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SYNTHETIC ATACAMITE, $Cu_2Cl(OH)_3$: A SUSPECTED SPIN GLASS BEHAVIOR IN LOW-TEMPERATURE HEAT CAPACITIES

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ABSTRACT

Heat capacities of synthetic atacamite, $Cu_2Cl(OH)_3$, were measured in an adiabatic calorimeter between 4 and 300 K with particular attention to the relaxation phenomenon below 8 K. A suspected spin glass behavior was observed, which was compatible with previous measurements of the magnetic susceptibility.

INTRODUCTION

Recent studies of the magnetic susceptibilities of synthetic atacamite, $Cu_2Cl(OH)_3$, revealed existence of a relaxation phenomenon below 8 K [1] similar to that in spin glasses. Thus, the magnetic susceptibility shows an unusual behavior below 8 K; there is a peak in the susceptibility at about 5.3 K when the crystal is cooled in zero external field and the magnetization was a very slow process following a logarithmic law. On the other hand, if the crystal has been cooled in a weak (~100 G) magnetic field, the susceptibility decreases monotonously as the temperature is raised. Since atacamite is a pure, well defined crystalline material, its glass-like behavior was considered particularly interesting and precision measurements of its heat capacities have been made.

EXPERIMENTAL

The specimen used for the heat capacity measurements was the same as used for magnetic susceptibility measurements; it was synthesized from mixed aqueous solutions of $Cu(HCOO)_2$ and KCl. The powdered sample thus obtained was identified as atacamite by the powder X-ray diffraction. The mass percentages of Cu and Cl were 58.74 (calcd. 59.51) and 16.16 (16.60), respectively, as determined by electro gravimetry, atomic absorption spectrophotometry, and gravimetric analysis. The powdered calorimetric specimen weighing 22.460 g (0.10517 mol) in

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vacuo was loaded into the calorimeter vessel with a small amount of helium gas for heat exchange. The adiabatic calorimeter used for the heat capacity measurements was the same as will be described elsewhere [2]. Platinum (model 8164, Leeds & Northrup Co.) and germanium (model CR-1000, CryoCal Inc.) resistance thermometers were used for the temperature measurements. Their temperature scales are based on the IPTS-68, helium gas thermometry and the 1958 ^{4}He vapor pressure scales [2,3].

RESULTS

The measured heat capacities of atacamite between 4 and 300 K are shown in Fig. 1. Existence of an anomaly below 8 K is evident in Fig. 1; i.e. the heat capacity becomes larger at lower temperatures. Furthermore, the time needed for the attainment of thermal equilibrium within the calorimeter after each energy input became rapidly longer as the temperature was lowered from 1 min above 8 K to about 40 min at 5.9 K and it became impractical, from considerations of uncertainty of the measured heat capacity, to wait for the complete equilibrium

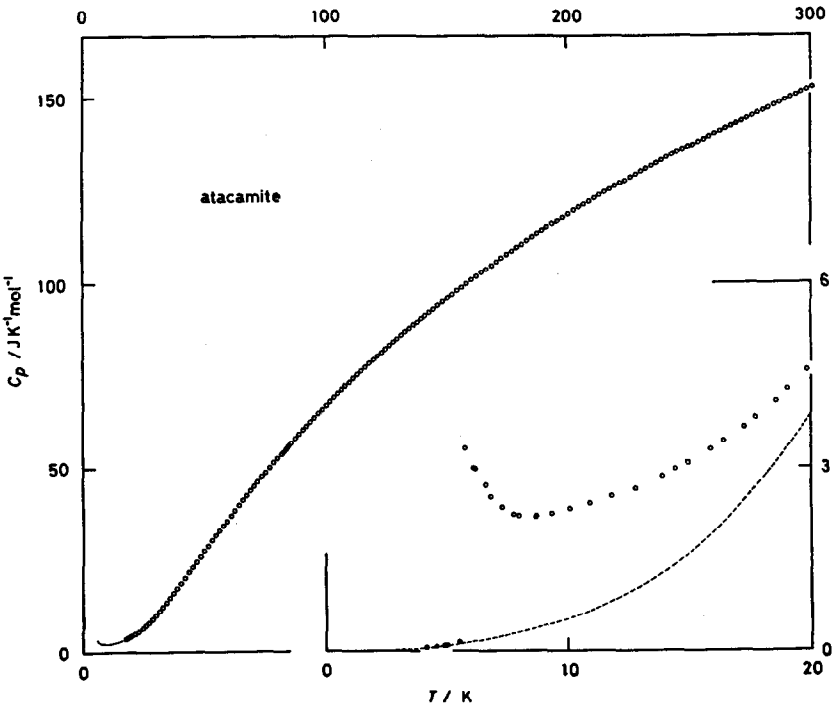

Fig. 1. Measured heat capacities of synthetic atacamite, equilibrium (open circles) and "instantaneous" (closed circles). The broken line shows the estimated lattice heat capacities.

