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MAGNETIC PHASE TRANSITIONS AND SPECIFIC HEAT OF SINGLE CRYSTALLINE CUPRIC OXIDE

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The antiferromagnetic phase transitions in a CuO single crystal are studied by specific heat in magnetic fields up to 6 T. The magnetic field dependence of the incommensurate-to-commensurate-antiferromagnetic transition at T_L is found to be highly anisotropic. T_L is observed to increase nonlinearly for $B_a \parallel c$-axis, whereas, a linear reduction is observed for $B_a \parallel b$-axis. The magnetic field dependence of T_L and the jumps in magnetic susceptibility at T_L are explained thermodynamically using the Clausius-Clapeyron equation.

Keywords: cupric oxide, magnetic phase transitions, specific heat

Introduction

The magnetic properties of cupric oxide (CuO) are unusual. It undergoes a second order paramegnetic-to-incommensurate-antiferromagnetic transition at a temperature $T_N \approx 230$ K [1–6]. This is followed by a first order incommensurate-to-commensurate-antiferromagnetic (IC-C) transition at a temperature $T_L \approx 213$ K [2–6]. The magnetic part of the heat capacity shows a broad maximum at ~600 K, characteristic of low dimensional systems [7]. The temperature dependence of magnetic susceptibility $\chi(T)$ also shows a broad maximum at ~550 K [8]. Neutron scattering experiments [2, 9] show large spin-wave velocity and anisotropic spin correlations above T_N. The magnetic susceptibility of CuO is also highly anisotropic with respect to the crystallographic axes [7, 10]. The origin of the anisotropy can be understood qualitatively from the crystal structure in the following way [8]. The superexchange interaction between the copper ions is through the Cu-O-Cu bond. The superexchange interaction strength also depends on the bond angle which is maximum when the bond angle is close to 180 degrees, and minimum when the angle is close to 90 degrees [11]. From this consideration, it appears that the superexchange interaction along (1, 0, −1) is considerably stronger than that in other directions. This can give rise to the observed anisotropy in CuO.

In this work, we study the effect of magnetic field on the magnetic transitions in a CuO single crystal. We find that the magnetic field dependence of the IC-C transition is highly anisotropic.

Experimental and discussion

Specific heat measurements were carried out by Nernst's step heating calorimetry [12] using a CuO single crystal weighing about 0.2 g. The crystal was grown at Oxford University by the flux growth method in a platinum crucible [13]. A given crystallographic axis was oriented with respect to the applied magnetic field (B_a) to within about 5 degrees using a support made of 0.3 mm thick copper foil. The CuO crystal was cemented to the copper support using Apiezon-N grease.

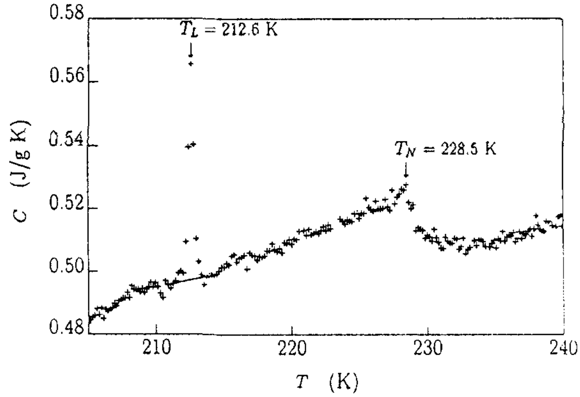

Fig. 1 Specific heat of a CuO single crystal (weight=0.197 g) as a function of temperature in the absence of magnetic field. The anomaly at 228.5 K corresponds to the second order paramagnetic-to-incommensurate-antiferromagnetic transition. The anomaly at 212.6 K corresponds to the first order IC-C antiferromagnetic transition. The straight line under the first-order peak at T_L shows the region used for the determination of the latent heat

This assembly was fixed to the Al_2O_3 sample holder using also Apiezon-N grease. The total amount of Apiezon-N grease was typically less than 5 mg, whose heat capacity was subsequently subtracted using the literature values [14]. The heat capacity contribution of the copper support was measured separately and subtracted. The sample temperature was measured with a calibrated platinum resistance thermometer (model PTXG65 of Rosemount Inc., Minneapolis, Minnesota 55435, U.S.A.) glued to the bottom side of the 0.1 mm thick

