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Effect of magnetic field on the spin-Peierls transition in single-crystal CuGeO*

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This paper reports that high quality $CuGeO_3$ single crystals were successfully grown by floating-zone technique and the magnetic property was studied. The temperature dependence of magnetic susceptibility below the spin-Peierls (SP) transition temperature (T_{sp}) under magnetic fields applying along both the *a*- and *c*-axis direction can be fitted well by a model of noninteracting dimmers. The spin gap derived from the fitting is consistent with other reports. There is a very weak anisotropy in the fitting parameters for different directions, which should be expected from a SP system. A small upturn in susceptibility at low temperature due to paramagnetic impurities and/or defects can be observed. A suppression of the upturn by magnetic field is first discovered in this system and the possible origins for this suppression are discussed.

Keywords: spin chain, spin–Peierls transition, spin dimmer, magnetic susceptibility
PACC: 7530F, 7530E, 7510J

1. Introduction

Low-dimensional spin systems have many interesting behaviours, such as spin density waves (SDW), charge density waves (CDW) and spin-Peierls (SP) transition. SP transition was first confirmed experimentally in organic materials.[1,2] Gemanate $CuGeO_3$ is the first inorganic material which exhibits the SP transition.[3] The discovery of SP transition in this inorganic material extends the research from organic to inorganic materials and shows that SP transition is a quite universal feature in spin-chain compounds. The magnetic property of SP systems is usually described by the one-dimensional Heisenberg model of antiferromagnetic (AFM) spin chains.[4] Some models also include anisotropic exchange interactions such as Dzyaloshinskii–Moriya interactions.[5]

The gemanate $CuGeO_3$ has an orthorhombic structure of space group Pbmm. The lattice parameters are $a = 0.481\,\text{nm}$, $b = 0.843\,\text{nm}$, and $c = 0.295\,\text{nm}$. The Cu–O spin chain is along the *c*-axis, which is separated by the Ge–O chain, and the SP transition mainly happens in the Cu–O spin chains. The adjacent Cu^{2+} ions are coupled through two O^{2-} ions and AFM interaction between spins of Cu^{2+} is proposed.[3,6] A sharp drop in the magnetic susceptibility has been observed when temperature is lower than T_{sp} of about 14 K.[3] The main difference between SDW and AFM ordering is that there is an easy-axis for magnetic moments in AFM ordering state. Thus the measurement of magnetic properties under different magnetic field directions is a good experimental method to distinguish SDW from AFM ordering. However such studies were mainly performed in polycrystalline samples in previous reports and a systematic study on the effect of magnetic fields on SP transition along different principal axes of single-crystal samples is still required. The comparison of the experimental data of $M(T, H)$ with the current theoretic models of spin dimmer state is also poor.[6]

In this paper, we report a systematic study on the magnetic properties of high quality $CuGeO_3$ single crystals grown by the optical floating-zone furnace. We found that the temperature dependence of magnetic susceptibility in the spin-Peierls state can be fitted well by a model of noninteracting dimmers. A suppression of the upturns in the magnetic susceptibility at low temperature by applied magnetic field is

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first discovered and the possible origins are discussed.

2. Experimental

The $CuGeO_3$ single crystals were grown by the floating-zone optical image furnace. First, the GeO_2(4N) and CuO (4N) powders were mixed thoroughly with the ball mill. Next, the well-mixed powders were heated at 850°C for 24 hours in air. Then, the reacted powders were re-grounded with the ball mill, and heated at 950°C in flowing O_2 for 24 hours. This procedure was repeated several times until the pure single phase was obtained. After re-grounding, the powders were filled in a rubber tube and were pressed into a cylindrical rod with the length of about 110 mm and the diameter of about 7 mm under 70 MPa pressure. The rod was annealed in a vertical furnace in flowing O_2 environment at 950°C for 24 hours. A part with a length of 20 mm of the rod was cut off as the seed rod during the crystal growing. The growth rate was 0.6 m/h in the flowing O_2 environment.

