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Ferromagnetic-phase transition in the spinel-type $CuCr_2Te_4$

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Abstract

Ferromagnetic-phase transition in spinel-type $CuCr_2Te_4$ has been clearly observed. $CuCr_2Te_4$ is a telluride–spinel with the lattice constant $a = 11.134$ Å, which has been synthesized successfully. The heat capacity exhibits a sharp peak due to the ferromagnetic-phase transition with the Curie temperature $T_C = 326$ K. This value of T_C corresponds exactly to that of the negative peak of dM/dT in low field of 1.0 Oe. The magnetic susceptibility shows the Curie–Weiss behavior between 380 and 650 K with the effective magnetic moment $\mu_{eff} = 4.14\,\mu_B$/Cr-ion and the Weiss constant $\theta = +357$ K. The low temperature magnetization indicates the spin-wave excitations, where the existence of first term of Bloch $T^{3/2}$ law and the next $T^{5/2}$ term are verified experimentally. This spin-wave excitation is detected up to approximately 250 K which is a fairly high temperature.

Keywords: Spinel-type $CuCr_2Te_4$; Telluride–spinel; Ferromagnetism; Heat capacity; Magnetization; Magnetic susceptibility; Spin-wave excitation

1. Introduction

Chalcogenide spinels including transition metals have a large variety of physical properties. In particular, much of the research for the metal–insulator transition in $CuIr_2S_4$ has been extensively done in the last decade [1]. Although extensive studies have been made, only just a few telluride–spinel compounds exist that are $CuCr_2Te_4$ [2–23], $AgCr_2Te_4$ [24], and $FeCr_2Te_4$ [25]. The spinel-type structure has a cubic symmetry of space group $Fd\bar{3}m$ (No. 227). For $CuCr_2Te_4$, Cu ions occupy A-site and Cr ions occupy the B-site. These cation sites are located at the center of tetrahedron and octahedron by Te^{2-} ions, respectively. Many investigations on the crystallographic study, NMR, Mössbauer effect study, and magnetic properties have been done for $CuCr_2Te_4$ by previous workers [2–15]. However, detailed study of thermal property has not been provided so far. This paper will present the heat capacity and magnetic properties, which verifies experimentally the clear accurate Curie temperature of $T_C = 326$ K. The heat capacity exhibits a sharp peak due to the ferromagnetic-phase transition at 326 K at which the inflection point of the magnetization is detected as a function of temperature, indicating the negative peak of dM/dT in a very low field of 1.0 Oe. Shchelkotunov et al. [23] have measured the heat capacity of $CuCr_2Te_4$; however, the temperature interval was 5 K and the accurate T_C was not determined. The basic results of heat capacity and magnetization are obtained and our new results are compared with that estimated by the previous workers. The present work provides direct evidence of ferromagnetic phenomena in $CuCr_2Te_4$.

2. Experimental methods

2.1. Sample preparation

The polycrystalline specimens were prepared by a direct solid-state reaction. Mixtures of high-purity fine powders of Cu (purity 99.99%, melting point 1357.5 K), Cr(99.99%, 2130 K), and Te(99.999%, 722.8 K) for the total weight of

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2.0 g with nominal stoichiometry were prepared, where excess 2 mg Te was added. These powders were heated in sealed quartz tubes ($\approx 4 \times 10^{-7}$ Torr) to 773 K with heating rate of 200 K/h and kept at this temperature for 160 h. The resultant powdered specimens were reground, heated again to 773 K and kept for 100 h, annealed at 673 K for 4 h, and then cooled in a furnace.

2.2. Measurements

The identification of the crystal structure and the determination of the lattice constant were carried out by the powder X-ray diffraction (XRD) method. XRD data were taken with Cu$K\alpha$ radiation and curved crystal monochrometer on a Bragg–Brentano-type powder diffractometer at room temperature. The heat capacity for 10.60 mg specimen was measured with a Quantum Design PPMS Heat Capacity Option (HC) Model P650 over the temperature range of 2.17–373 K in zero magnetic field. The obtained data were less accurate above 350 K. The magnetization M and the DC magnetic susceptibility χ of the powder specimens were measured with a Quantum Design superconducting quantum interference device (MPMS, *rf*-SQUID) magnetometer over the temperature range of 4.2–650 K for various external fields H. Demagnetizing-field corrections were made for the susceptibility.