Al_2O_3 disk serving as the sample holder. The magnetoresistance of platinum thermometers is negligible in this temperature and magnetic field range [15]. The resistance of the sample holder thermometer was measured with a resolution better than 1 ppm using an ASL model F17A ac resistance bridge [16]. The temperature of the isothermal radiation shield was controlled to better than 5 mK using an ASL model 300 temperature controller in conjunction with an ASL model F26 ac resistance bridge [16]. The data acqisition was automated. The heat capacity of CuO constituted about 25 percent of the total measured heat capacity, which had an average scatter of 0.07 percent. This low scatter is obtained by describing the temperature drift curve by an exponential function [17], instead of the usual linear function of time. Figure 1 shows the specific heat of CuO crystal as a function of temperature in the absence of magnetic field. The absolute value of the specific heat agrees with the previous literature values to within 10 percent which are higher in value than the present one [4–6]. The present data are the first adiabatic (precision) measurements on CuO near the magnetic phase transitions. The first order IC-C antiferromagnetic transition has a width less than 1.5 K with the peak at T_L=212.6 K. The latent heat (L) associated with this transition is about 36 mJ/g. The second-order paramagnetic-to-incommensurate antiferromagnetic transition is found to be nearly 4 K wide, with the peak at T_N=228.5 K. The discontinuity in the specific heat is about 29 mJ/gK. The paramegnetic-to-incommensurate-antiferro- magnetic transition at T_N was studied in magnetic fields up to 5 T applied parallel to the b- and c-axes. The change of T_N in magnetic fields up to 5 T is found to be less than 0.2 K. Changes less than 0.2 K could not be resolved unambiguously due to the large width of the transition at T_N. Figure 2 shows specific heat in a magnetic field of 5 T applied parallel to the c-axis. The rather negligible shift in T_N re-

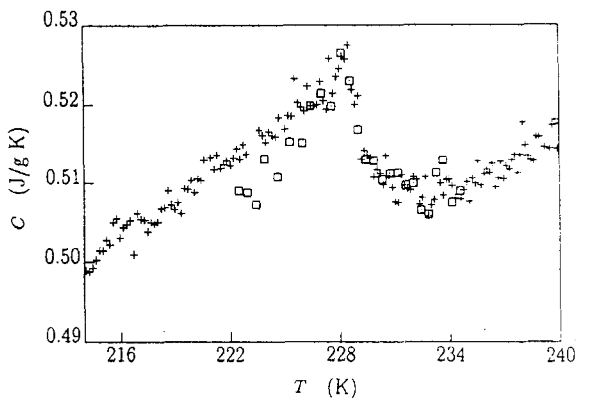

Fig. 2 The temperature dependence of specific heat near T_N in the absence of magnetic field (+) and for an applied field of 5 T parallel to the c-axis (⊡). The shift in T_N is less than 0.2 K

flects the relatively strong coupling between the copper ions and the large fraction of transition entropy above T_N [7].

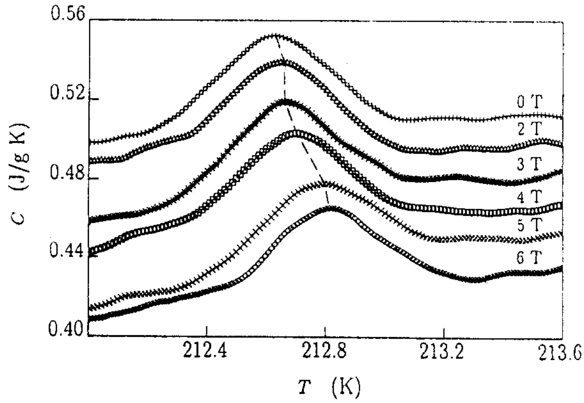

Fig. 3 The incommensurate-to-commensurate antiferromagnetic transition for several values of $B_a \parallel c$ -axis, obtained by the continuous-heating method. The data in the presence of magnetic field is shifted downwards with respect to the data in the absence of magnetic field, for clarity. With increasing field, the transition shifts to higher temperatures with negligible change in the shape

The IC-C transition at T_L was also studied by the continuous-heating method [18], adapted to the same calorimeter. For this purpose the sample was heated at a rate of about 1 mK/sec and the sample temperature was measured approximately every 20 seconds interval. The rate of temperature rise dT/dt was obtained by least-squares-fitting twenty temperature-*vs.*-time data to a second order polynomial. T_L did not change by more than 15mK by doubling the sample heating rate. Measurements were carried out in magnetic fields up to 6 T applied parallel to the b- and c-axes. The contributions of the Apiezon-N grease and the copper support were subtracted as mentioned previously. We define T_L as the temperature corresponding to the position of the peak, which could be located with a temperature resolution better than 10 mK. We obtain $T_L(B_a=0)=212.63$ K. Figure 3 displays the IC-C transition for several values of $B_a \parallel c$-axis. It is seen that on increasing the magnetic field, T_L shifts to higher temperatures. There is however, negligible change in the shape of the peak. On the other hand, application of magnetic field parallel to the b-axis has a contrary effect and is found to reduce T_L. From the results shown in Fig. 3, the magnetic field dependence of T_L is found to be nonlinear for $B_a \parallel c$-axis, which is given by:

$$T_L(B_a)=T_L(0)[1+\gamma B_a^2] \tag{1}$$

We obtain, $\gamma=(2.6\pm0.2)\times10^{-5}$ T^{2} from the least squares fitting. Whereas T_L appears to decrease linearly for $B_a \| b$-axis, which is given by:

$$T_L(B_a)=T_L(0)[1-\delta B_a] \quad (2)$$

where $\delta=(7.9\pm0.6)\times10^{-5}$ T^{-1}, is obtained from the least squares fit. The qualitative nature of the field dependence of T_L has one-to-one correspondence with the temperature dependence of magnetic susceptibility [7, 10]. When $B_a \| b$-axis, $\chi(T)$ shows a positive jump at T_L with increasing temperature (i.e., the susceptibility for $T > T_L(\chi_h)$ is greater than that for $T<T_L(\chi_l)$). This jump in $\chi(T)$ is equal in magnitude and opposite in sign to that observed for $B_a \| c$-axis. This can be understood thermodynamically, using the magnetic analog of the Clausius-Clapeyron equation, which is written by replacing p and V by B_a and $-M$, respectively:

$$dT_L/dB_a=(M_l-M_h)T_L/L \quad (3)$$

where M_l and M_h are the magnetizations corresponding to the low ($T<T_L$) and the high ($T>T_L$) temperature phases, respectively. Here $B_a=\mu_0 H$ and the latent heat (L) is positive in the case of CuO. When $B_a \| c$-axis, $M_l>M_h$ since $\chi_l>\chi_h$. Therefore, we see from the Clausius-Clapeyron equation that dT_L/dB_a should be positive for $B_a \| c$-axis. Whereas, for $B_a \| b$-axis, dT_L/dB_a should be negative, because $M_l<M_h$. This is consistent with our results.

We see from Eqs 1 and 2 that only for an applied field of 2 T, dT_L / dB_a ($B_a \| c$–axis) $\approx -dT_L / dB_a$ ($B_a \| b$–axis). Therefore, the equal-in-magnitude and opposite-in-sign jump observed in $\chi(T)$ at T_L for a magnetic field of 2 T applied parallel to the b- and c-axes, is a coincidence as can be seen from the Clausius-Clapeyron equation (Eq. 3).

We next estimate the latent heat using the experimental values of (M_l-M_h) and dT_L / dB_a. We take $\chi_l-\chi_h=0.17\times10^{-3}$ cm^3/mole from Ref. 10 and use the density $\rho=0.082$ mole/cm^3. We obtain L=33 mJ/g using dT_L/dB_a for $B_a \| c$-axis and 43 mJ/g using dT_L/dB_a for $B_a \| b$-axis. The average latent heat is about 38 mJ/g, which is smaller compared to the earlier reported values (57–100 mJ/g) [4–6]. This difference can be partly due to the difficulty in subtracting the large background contribution, when determining L using the area under the peak at T_L.

Conclusion

In summary, we have studied the effect of an applied magnetic field on the specific heat of a CuO single crystal. The IC-C transition temperature T_L is found to increase nonlinearly for $B_a \parallel$ c-axis, whereas a linear reduction of T_L is observed for $B_a \parallel b$-axis. There is one-to-one correspondence between the magnetic field dependence of T_L and the jump in magnetic susceptibility at T_N. We have explained this thermodynamically using the magnetic analog of the Calusius-Clapeyron equation. We have also shown that in general, the jump in $\chi(T)$ at T_L for $B_a \parallel b$- and c-axes are not equal in magnitude.

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Zusammenfassung — Anhand der spezifischen Wärme wurde in magnetischen Feldern bis zu 6 T die antiferromagnetische Phasenumwandlung in einem CuO-Einkristall untersucht. Die Abhängigkeit der antiferromagnetischen Phasenumwandlung inkommensurabel/kommensurabel vom magnetischen Feld bei der Temperatur T_L ist äußerst anisotrop. T_L steigt für $B_a \parallel c$-Achse nichtlinear zu und nimmt für $B_a \parallel b$-Achse linear ab. Die Abhängigkeit von T_L vom magnetischen Feld und die Sprünge der magnetischen Suszeptibilität bei T_L wurden unter Zuhilfenahme der Gleichung von Clausius-Clapeyron erklärt.