Magnetic specific heat and susceptibility of cupric oxide (CuO) single crystals

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Abstract. We investigated the magnetic specific heat and entropy of a CuO single crystal in the wide temperature range from 1.5 K to 1000 K and determined the anisotropy of its magnetic susceptibility below 300 K. CuO behaves like an anisotropic low-dimensional antiferromagnet. The magnetization discontinuity is most clearly visible at $T_{N2} = 214$ K for fields in the b - c plane. The measured magnetic entropy at 1000 K, $S_m(1000) = 5.67$ J/mol K, approaches the expected value of $S_m = R \ln 2 = 5.76$ J/mol K.

Keywords. CuO; specific heat; susceptibility; magnetic properties; high temperature superconductors.

1. Introduction

Copper ions, Cu^{2+} , in high temperature superconductors (HTSC) have a square-planar coordination as in CuO and the antiferromagnetic behaviour of these systems shows striking similarities. The magnetic properties of CuO are unusual and not yet fully understood. Recently, the two magnetic transitions at 213 K and 230 K have been investigated by neutron scattering experiments (Forsyth *et al* 1988; Yang *et al* 1989) and specific heat measurements (Junod *et al* 1989; Loram *et al* 1989; Gmelin *et al* 1990). Earlier work on the specific heat of CuO, before 1960, has been reviewed by Junod *et al* (1989) and Gmelin *et al* (1990). The susceptibility behaves anomalously (Parkin *et al* 1988; for earlier references see Junod *et al* 1989). The temperature dependence of the susceptibility follows neither a Curie-Weiss behaviour ($\mu_{\text{sat}} = 0.65 + 0.1 \mu_B$) nor does it show a cusp at T_N , but a broad hump was observed near 550 K (O'Keefe *et al* 1963; Perakis *et al* 1956). Nearly all the known structural, magnetic and thermal properties of CuO have been summarized in the recent papers by Junod *et al* (1989) and Gmelin *et al* (1990). However, the published results on the specific heat and susceptibility refer only to CuO powder. Until now, no data have been reported for single crystals, and the magnetic specific heat above room temperature is unknown. We have, therefore, measured the heat capacity C and susceptibility χ of *single crystalline* CuO in order to get first information on the anisotropy of χ and the magnetic contribution to C at higher temperatures. Cupric oxide has been investigated also to understand better the magnetic properties of HTSC. We point out, for the first time, that CuO displays the full entropy expected for a spin ($\frac{1}{2}$) Heisenberg antiferromagnet and report measurements of the temperature dependence of the specific heat up to 1000 K.

2. Experimental

Specific heat and susceptibility are measured on single crystals grown in a platinum crucible by the flux growth method as described by Wanklyn and Garrard (1983). The study was performed with two single crystals with a total weight of 276.4 mg. An adiabatic microcalorimeter (Brill and Gmelin 1987), high temperature scanning calorimeters (Netsch DSC 404, Perkin–Elmer DSC-2) and a sensitive Faraday balance magnetometer (using a field of $B = 2$ Tesla) were used to determine specific heat and susceptibility.

3. Results and discussion

3.1 Susceptibility

In figures 1a,b the susceptibilities $\chi(T)$ are shown for three selected crystal orientations. (Note that a $1/T$ -like susceptibility contribution due to about 0.3% paramagnetic impurities has been subtracted). While measurements on powder samples reveal only the magnetic transition T_{N1} (second order, Néel point) near 230 K as a weak shoulder on an otherwise increasing χ curve with increasing temperature, both magnetic transitions can be clearly detected in a single crystal study. It turns out that for all orientations the $\chi(T)$ curves show a parallel behaviour around T_{N1} and that the characteristic symmetry breaking does occur only below the χ -discontinuity at T_{N2} (first order, commensurate to incommensurate phase transition). Thus T_{N1} can be observed on powder samples since $\chi(T)$ is qualitatively the same for all crystal orientations whereas at T_{N2} , depending on the orientation, either a positive or a negative jump in χ occurs, such that in a powder the effect vanishes. The largest positive discontinuity in χ (with increasing T) is observed for $B_0 \parallel b$ and the strongest negative one for $B_0 \parallel c$. No detectable jump is seen for $B_0 \parallel a$ and within the crystallographic (023) and (0 $\bar{2}$ 3) planes (see figure 1).