The structure of the powder samples and single crystals was measured by room-temperature x-ray diffraction (XRD). The magnetic properties were measured on a Quantum Design MPMS-5 SQUID magnetometer. The large size single crystals grown in this work make it possible to perform high resolution magnetic measurements with magnetic field applying along the three principal axes of the crystalline samples.

3. Result and discussions

The grown single-crystal rod of $CuGeO_3$ is blue and transparent. Its cross-section has an elliptical shape and the a-axis is almost along the growth axis. It is easy to cleave along the (100) plane. The long axis of the ellipse is along the c-axis direction (the spin-chain direction) and the short axis is along the b-axis direction. The XRD pattern of a cleaved crystal is shown in Fig.1, and a XRD pattern of the powder sample is shown in the inset of Fig.1. As seen in Fig.1, the sharp (l00) peaks in the XRD pattern indicate that the crystal is well orientated. The lattice constants are $a = 0.4803$ nm, $b = 0.8426$ nm, $c = 0.2946$ nm, according to the powder XRD patterns, which are consistent with previous reports.[6]

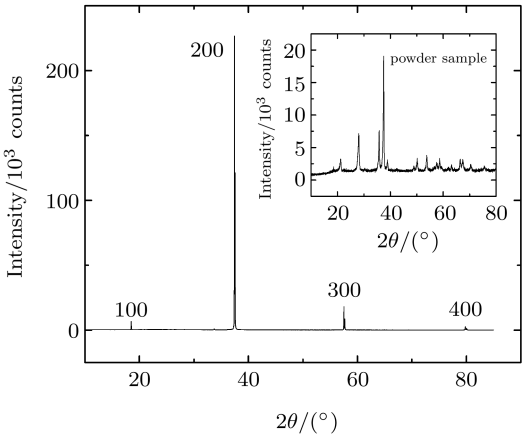


Fig.1. The XRD pattern of a cleaved single crystal. Inset: the XRD pattern of the powder sample.

Figure 2 shows the temperature dependence of magnetic susceptibility, $\chi(T)$, as the magnetic field, $\mu_0 H$ of 0.1 T, is applied along the a-, b-, and c-axis direction respectively. The inset shows the effect of magnetic field on the transition temperature T_{sp} (see below). The magnetic susceptibilities have similar temperature dependence for the three principal axes. There exists a broad peak around T_m of about 60 K and a sharp decrease near $T_{sp}(0)$ of 14 K. The sharp decrease near 14 K is caused by the SP transition.[3,6] The weak anisotropy in the temperature dependence of magnetic susceptibility for the three principal axes indicates that the magnetism of this compound can be described by a Heisenberg model.[3] A remarkable feature in the susceptibility $\chi(T)$ above T_{sp} is that there exists a maximum around $T_m \sim 60$ K. Such a maximum in $\chi(T)$ is expected in low-dimensional

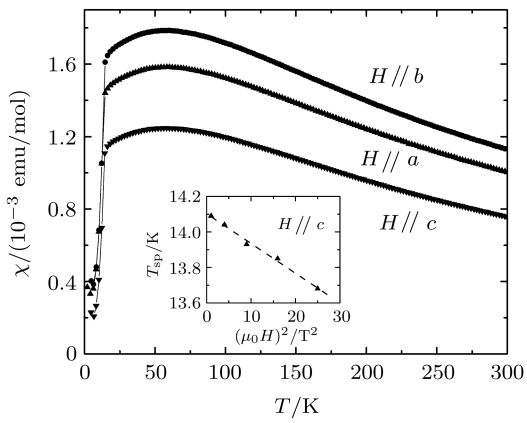


Fig.2. The temperature dependence of magnetic susceptibility of a $CuGeO_3$ crystal. A magnetic field, $\mu_0 H$ of 0.1 T, is applied along the a-, b-, and c-axis direction respectively. Inset: plot of $T_{sp}(H)$ vs $(\mu_0 H)^2$. The solid triangles are the experimental data, and the dash line is the fitting line according to the Eq.(1).

