Growth of (CH$_3$)$_2$NH$_2$CuCl$_3$ single crystals using evaporation method with different temperatures and solvents

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Abstract

The bulk single crystals of of low-dimensional magnet (CH$_3$)$_2$NH$_2$CuCl$_3$ (DMACuCl$_3$ or MCCL) are grown by a slow evaporation method with different kinds of solvents, different degrees of super-saturation of solution and different temperatures of solution, respectively. Among three kinds of solvent, methanol, alcohol and water, alcohol is found to be the best one for growing MCCL crystals because of its structural similarity to the raw materials and suitable evaporation rate. The best growth temperature is in the vicinity of 35 °C. The problem of the crystals deliquescing in air has been solved through recrystallization process. The crystals are characterized by means of x-ray diffraction, specific heat and magnetic susceptibility.

Keywords:
A1. X-ray diffraction, A1. Recrystallization, A2. Growth temperature, A2. Solvent
1. Introduction

Catena (dimethylammonium-bis(µ₂-chloro)-chlorocuprate) ($\text{CH}_3\text{2NH}_2\text{CuCl}_3$ (DMACuCl$_3$ or MCCL) is an organic-metallic magnetic material with quasi-one-dimensional alternating antiferromagnetic-ferromagnetic (AFM-FM) Heisenberg chain ($S = 1/2$). MCCL is very interesting in the regard that it has a rather complex $H-T$ phase diagram and multiple magnetic-field-induced phase transitions. Willett first proposed that Cu$^{2+}$ ions ($S = 1/2$) coupled via Cu-halide-Cu bridges to form magnetic chains along the crystallographic $a$ axis, but Stone et al. recently found that there was a significant dispersion along the $b$ axis by inelastic neutron scattering, indicating that the $b$ axis is the one-dimensional magnetic axis [1, 2, 3, 4]. It is found that the magnetization shows a 1/2 plateau, corresponding to a field-induced gapped state, with magnetic field range from 2 to 3.5 T [5]. There are a spontaneous AFM ordering and a field-induced one below and above the plateau, respectively [6, 7]. It would be very useful for studying the mechanisms of these magnetic transitions if one can get high-quality single crystals of MCCL.

A slow evaporation method using water, methanol or alcohol as a solvent was originally introduced in 1960’s to grow MCCL crystals [1]. Recently, several groups also obtained MCCL crystals, including the deuterated crystals, by using Willett’s method [2, 3, 5, 6, 7]. However, the conditions of the crystal growth, the sizes and the quality of the obtained crystals are not clearly mentioned in these papers. It is therefore still important to investigate the appropriate growth procedure. In this work, we report a detailed study on the MCCL crystal growth using this method. It is found that the MCCL single crystals can be synthesized in different kinds of solvents, including methanol, alcohol and water. The sizes and the shapes of the crystals, however, are dependent not only on the type of solvent but also on the degree of super-saturation of solution and the growing temperature. The biggest crystal with size of $12 \times 7 \times 4 \text{ mm}^3$ is obtained from 100 ml alcohol solution (containing raw materials of 15 mmol CuCl$_2$·2H$_2$O and 15 mmol ($\text{CH}_3\text{2NH}_2\text{Cl}$) at 35 °C. A common problem of the crystal deliquescing in air can be overcome by using a recrystallization process.
2. Crystal Growth

(CH$_3$)$_2$NH$_2$Cl and CuCl$_2$·2H$_2$O in the molar ratio 1:1 are used as the starting materials for synthesizing MCCL. The chemical reaction formula between the two raw materials is

$$(\text{CH}_3)_2\text{NH}_2\text{Cl} + \text{CuCl}_2\cdot2\text{H}_2\text{O} \rightarrow (\text{CH}_3)_2\text{NH}_2\text{CuCl}_3 + \text{H}_2\text{O}.$$ 

At first, 15 mmol CuCl$_2$·2H$_2$O is dissolved in a selected solvent (methanol, water or alcohol) at different temperatures. Then, the same mole amount of (CH$_3$)$_2$NH$_2$Cl is added to the solution slowly with continuously stirring. Keeping the solution in the super-saturation state, then the crystals can grow gradually with the solution continuously evaporating.

