1)$$

low temperature for ZFC magnetization (Fig. 4). The AC magnetic susceptibility x' shows a sharp peak at 5.8 K(Fig. 5), which shifts to higher temperature with increasing AC-field frequency($\Delta \ln T_{max.} / \Delta \ln \nu$ =0.0034)(Inset Fig. 5).

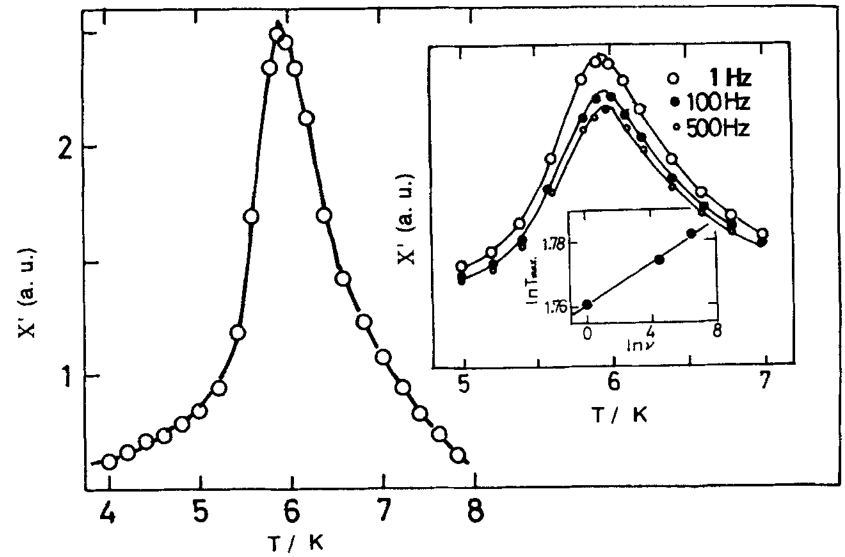

Fig. 5 AC magnetic susceptibility X' (real part) of $Cu_2Cl(OH)_3$.
Inset reveals frequency dependence of cusp.

DISCUSSION

The atacamite, whose crystal structure was reported by Wells[2], has two types of Cu, Cu_I and Cu_{II}, as shown in Fig.6. Judging from the structure, the strongest magnetic interaction, which exists in the OH bridged linear Cu_{II} chain, is responsible for the magnetic behavior in the high temperature range. The experimental data can be reproduced well by Heisenberg linear chain model for Cu_{II} chain and Curie-Weiss model for Cu_I (with J/k=-140 K, C=0.400 emu K mol^{-1}, θ=-12 K).

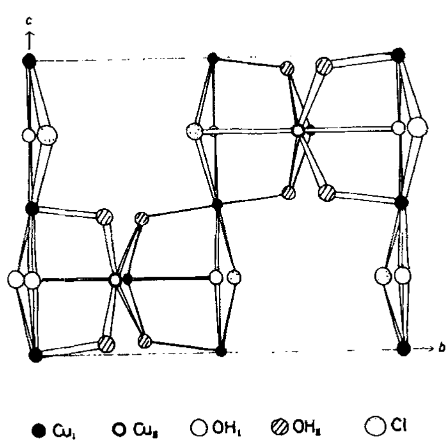

Fig. 6 Crystal structure of atacamite[2].

The magnetic behavior in the temperature range 6-30 K indicates the transition from a paramagnetic state to a ferrimagnetic one. The solid line in the inset of Fig. 2 is theoretical curve for the ferrimagnetic transition[4]. From the crystal structure, a spin arrangement for ferrimagnetic sate is deduced as Fig.7(a). The sharp cusp of ZFC-magnetic susceptibility (Fig. 3), the frequency-dependence of the cusp(Fig. 5), and time-dependence of ZFC-magnetization(Fig. 4) all are the characteristic phenomena observed in spin glass.