3. Results and discussion

3.1. Crystal structure

The color of powder specimen $CuCr_2Te_4$ is dark gray. Fig. 1 shows the powder XRD pattern with the cubic spinel-type symmetry of $CuCr_2Te_4$. The lattice constant is $a = 11.134$ Å at room temperature which is in good agreement with data of previous researchers [3,4,6]. The indices, the comparisons of d spacing between the calculated and the observed values, and observed peak intensities are listed in Table 1. A small amount of unknown impurities are found as weak peaks in Fig. 1, where it was too difficult for us to extinguish these impurities. Kanomata and Ido [3] also reported that three extra lines in XRD pattern were observed in $CuCr_2Te_4$.

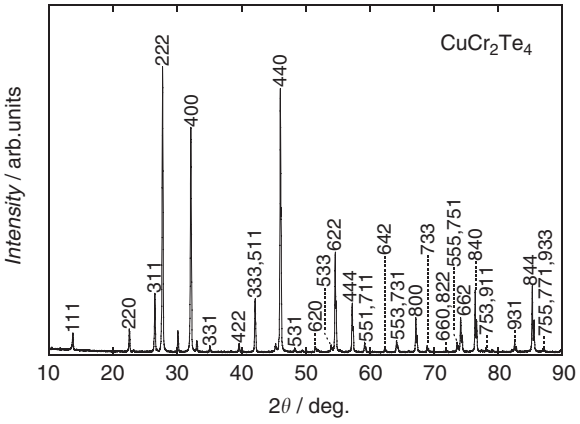

Fig. 1. Powder X-ray diffraction pattern of $CuCr_2Te_4$ at room temperature with the lattice constant $a = 11.134$ Å.

Table 1
Indices, observed and calculated values of d spacings and observed peak intensities for $CuCr_2Te_4$ with the lattice constant $a = 11.134$ Å

h	k	l	d_{obs} (Å)	d_{cal} (Å)	I_{obs}
1	1	1	6.4583	6.4280	5
2	2	0	3.9483	3.9363	7
3	1	1	3.3632	3.3569	19
2	2	2	3.2201	3.2140	93
4	0	0	2.7878	2.7834	77
3	3	1	2.5573	2.5542	2
4	2	2	2.2751	2.2727	3
3	3	3	2.1445	2.1427	19
5	1	1		2.1427	
4	4	0	1.9698	1.9682	100
5	3	1	1.8835	1.8819	1
6	2	0	1.7616	1.7604	1
5	3	3	1.6990	1.6979	3
6	2	2	1.6795	1.6785	39
4	4	4	1.6081	1.6070	20
5	5	1	1.5599	1.5590	4
7	1	1		1.5590	
6	4	2	1.4887	1.4878	2
5	5	3	1.4503	1.4495	5
7	3	1		1.4495	
8	0	0	1.3923	1.3917	13
7	3	3	1.3610	1.3602	2
6	6	0	1.3127	1.3121	1
8	2	2		1.3121	
5	5	5	1.2862	1.2856	4
7	5	1		1.2856	
6	6	2	1.2776	1.2771	13
8	4	0	1.2453	1.2448	25
7	5	3	1.2224	1.2221	2
9	1	1		1.2221	
9	3	1	1.1676	1.1671	4
8	4	4	1.1367	1.1363	27
7	5	5	1.1194	1.1190	1
7	7	1		1.1190	
9	3	3		1.1190	

3.2. Heat capacity

3.2.1. Lattice heat capacity

Fig. 2 depicts the molar (formula-unit) heat capacity C for $CuCr_2Te_4$ as a function of temperature over the temperature range of 2.17–373 K. The compound $CuCr_2Te_4$ exhibits a sharp peak due to the ferromagnetic-phase transition at 326 K. Fig. 3 indicates the lattice contribution $C_{lattice}$, following the Debye T^3 approximation, below 10 K,

$$C_{lattice} = \left(\frac{12}{5}\right)\pi^4 N_A k_B r\left(\frac{T}{\Theta_D}\right)^3, \\ = 1943.8r\left(\frac{T}{\Theta_D}\right)^3, \quad (1)$$