Heisenberg AFM spin system by theoretic models.[7] However, the agreement between the experimental $\chi(T)$ data and the theoretic prediction made by Bonner and Fisher based on the uniform Heisenberg AF linear chains is rather poor.[3] Castilla *et al* have pointed out that competing nearest-neighbour (NN) (J_1) and next-nearest-neighbour (NNN) interactions (J_2) play an important role in $CuGeO_3$.[4] They have shown that the maximum behaviour in the susceptibility above T_{sp} can be well described by the Heisenberg model with a competing interaction with the ratio of $J_2/J_1 \approx 0.24$.

It is well established that the sharp drop of magnetic susceptibility below T_{sp} of 14 K results from the SP transition and therefore $CuGeO_3$ is a good example of inorganic SP system.[6] The change of T_{sp} with the magnetic field H can be well described by the equation:

$$T_{sp}(H) = T_{sp}(0)\left[1 - \alpha\left(\frac{\mu_B \mu_0 H}{k_B T_{sp}(0)}\right)^2\right], \qquad (1)$$

where μ_B is the Bohr magneton and k_B is the Boltzmann constant. This equation is predicted by the Hartree–Fock theory of Bulavevskii, Buzdin, and Khomaskii (BBK)[8] and also by the Luther–Peschel-type treatment of the spin-correlation functions of Cross.[9] The coefficient α derived by fitting to the experimental data of $T_{sp}(H)$ with this equation is about 0.5 as shown in the inset of Fig.2 for the $H//c$ case, more consistent with the BBK theory.[8] Bulavevskii[10] also calculated the temperature dependence of susceptibility $\chi(T)$ in spin dimmer state based on the Heisenberg model of AFM linear chains with temperature-independent alternating J. Although the theoretic curve of this model can describe the basic feature of $\chi(T)$, the discrepancy between the theoretic curve and experimental data is obvious, especially for the temperature range close to T_{sp}.[6]

We have performed careful measurements of the magnetic susceptibility in the SP state for both $H//a$ and $H//c$ of $CuGeO_3$ single crystal. Figure 3 shows the temperature dependence of susceptibility measured

