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Article

Drastic and Sharp Change in Color, Shape, and Magnetism in Transition of $CuMoO_4$ Single Crystals

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The change in the chromic, volumetric, and magnetic properties of copper molybdate $CuMoO_4$ by the structural phase transition is tremendous; however, the change is gradual, and its reliable data are lacking for polycrystalline samples, possibly due to a size effect of the constituent crystallites. To investigate intrinsic properties, we used single crystals of the material, which can be considered as a system in a limit of infinite dimension. We found a sudden jump and relatively narrow hysteresis loop in the temperature dependence of magnetization for single crystals. This result indicates that the phase transition is intrinsically sharp and suggests that the supercooling and the superheating become enhanced with decreasing the size of crystallites and that the gradual change of the properties in a polycrystalline sample is caused by the distribution in the size of crystallites. We will also discuss a model for the spin state that is justified quantitatively by the temperature dependence of anisotropic magnetization of single crystals.

Introduction

Copper molybdate $CuMoO_4$ exhibits first-order structural phase transition by the change of temperature or pressure, accompanied by the change of volume and color.[1−3] Possible applications using these properties, such as thermochromic and piezochromic indicators, have been studied extensively.[4] Although fundamental physical properties of the compound have been investigated,[5] reliable intrinsic properties, which are necessary to design applications, have not been obtained so far. It is pointed out that the properties are sensitive to the size of the micro(nano)crystals.[5] To obtain intrinsic properties of the compound, we have investigated the properties of the single crystals of the compound, which can be considered as in a limit of infinite dimension. An investigation of anisotropic properties is another purpose of this study. We have succeeded in the growth of single-crystal ingots with large dimensions, which would be also important for applications. Since the change of the volume of crystals may be applicable for mechanical motion such as actuators, we made an observation on the modification of a crystal with a change of temperature.

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The structural phase transition occurs at $T_c \sim 200-250$ K.[1−3] The phases above and below the transition temperature are called as α- and γ-phases and have colors of yellow-green and red-brown, respectively.[1−3] At the transition from α- to γ-phases, the volume is reduced as large as 13%, and the lattice constants shrink up to ∼7% (largest along the *b* axis).[1−3] On the transition, a change in the environment surrounding the copper cations occurs as shown in Figure 1.[1,2] Whereas the coordination number of oxygen anions surrounding copper cation is five (pyramidal coordination) or six (octahedral coordination) depending on the copper sites in the α-phase, it is always six (octahedral coordination) in the γ-phase. Each pyramid or octahedron in both phases is distorted. The difference of the color of each phase is explained by the change of the charge-transfer gap and the crystal-field transition.[3] In the α-phase, the system consists of isolated clusters with six Cu−O polyhedra connected each other. In the γ-phase, on the other hand, Cu−O polyhedra are connected one-dimensionally. This change of the connection of the polyhedra looks similar to polymerization of molecules. Such a drastic change is the origin of large shrink of the lattice constants. Below the structural phase transition temperature, gradual decrease of the magnetization with hysteresis is reported using polycrystalline samples.[5]

Experimental Methods

The crystal growth of $CuMoO_4$ was performed by the traveling solvent floating zone method. The details of the crystal growth and the characterization of the single crystals are found in Supporting Information. We have obtained the ingots of the

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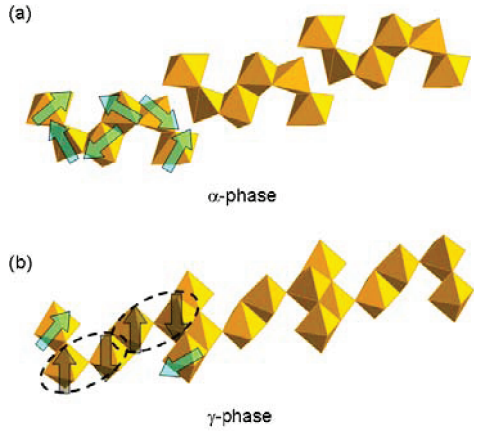

Figure 1. Arrangements of Cu−O polyhedra in $CuMoO_4$ for (a) α- and (b) γ-phases. Cu^{2+} $S = 1/2$ spins are shown schematically by arrows; green arrow depicts free spin and a pair of gray ones a dimerized spin singlet. The structural parameters are taken from refs 6 for (a) and 2 for (b).

single crystals of typical size of 6 mmϕ × 30 mm. The ingots are easily cleaved mechanically. We observed change in color and shape of cleaved single crystals under a microscope with changing temperature.