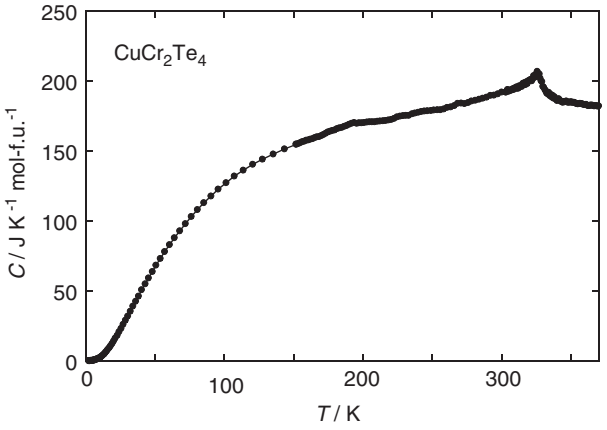

Fig. 2. Molar heat capacity of $CuCr_2Te_4$ over a wide temperature range of 2.17–373 K.

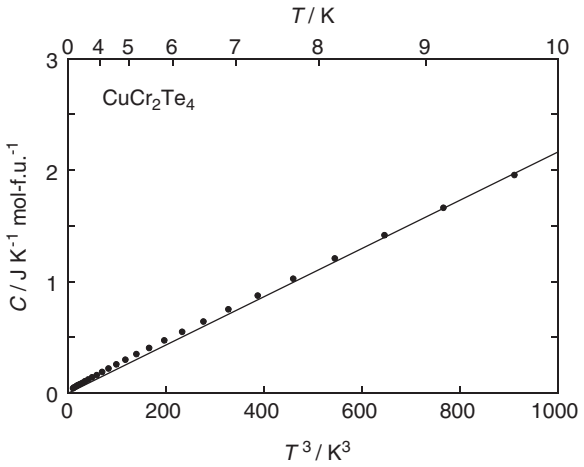

Fig. 3. The Debye T^3 approximation of low-temperature lattice heat capacity for $CuCr_2Te_4$.

where N_A is the Avogadro's number, k_B the Boltzmann's constant, Θ_D the Debye temperature, T the temperature and r the number of atoms per formula unit, which is found to be $r = 7$ for spinel compound. The Debye temperature Θ_D is obtained to be 184 K ($r = 7$) and 96.4 K ($r = 1$). The results of Curie temperature by Belov et al. [20] is $T_C = 324$ K. The Debye temperature is $\Theta_D = 260 \pm 5$ K by Shchelkotunov et al. [23]

3.2.2. Magnetic heat capacity

Fig. 4 shows the temperature dependence of the magnetic heat capacity C_m of $CuCr_2Te_4$. The magnetic heat capacity is obtained after the subtraction; $C_m = C - C_{lattice}$. However, the accurate subtraction of the lattice contribution was not possible. The lattice heat capacity was assumed to be a straight line, for the simplicity, from 200 to 373 K; here, all the value comes from the lattice heat capacity at 200 and 373 K. The experimental observation of the magnetic entropy change S_m over the temperature range of 200–373 K is presented in