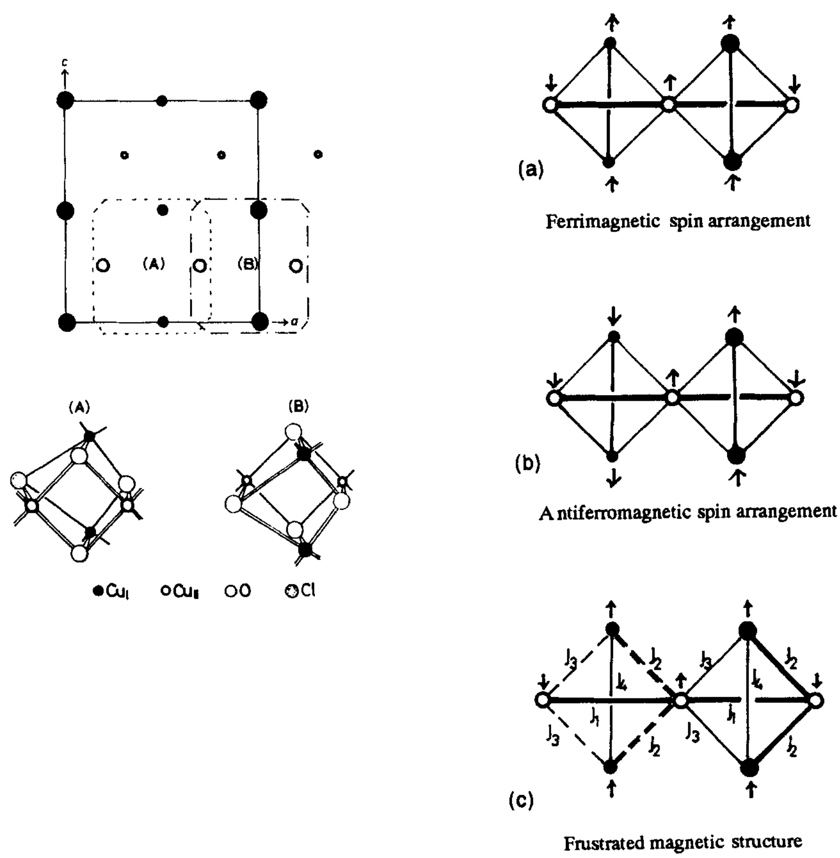

Fig. 7 Ferrimagnetic(a) and antiferromagnetic(b) spin arrangement,and frustrated structure(c).

The antiferromagnetic spin arrangement(Fig. 7(b)) may be more stable than ferrimagnetic one. When the sample is cooled rapidly, the spin may be frozen in the course of transition from ferrimagetic state to antiferromagnetic one. A frustrated magnetic structure is expected from the crystal structure(Fig. 7 (c)).

The mineral atacamite shows the same magnetic behavior as synthetic atacamite in the temperature range T > 15 K, however, does not show spin glass behavior(Fig. 8). A small difference probably exist between synthetic and mineral atacamite crystals (the randomness in synthetic atacamite, and/or the chemical impurities in the mineral).

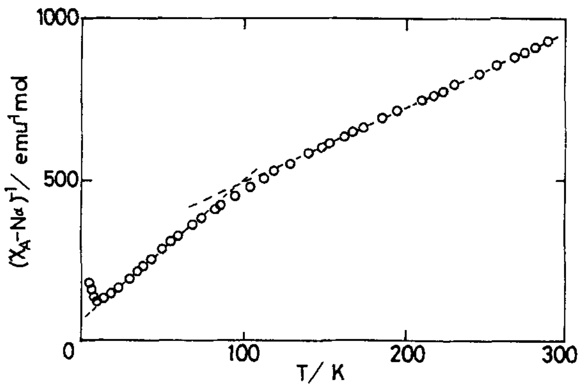

Fig. 8 Reciprocal magnetic susceptibility of mineral atacamite.

We are grateful for the financial support of the Ministry of Education Science and Culture of Japan (Specially Promoted Research No. 06101004).

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