The measurements of the magnetization were performed using cleaved single crystals. The crystal symmetry is triclinic, and therefore we took field directions that are orthogonal to each other and are not always parallel to the principle crystallographic axes. The measurements were performed with decreasing the temperature from room temperature to $T = 5$ K and then increasing it in the same temperature range. After each measurement, the used crystal was broken into small pieces or powder, so a different crystal was used for each measurement. Such destruction of the sample occurs even if the temperature sweep rate is as slow as 1 K/h. The details of the measurement are described in Supporting Information.

Results and Discussion

Photographs of a cleaved crystal of the size of ∼1 mm at various thermal conditions are shown in Figure 2. The crystals are usually cleaved parallel to the $b-c$ plane, and the longest dimension is along the b axis. The color of the crystal is transparent yellow-green at room temperature as shown in (a). On cooling the crystal below the transition temperature using liquid nitrogen, the color suddenly becomes dark red-brown as shown in (b). The size of the crystal in the longest dimension (parallel to the b axis) shrinks by ∼7%, which reproduces the shrink rate (∼7%) of the b axis lattice constant at the transition.[1,2] On warming the crystal, it becomes mottled with yellow-green and red-brown and then entirely yellow-green, as shown in (c) and (d), respectively. The crystal becomes broken into small pieces by the sudden thermal expansion at the transition temperature. From this result, applications for mechanical purposes seem difficult, and a proper thermal gradient inside a crystal may be necessary to avoid such destruction. The thermochromic property observed in polycrystalline samples is reproduced and rather sharpened in single crystals.

The temperature dependence of the anisotropic magnetization at several fields is shown in Figure 3.

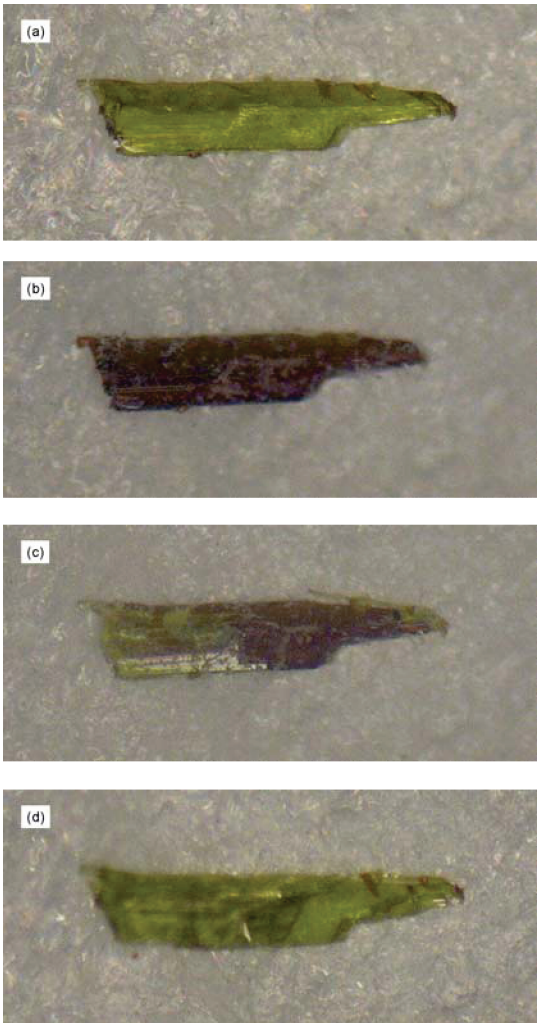

Figure 2. Change in color and shape of a cleaved single crystal $CuMoO_4$ of a length of ∼1 mm by the temperature change. The magnification of a microscope was kept constant. (a) The sample at room temperature at the beginning. (b) The sample cooled down using liquid nitrogen below the transition temperature. (c) The sample at around the transition temperature on warming. (d) The sample whose temperature is raised to room temperature.