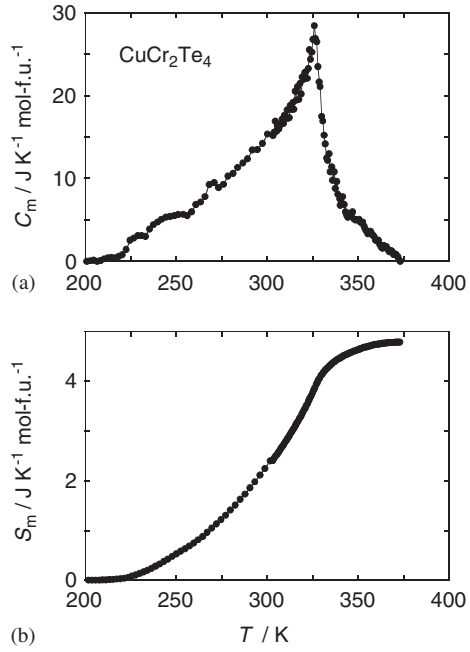

Fig. 4. Magnetic molar heat capacity of $CuCr_2Te_4$ as a function of the temperature (a) After the subtraction of lattice contribution, see text. The Curie temperature is 326 K. (b) Magnetic entropy change as a function of the temperature, using (a).

Fig. 4 using the following expression:

$$S_m = \int_0^T \frac{C_m}{T}\,dT. \tag{2}$$

The calculated total magnetic entropy change is small in comparison with the expected value for $S = \frac{3}{2}$ (Cr^{3+} ion). Presumably, the magnitude of subtraction on the lattice heat capacity is over estimated, therefore, the magnetic entropy change would be underestimated as shown in Fig. 4. Consequently Fig. 4 provides only the qualitative feature of the magnetic heat capacity without the accuracy for the absolute value. In addition, the ratio of the magnetic entropy change below and above T_C is evaluated to be ΔS_m ($200\,K < T < T_C$) = 80% and ΔS_m ($T_C < T < 373\,K$) = 20%.

3.3. Magnetic properties

3.3.1. Magnetization and magnetic susceptibility

Fig. 5 displays the temperature dependence of magnetization in an applied field $H = 10.0$ kOe for polycrystalline specimens of $CuCr_2Te_4$. Fig. 6 indicates the result of the magnetization near the Curie point in a very low field of 1.00 Oe and presents the temperature derivative of M, dM/dT, as a function of the temperature. This negative peak temperature of dM/dT corresponds to that of the sharp peak of the heat capacity. The accurate Curie temperature has been now determined for $CuCr_2Te_4$ for the first time. It should be noted that the difference of value of magnetization between Figs. 5 and 6 is critically important to discuss precise T_C. In Fig. 6, the magnetization was measured in extremely low magnetic field of

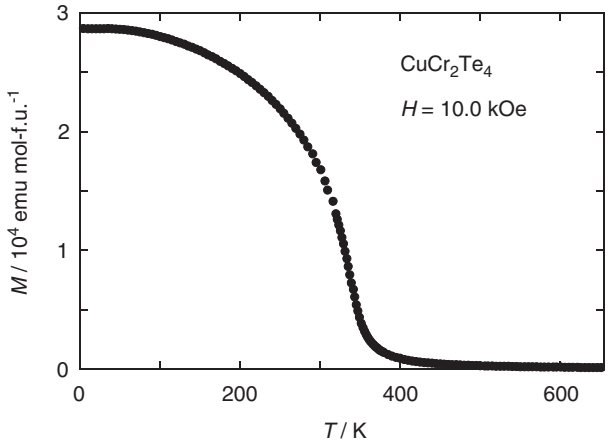

Fig. 5. Magnetization versus temperature for $CuCr_2Te_4$ per formula unit at constant magnetic field of 10.0 kOe.