We study the influence of the temperature on the crystal growth under the condition that both the amount of raw material and the degree of super-saturation solution are invariant. The volumes of solvents are chosen to be 150 ml. For aqueous solvent, the solution evaporates too fast to form single crystals at temperatures above 50 °C, while we can obtain shining tiny slice-like crystals and big crystals with thin smooth surface at 35 °C and 20 °C, respectively. In addition, the solution at 20 °C evaporates very slowly and it takes a very long time (about three months) to get crystals. These results are listed in Table 1. The similar investigations and results by using alcohol as the solvent are given in Table 2. There are no crystals at temperatures above 40 °C; while many high-quality single crystals with typical size of (3–7)×(2–3)×(2–4) mm$^3$ can be obtained after one week at 35 ± 2 °C. If we keep the growing temperature at 20 °C, the obtained crystals have considerably big sizes but poor quality, checked by the x-ray diffraction (XRD). For methanol solvent, there are no any high-quality single crystals though we make many attempts, see results in Table 3. From the above, there is notable difference among the results of three solvents at the same growth temperatures. The main reason is that the ability of crystal growth may strongly depend on the similarity of structure between the solute and the solvent. Another possible reason is that the different solvent molecules have different adsorption choices to the faces of the crystals, leading to different growth rates of the crystallographic planes and consequently forming different shapes of the crystals [8, 9, 10]. Moreover, the growth temperatures have significant effect on the quality and shape of crystals even in the same solvent. Figure
1 shows the shapes of MCCL crystals grown at different temperatures in alcohol. The temperature can be considered as an activation energy to affect the processes of the crystal growth, which is either a pure surface reaction process or a pure diffusion process. In general, the surface reaction of the crystallization process plays the main role at low temperature. When the temperature rises, the growth rate becomes faster and the diffusion process will gradually dominate the growth of the crystals. The crystals grown at an appropriate higher temperature usually has better quality than those grown at low temperature (but too high temperature causes too fast evaporation to generate crystals), because the driving force of the crystallization, which is the ability of crystallized particles rejecting impurities, is enhanced with increasing temperature [11]. Generally, the sample has a flat irregular shape and normally grows with the (110), (011) and (001) planes developed. The largest crystal face is the (110) plane.

One problem we meet is that the MCCL single crystals deliquesce in air so easily that they can completely be destroyed after keeping in air for two days, which makes both the sample preservation and the measurement very difficult. We adopt the following method to solve this problem. After the first-run growth is nearly finished, the same amount of solvent is added to the beaker, which contains the crystals. The solution is kept at the same condition and then the crystals are partially dissolved and re-crystallized. The re-crystallized single crystals have the similar shapes to those from the first run but do not deliquesce any more. It is likely that the purity of the synthesized crystals can be improved by the recrystallization process.

The different degree of super-saturation of the solution also affects the crystal quality. As shown in Fig. 2, the ratio of 15 mmol raw materials to 80 ml alcohol makes the solution at an unstable super-saturated state and can not form good crystals. From the solution of 15 mmol raw materials dissolved into 100 ml alcohol, the obtained crystals are very large and the biggest one reaches 230 mg. However, the crystal size becomes smaller with further reducing the degree of super-saturation, as shown in Fig. 2(c). This result indicates that the initial concentration of the solution is very important in determining the crystals formation and their growth.
To sum up, we compare the results of the crystal growth from different types of solvent, different temperatures of solution and different degrees of super-saturation solution, respectively. We obtain the best crystal growth condition: prepare a super-saturated solution with the ratio of 1 mmol raw materials to 10 ml solvent and grow crystals by continuously evaporating the solution at 35 °C. The alcohol is a much better solvent than water and methanol.

3. Structural characterization

Figure 3(a) shows the x-ray powder diffraction pattern for the crystals we obtained from the best growing procedure discussed above. The data are consistent with the monoclinic structure (space group I2/a) with lattice parameters $a = 11.97$ Å, $b = 8.6258$ Å, $c = 14.34$ Å, and $\beta = 97.47^\circ$ [3]. Figure 3(b) shows a rocking curve of (002) diffraction for a selected single crystals. The peak is very narrow with the full width at half maximum of 0.07°, indicating a high quality of this sample.

4. Magnetic susceptibility and specific heat

Figure 4 shows the temperature dependence of magnetic susceptibility measured in 4 T magnetic field perpendicular to the $ab$ plane using a SQUID-VSM (Quantum Design). The susceptibility increases monotonically with decreasing temperature, showing a Curie-like behavior [12]. There is no magnetic transition down to 2 K, which is consistent with the former studies.