A hysteresis is observed, where the magnetization jumps suddenly at 210 K on cooling and at 260 K on warming. This hysteresis with supercooling and superheating supports that the transition is of the first order. The transition temperature does not depend on the magnitude and the direction of the field. The sudden magnetization jump indicates that the transition is intrinsically sharp. The hysteresis loop (the width of ∼50 K) is narrower than that of a polycrystalline sample (the width of ∼100 K),[5] suggesting that the supercooling and the superheating become enhanced with decreasing the size of crystallites. Such a wide hysteresis loop looks similar to that of the solid−liquid transition of Ge on decreasing the size of crystals, where the surface energy and the kinetics of the nucleation play an important role.[7] Since a polycrystalline

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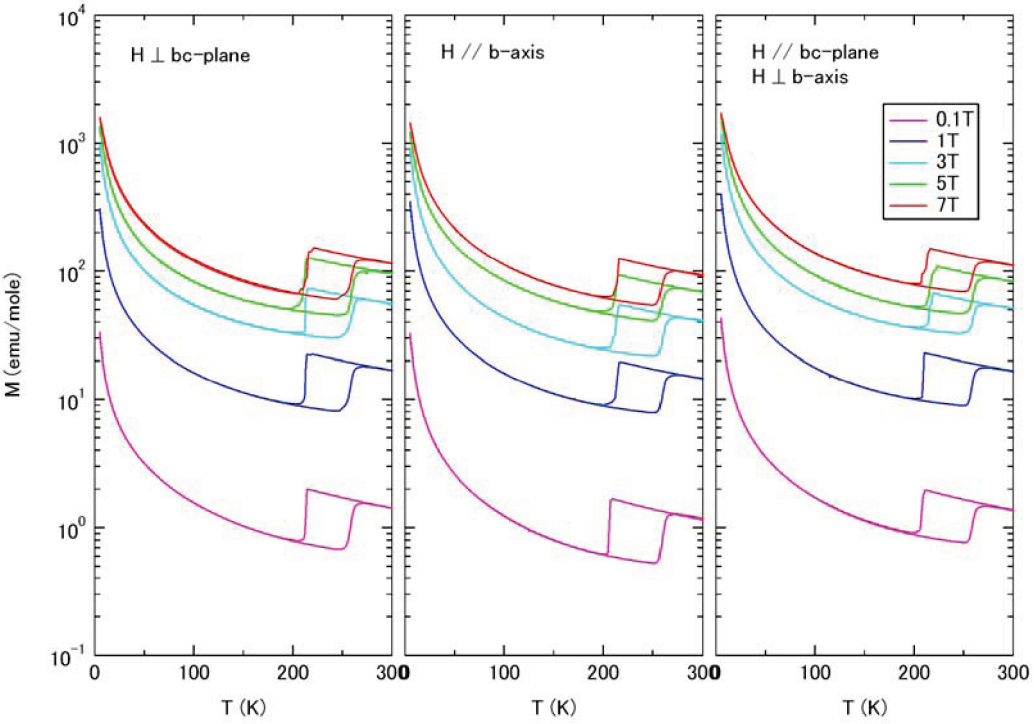

Figure 3. Temperature dependence of magnetization of cleaved $CuMoO_4$ single crystals for three field directions.

sample consists of crystallites with widely distributed size, they show successive phase transitions and therefore the change of magnetization would become gradual. It is also suggested that crystallites with the size smaller than a critical dimension may lose the phase transition.[5] In a single crystal sample, on the other hand, the transition occurs simultaneously and sharply. Even for a single crystal sample, multiple steps caused by successive transitions are sometimes observed on cooling, possibly due to the creation of domains by cracking. On warming, the transition width becomes broader, which is consistent with the crystal breaking into small pieces, as shown in Figure 2d.