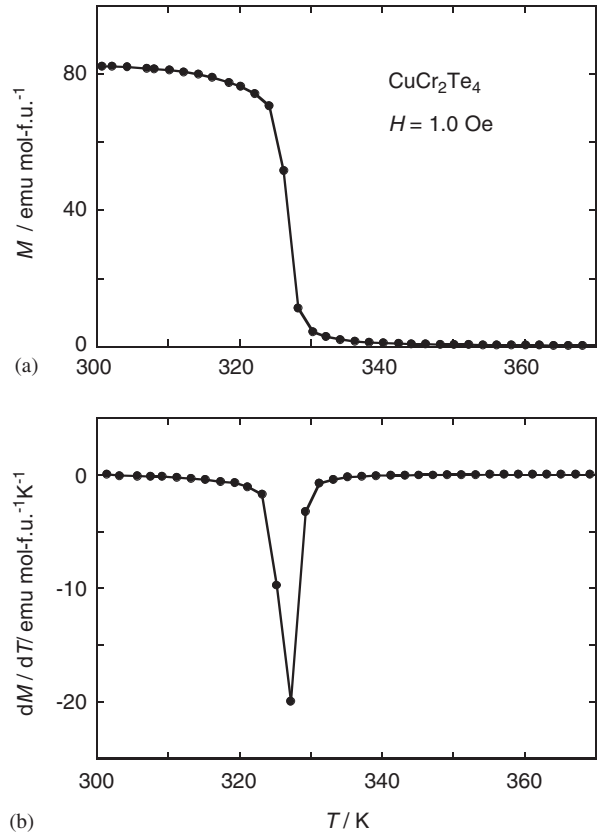

Fig. 6. Determination of the Curie temperature using the inflection point in the magnetic data: (a) magnetization versus temperature for $CuCr_2Te_4$ in very low magnetic field of 1.00 Oe and (b) temperature derivative of M, dM/dT, as a function of temperature. This negative peak temperature corresponds to the sharp peak of the heat capacity.

1.0 Oe; the temperature variation of dM/dT in low field enables us to determine the accurate T_C because of the avoidance of a great influence of domain structure in the ferromagnetic phase.

The inverse magnetic susceptibility in an applied magnetic field H of 10.0 kOe is indicated in Fig. 7. The

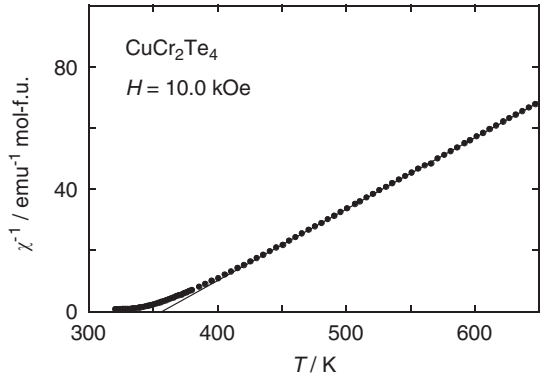

Fig. 7. Inverse magnetic susceptibility for $CuCr_2Te_4$ as a function of temperature in a magnetic field of 10.0 kOe.

susceptibility of $CuCr_2Te_4$ is well fitted to a modified Curie–Weiss law over the temperature range of 450–650 K,

$$\chi = \frac{C}{T-\theta} + \chi_0, \tag{3}$$

where C is the Curie constant, the Weiss constant θ and χ_0 a temperature independent term and T the temperature. The experimental result of χ_0 is found to be -2.89×10^{-3} emu mol-f.u.$^{-1}$. The amount of diamagnetic contribution caused by the atomic core electrons for $CuCr_2Te_4$ is evaluated to be $\chi_{dia} \approx -3.1 \times 10^{-4}$ emu mol − f.u.$^{-1}$ [26]. The Weiss constant θ is + 357 K, the Curie constant C is 4.28 K emu mol-f.u.$^{-1}$. The magnitude of the effective magnetic moment μ_{eff} is evaluated to be 4.14 μ_B Cr-ion^{-1}, which is close to the spin only value 3.87 μ_B expected for $S = 3/2$ (Cr^{3+} ion). In addition, this evaluated magnitude of μ_{eff} is equivalent to 5.85 μ_B mol-f.u.$^{-1}$

Fig. 8 shows the magnetization curve at 5.0 K up to $H = \pm 10.0$ kOe. The value of magnetization at $H =$ 10.0 kOe is 2.85×10^4 emu mol-f.u.$^{-1}$, which leads to the value of the magnetic moment n_B ($n_B = gS$, where g is the Lande's g-factor) at $H = 10.0$ kOe is $n_B = M/(N_A\mu_B) = 2.55\,\mu_B$/Cr-ion. The value of n_B is much less than the effective Bohr magneton number $p_{eff} = 4.14$/Cr-ion. The magnetization is not saturated at 10.0 kOe. A possible mechanism may be a non-collinear spin alignment [27,28].