below 5.9 K. The approach of the thermometer reading to a steady drift rate at each temperature was fitted to an exponential function of the form,

$$T - T_\infty = (T_0 - T_\infty)\exp(-t/\tau), \tag{1}$$

to obtain the time constant τ, which was then plotted against $1/T$ in Fig. 2.

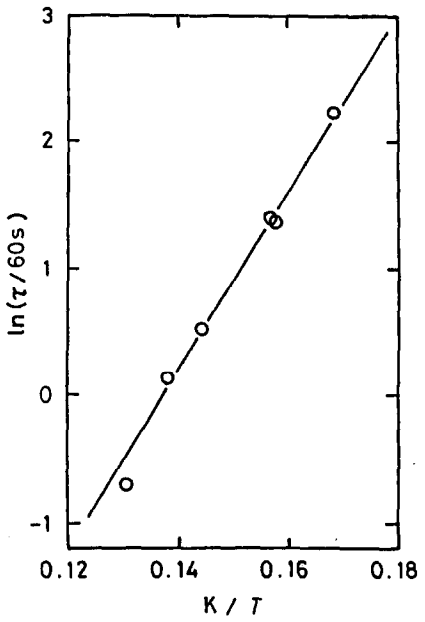

Fig. 2. Arrhenius plot of the relaxation time τ of synthetic atacamite.

The straight line of Fig. 2 gave the activation energy of the process governing this relaxation a value of about 0.6 kJ•mol^{-1}.

Below 5.6 K, we attempted to determine the "instantaneous" heat capacities, which were obtained by ignoring the long time process. These measured points are shown in Fig. 1 by filled circles. Since thermal equilibration in ordinary substances is attained in less than a minute, the "instantaneous" heat capacities of atacamite correspond to the heat capacities of the crystal lattice. The "instantaneous" heat capacities agree with the equilibrium values above 7 K, where τ becomes as short as 1 min. Therefore, the lattice heat capacities were estimated by smooth interpolation between 5.9 K and 30 K using the Debye characteristic temperature 200 K for 6 degrees of freedom per formula unit, and they are drawn in Fig. 1 with the broken line. The entropy gain due to the portion of the excess heat capacities above 5.5 K is 2.4 J•K^{-1}•mol^{-1}, which account for 40 per cent of the expected magnetic entropy (Rln2). It would take an extremely long time to remove all the magnetic entropy through either a phase

transition or Schottky type of anomaly. Therefore, magnetic spins become frozen, from experimental point of view, in the low temperatures. Measurements of the heat capacity in a weak magnetic field did not reveal any difference from those without the applied field.

A total thermal analysis was done with the crystal which had been kept at about 5 K for more than 10 h at a constant rate of energy input while maintaining the adiabatic condition. The result shown in Fig. 3 is interesting in that the temperature recording begins to decrease when it reaches about 8 K. This is considered as another manifestation of the relaxation phenomenon.

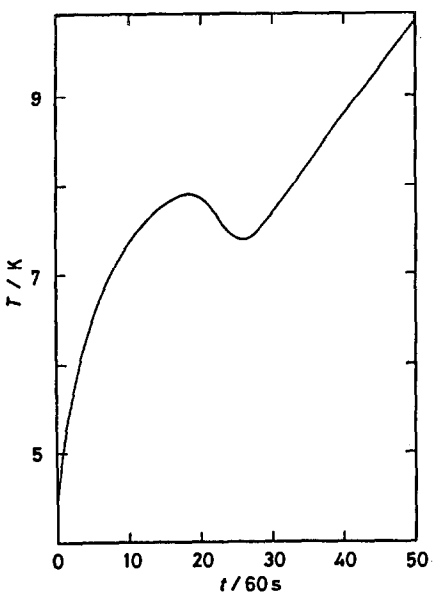

Fig. 3. Temperature records in a continuous heating experiment under the adiabatic conditions.

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