The temperature dependence of the magnetization is nearly isotropic, and the magnetization is linear in the magnetic field, which indicates that the decrease in the magnetization below the transition temperature is not due to antiferromagnetic ordering. The temperature dependence of the magnetization nearly obeys the Curie law and free spins contribute to the magnetization both above and below the transition temperature. These results indicate that the jump in the magnetization curve is due to partial quench of nearly free spins. Deviation from the Curie law is observed at high fields and low temperatures as shown clearly in Figure S2 (Supporting Information), possibly originating from the moment saturation. To avoid the effects of the deviation, the magnetization curves at $H = 0.1$ T for three field directions were fitted with the Curie−Weiss law, $\chi = M/H = C/(T - \theta) + \chi_0$ with $C = Ng^2\mu_B{}^2S(S + 1)/3k_B$, where C is Curie constant, θ Weiss temperature, χ_0 sum of constant terms like the diamagnetism of the closed shell, N number of spins, g g-factor, μ_B Bohr magneton, S spin quantum number, and k_B Boltzmann constant. Since the g-factor is estimated to be 2.10 from the ESR measurements of the polycrystalline sample below the transition temperature[8] and $S = 1/2$ for the Cu^{2+} ion, the Curie constant for the contribution of all Cu spins, C_{all}, is 0.413 emu/Cu mol K. The obtained fitting parameters are summarized in Table S1 (Supporting Information). The Curie constant C shows that nearly all the spins are free in the α-phase and nearly 1/3 of the spins are free in the γ-phase. The Curie constant in the γ-phase for our single crystal samples is much smaller than that for a polycrystalline sample.[5] The Weiss temperature θ is ~ -10 K (antiferromagnetic) in the α-phase and $\sim$1 K (ferromagnetic, but weak) in the γ-phase. The constant term χ_0 is negligibly small in both phases.

Let us discuss the relationship between the magnetic properties and the magnetic interactions expected from the crystal structures. We only consider the superexchange interactions through Cu−O−Cu paths (of the order of 1000 K for corner sharing and 100 K for edge sharing) and ignore the supersuperexchange interactions through Cu−O−O−Cu paths (of the order of 10K).[9] In the α-phase, all the polyhedra are connected by edge sharing, where the magnetic interaction between Cu ions is relatively weak.[9] All the spins are likely nearly free. Cu−O−Cu bond angles listed in Figure S3a (Supporting Information) are in the range between 91.6 and 106.0°.

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It is shown that the magnetic interaction between Cu ions for the Cu−O−Cu bond angle below and above ~94° is ferromagnetic and antiferromagnetic, respectively.[9] Negative Weiss temperature suggests that antiferromagnetic interactions overcome ferromagnetic ones in the α-phase. In the γ-phase, corner sharing appears between Cu(2) and Cu(3) polyhedra. (See the definition of Cu sites in Figure S3, Supporting Information.) The magnetic interaction between Cu ions in corner-shared polyhedra is much stronger than that in edge-shared ones.[9] Therefore, adjacent Cu(2) and Cu(3) spins are connected by strong antiferromagnetic interaction and likely become a spin singlet state, as is pointed out by Thiry et al.[5] The remaining Cu(1) spin would be left nearly free and isolated, which is consistent with very small Weiss temperature. Schematic pictures of spin states are shown in Figure 1. Our experimental results using single crystals have justified this model quantitatively for the first time.

Conclusion

We have successfully fabricated $CuMoO_4$ single-crystal ingots and clarified their intrinsic physical properties in a limit of infinite dimension, which are reliable and reproducible. With lowering the temperature across the transition, the crystal shrinks as large as ~7% along the *b* axis direction. However, the large change of the lattice destroys the crystals themselves. The color of $CuMoO_4$ changes from yellow-green in the α-phase to red-brown in the γ-phase. The temperature dependence of the magnetization for each field direction shows a sharp jump at the transition temperature, which is different from gradual change observed in polycrystalline samples, possibly originating from the distribution of crystallite size. It obeys the Curie−Weiss law in both the α- and the γ-phases. The values of the Curie constant, as well as no anisotropy in the magnetization, quantitatively show that 2/3 of the nearly free Cu^{2+} $S = 1/2$ spins in the α-phase are dimerized into the spin singlet state in the γ-phase, which is consistent with the magnetic interactions expected from the crystal structures.

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Supporting Information Available: Experimental section, Table S1, and Figures S1, S2, and S3 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.