Specific heat is measured by the Physical Property Measurement System (PPMS, Quantum Design). Figures 5(a), 5(b) and 5(c) show the effects of magnetic field on $C(T)$ for three characteristic field ranges, which are separated by the 1/2 magnetization plateau. In general, all these data are consistent with those in a former report [7]. The temperature dependence of the specific heat at low field has a well-defined peak in the low temperature regime, as shown in Fig. 5(a). In zero field, there is a sharp peak at the Néel transition temperature $T_N = 0.8$ K. The height of the peak decreases gradually with increasing field, indicating the
suppression of AFM ordering by the external field. The peak disappears completely in the 1/2-plateau field range (2–3.5 T), as shown in Fig. 5(b), suggesting a transition from the AFM magnetic ordering into the field-induced gapped state. When the field is above 3.5 T, another peak appears and increases rapidly with increasing field, as shown in Fig. 5(c), indicating that the spin gap is closed and the system turns into the field-induced magnetic ordering state. All such peculiarities originate most likely from the interplay between the coexisting FM and AFM dimers [4, 5, 6, 7].

Therefore, both the magnetic susceptibility and the specific heat measurements of our MCCL single crystals are essentially same as those reported in earlier papers [4, 5, 6, 7], in which these physical properties have already been discussed in details. In this regard, the quality of our crystals are also confirmed and it is possible to carry out more experimental investigations, like low-temperature heat transport measurements, by using these high-quality crystals.

5. CONCLUSIONS

MCCL single crystals are grown at different temperatures in alcohol, aqueous and methanol solutions, respectively. The most appropriate condition for MCCL crystal growth is starting from a super-saturation solution with ratio of 1 mmol each raw material to 10 ml alcohol solvent and keeping the growth temperature at 35 °C. The problem of the crystals deliquescing is solved by recrystallization method. The x-ray diffraction data indicate single phase and good crystallinity of the obtained crystals. The magnetization measurement confirms the absence of magnetic ordering above 2 K, while the specific heat measurements at very low temperatures and in high magnetic fields demonstrate the low-field AF ordering, the field-induced spin gapped state and the field-induced magnetic ordering upon increasing field.

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Figure 1: The crystals grown at different temperatures in alcohol. They have very different shapes. In panel (a), the irregular crystal has four bright planes and good quality. In panel (b), the flat crystal has a big shining plane but poor quality.
Figure 2: Crystals grown from alcohol solvent at 35 °C with different amounts of solvent. 15 mmol of each raw material is dissolved in 80 ml, 100 ml and 150 ml alcohol, respectively.
Figure 3: (a) X-ray powder diffraction pattern. (b) Rocking curve of (002) peak for a piece of single MCCL crystal.
Figure 4: Temperature dependence of magnetic susceptibility measured in 4 T magnetic field perpendicular to the $ab$ plane.
Figure 5: Specific heat of MCCL crystal as a function of temperature for magnetic field applied perpendicular to the $ab$ plane.
Table 1: Results for different growth temperatures in 150 ml solvent of water.

| Temperature | Crystal State                          |
|-------------|----------------------------------------|
| 20 °C       | big bright pieces, size about (5–9)×(3–5) mm² |
| 35 °C       | bright tiny slice                      |
| 40 °C       | none                                   |
| 50 °C       | none                                   |
Table 2: Results for different growth temperatures in 150 ml solvent of alcohol.

| Temperature | Crystal State                          |
|-------------|---------------------------------------|
| 20 °C       | flat crystal, but poor quality        |
| 35 °C       | high quality crystals, size about (3–7)×(2–3)×(2–4) mm³ |
| 40 °C       | none                                  |
| 50 °C       | none                                  |
Table 3: Results for different growth temperatures and different volumes for methanol solvent. The amount of starting raw materials is 15 mmol.

| Volume | Temperature | Crystal State                                      |
|--------|-------------|----------------------------------------------------|
| 60 ml  | 20 °C       | thin bright pieces, size about (4–7)×(2–3) mm²   |
| 70 ml  | 20 °C       | small crystals, size is (0.5–2)×(0.3–1)×(0.1–0.8) mm³ |
| 150 ml | 20 °C       | bright thin pieces, size about 5×4 mm²             |
| 150 ml | 35 °C       | none                                              |
| 150 ml | 35 °C       | none                                              |
| 150 ml | 40 °C       | none                                              |
| 150 ml | 50 °C       | none                                              |