3.4. Spin-wave excitation

The low-lying elementary excitations due to the spin wave have been examined for $CuCr_2Te_4$. The spin-wave dispersion relation for the long-wave ($k \sim 0$) takes the form:

$$\varepsilon_k = Dk^2 + Ek^4, \tag{4}$$

where D is the stiffness constant and E is the constant of proportionality for the k^4 term. At low temperatures, the magnetization is expected to follow the Heisenberg-model theoretical prediction as,

$$\frac{M(0)-M(T)}{M(0)} = \alpha T^{3/2} + \beta T^{5/2}, \tag{5}$$

where $\Delta M = M(0) - M(T)$ indicates the difference of the magnetization and, α and β are constants.

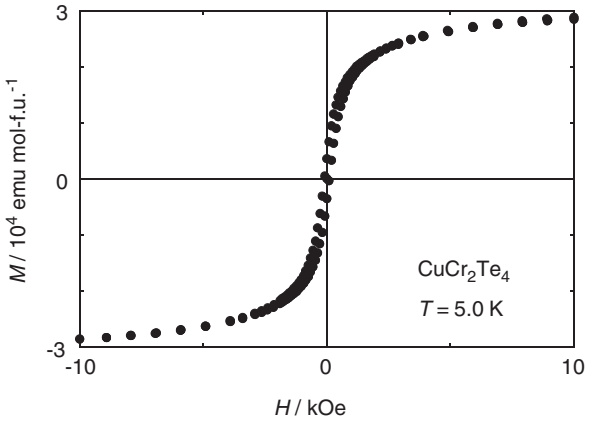

Fig. 8. Magnetization as a function of magnetic field H for $CuCr_2Te_4$ at 5.0 K in the range of $-10 \leqslant H \leqslant 10$ kOe.

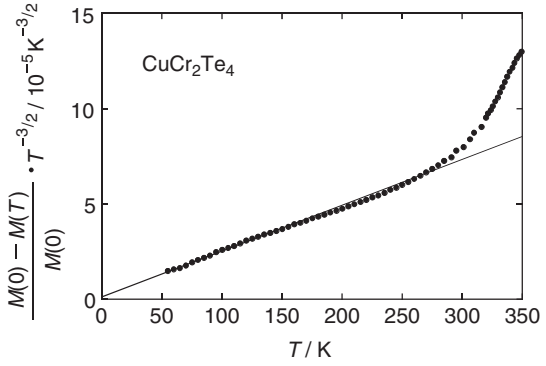

Fig. 9. A spin-wave ferromagnetic excitation analysis. The fractional change of the magnetization $\Delta M/M(0) = \alpha T^{3/2} + \beta T^{5/2}$ is detected up near 250 K, where $\Delta M = M(0) - M(T)$. The first term indicates the Bloch $T^{3/2}$ law. It is noted that the value α is not zero, corresponding to the value of the ordinate at the extrapolated abscissa to $T = 0$ K.

Fig. 9 shows the experimental result on the basis of Eq. (5). In the presence of a magnetic field, formulae (4) and (5) must be changed a little. Nevertheless, we neglected the influence of the applied magnetic field of 10 kOe. The low temperature magnetization is found to fit Eq. (5). The first term indicates the Bloch $T^{3/2}$ law. In order to obtain the values of α and β, Fig. 9 presents $\Delta M/M(0) \times T^{-3/2}$ versus T. It is noted that the value α is not zero in the Fig. 9, corresponding to the value of the ordinate at the extrapolated abscissa to $T = 0$ K. The straight line is observed up near 250 K. The low-temperature data below 50 K are not given in Fig. 9 because the results of magnetization were not accurate in our samples, because of the sample dependence. The values of α and β are evaluated to be $\alpha = 1.29 \times 10^{-6}\,K^{-3/2}$ and $\beta = 2.40 \times 10^{-7}\,K^{-5/2}$, respectively. It is pointed out that more precise analysis for the spin-wave excitation should be made taking into account the external magnetic field, see Ref. [29].

Acknowledgments

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