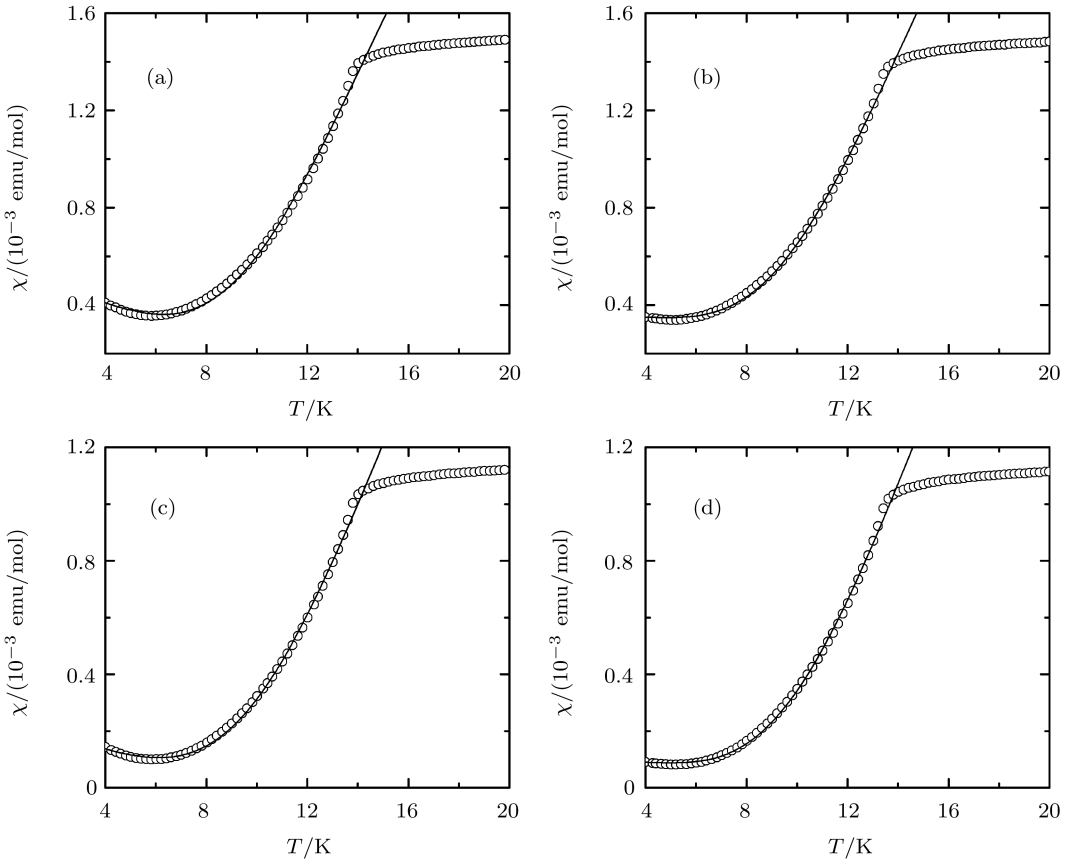


Fig.3. The magnetic susceptibility versus temperature under different magnetic fields in the temperature range between 4–20 K. (a) $\mu_0 H//a$, 1 T; (b) $\mu_0 H//a$, 5 T; (c) $\mu_0 H//c$, 1 T; (d) $\mu_0 H//c$, 5 T. The solid lines are the fitting curves based on the model of noninteracting dimmers (see text).

under $\mu_0 H$ of 1 T and 5 T along the a- and c-axis respectively. As we mentioned aforetime in this paper, the sharp drop in $\chi(T)$ below T_{sp} cannot be described quantitatively by the BBK theory. Another feature is that there is an obvious upturn in $\chi(T)$ at the low temperature ($T < 7$ K) no matter which direction the magnetic field is applying. Such an upturn has also been observed in the organic chain compounds and it has been interpreted as the Curie–Weiss term from the randomly distributed paramagnetic impurities and/or defects which do not form the spin dimmers.[11] Furthermore, it can be easily found by comparing Fig.3(a) with Fig.3(b), and Fig.3(c) with Fig.3(d), that the upturn is significantly suppressed under magnetic field $\mu_0 H$ of 5 T. Such a suppression of the Curie–Weiss term by strong magnetic field is first observed in this spin chain compound. We will discuss this magnetic effect thereafter.

Matsuda and Katsumata[12] reported that the spin-chain part of the magnetic susceptibility in the spin dimmer state of $Sr_{14}Cu_{24}O_{41}$ can be well described by a model of noninteracting spin dimmers. According to this model, the temperature dependence of susceptibility is given by the equation:

$$\chi = \frac{Ng^2\mu_B}{k_B T} \cdot \frac{1}{3 + \exp(2J/k_B T)}, \qquad (2)$$

where N is related to the number of spin dimmers, μ_B is the Bohr magneton, and J is the exchange interaction between nearest-neighbour Cu moments. In the case of $Sr_{14}Cu_{24}O_{41}$, there are spin chains and spin ladders, and the spin dimerization is claimed to occur in the spin chains. There is no observation of SP transition from the structure, magnetic, and specific heat measurements in this system.[12,13] In the case of $CuGeO_3$, there is a clear structure distortion around T_{sp}, and it is well established that the SP transition leads to the structure distortion and spin dimerization.[3,6] However, there should be some universal features related to the spin dimmer state in different compounds. Indeed, we found that the $\chi(T)$ of $CuGeO_3$ can be fitted well by the Eq.(2). In order to include the low temperature Curie–Weiss term, we use the following equation to fit our $\chi(T)$ data below T_{sp}:

$$\chi = \frac{C}{T-\theta} + \frac{C_1}{T} \cdot \frac{1}{3 + \exp(2J/(k_B T))}, \qquad (3)$$

where $C = \frac{N_A \mu_{eff}^2}{3k_B}$, and $C_1 = \frac{Ng^2\mu_B^2}{k_B}$. N_A is the Avogadro's number. Because the core diamagnetic susceptibility is usually as small as -10^{-5} emu/mol, it is neglected in the fitting procedure. From Fig.3, we can find that the Eq.(3) fits the experimental data very well regarding the direction of the magnetic field. The fitting parameters are listed in Table 1. The C values are very small (only corresponding to $\mu_{eff} \approx 0.2\mu_B$), indicating that the number density of impurities or defects is very small. The negative θ values mean that the exchange interaction between these paramagnetic moments is AFM coupling. The J values are very close to the spin gap Δ value of 24 K, but it is not consistent with the J value of about 88 K fitted by the BBK theory.[3] As mentioned in Ref.[12], probably the J value in Eq.(2) is just a scale of the energy gap between the singlet and first excited triplet state instead of the exchange coupling constant between the magnetic moments. Therefore it is reasonable that the J value is comparable to the spin gap (Δ) value. It should be noted that the anisotropy of these parameters related to the spin dimmers regarding the field direction is very weak, for example, there is only 6% difference in the J values for $H//a$ and $H//c$. This result of the isotropic fitting parameters provides another evidence to support the SP transition occurring at T_{sp} of 14 K in $CuGeO_3$.

Table 1. The fitting parameters based on the model of noninteracting dimmers (i.e., according to the Eq.(3)).

applying field		C/(emu/mol· K)	θ/K	C_1/(emu/mol· K)	J/K
$\mu_0 H//a$	1 T	0.0048	–7.74	0.9317	28.14
	5 T	0.0294	–80.1	0.9430	28.31
$\mu_0 H//c$	1 T	0.00066	–1.08	0.9549	29.94
	5 T	0.00214	–21.0	0.9617	29.60

It is remarkable that the upturn in $\chi(T)$ is suppressed by applying magnetic field. Usually the suppression of Curie–Weiss term in the susceptibility at low temperature means that the AFM interaction between free moments is enhanced or even long-range AFM ordering forms. However, the suppression of the

upturn is also almost isotropic regarding the field direction, which means that the suppression should not be caused by the enhancement of AFM ordering because AFM state has an unique easy-axis direction. Moreover, the moments from impurities or defects are well separated in space so that the AFM ordering between these moments is unlikely. We propose that the increase in the absolute value of the θ parameters with magnetic field might imply that the interaction between these free moments and the spins of Cu ions in spin dimmer state is AFM type, and this interaction could be enhanced by applying magnetic field. Another possibility is that the SP transition could be enhanced by the magnetic field and the free moments from the impurities and/or defects also start to form the spin dimmers with their neighbouring spins of Cu ions. Such a scenario is not so exotic. In usual low dimensional systems which undergo a Peierls transition so that CDW form, the enhancement of the CDW gapping with magnetic field has been observed in $NbSe_3$.[14−16] We propose that the applying magnetic field might help on turning the free magnetic moments of the impurities and/ or defects into the spin dimmer state in $CuGeO_3$. This proposal should be testified by further studies including the structure measurements under magnetic field.

4. Conclusion

Large high quality single crystals of $CuGeO_3$ were grown by floating-zone method and it allows us to study magnetic properties of the spin dimmer state in details. The temperature dependence of magnetic susceptibility below T_{sp} can be fitted well by a model of noninteracting dimmers and the spin gap is estimated from the fitting. The isotropic fitting parameters for different magnetic field directions indicate that magnetic property of $CuGeO_3$ is indeed isotropic in SP state. We first report that the upturn in susceptibility at low temperature due to paramagnetic impurities and/or defects is strongly suppressed by magnetic field and the origins of this suppression are discussed.

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