Assuming the simplified view that there is only one phase transition at T_{N2} , we are led to conclude that there is no critical behaviour in the (023) and (0 $\bar{2}$ 3) planes but only in directions between these planes. Thus, T_{N2} may be characterized as a two-fold degenerate one-dimensional transition and the critical behaviour occurs in the b – c

Figure 1a, b. Susceptibility of a CuO single crystal in three different crystallographic orientations. T_{N1} (Néel point) and T_{N2} denote the two magnetic phase transitions.

Table 1. Absolute values of susceptibility of a CuO single crystal (in $10^{-3} \text{ cm}^3/\text{mol}$)

$T(\text{K})$	χ_{010}	χ_{100}	χ_{001}
250	3.51	3.3	2.96
100	1.97	2.97	2.98

plane. T_{N2} seems to be the main transition where the spins rearrange and lock-in whereas the T_{N1} transition is a minor precursor.

Absolute values of χ along the main crystal orientations are listed in table 1 for $T=250 \text{ K}$ (paramagnetic phase) and for $T=100 \text{ K}$ (antiferromagnetic phase). For $T > T_{N1}$, the susceptibility is smallest for $B_0 \parallel c$. We interpret this as a consequence of strong diamagnetic contributions owing to extended covalent Cu–Cu bonds in the a – b plane. At 100 K the χ -tensor is a rotational ellipsoid with the small axis along the crystallographic b -direction which indicates that the orientation of the magnetic moment is along b -direction. This result is in good agreement with conclusions drawn from neutron scattering experiments (Forsyth *et al* 1988) from which, at 100 K, a moment orientation along the b -axis was deduced by intensity relations between different hkl magnetic scattering lines.

3.2 Specific heat

The specific heat is shown in figure 2 (continuous line) in a plot of the equivalent Debye-temperature $\Theta(T)$, as calculated from the more than 800 individual measuring points, as a function of temperature. The specific heat below 10 K is shown in detail in the inset of figure 3 as a plot C_p/T vs T^2 . In figure 3 the total molar heat (at constant pressure),

Figure 2. Debye temperature Θ vs T for single crystalline CuO, as calculated——from the specific heat $C_p - \gamma T$, ————according to equation 1 from $C_v - \gamma T$, ---- extrapolated from harmonic part.

Figure 3. Molar heat capacity of single crystalline CuO: ——— total specific heat at constant pressure, C_p ; ---- total specific heat at constant volume, C_v ; — · — lattice heat capacity, derived from extrapolation of the harmonic part of C_p at low temperatures according to Barron *et al* (1957); + + + data of Wöhler and Jochum (1933).

C_p is plotted for the temperature range from 250 K to 1000 K (continuous line). Our results agree within a few per cent with earlier higher temperature C_p data (Wöhler and Jochum 1933). $C_p(T)$ displays an unusual temperature dependence above 800 K: C_p obviously decreases.

From the low temperature results we deduce a nearly zero electronic term, $\gamma < 0.1 \text{ J/mol K}^2$, and a Debye temperature $\Theta_0(0 \text{ K}) = 391 \text{ K} \pm 10 \text{ K}$ if we disregard the additional $\Delta C \sim T^{-2}$ term at lowest temperatures. These γ and Θ_0 -values are in excellent agreement with the data reported for powder samples (Junod *et al* 1989; Loram *et al* 1989). We have reported and analysed the intermediate range ($10 \text{ K} < T < 250 \text{ K}$), where the two phase transitions occur, elsewhere (Gmelin *et al* 1990) and we merely summarize it here. For single crystals, in comparison to powder samples, the magnetic transitions T_{N1} and T_{N2} are located nearly 1 K higher in temperature, at 214 K and $230 \text{ K} \pm 0.4 \text{ K}$, respectively, and the specific heat anomalies are much higher and narrower than the earlier reported ones. The latent heat at T_{N2} amounts to $\Delta H = 7.96 \pm 0.25 \text{ J/mol}$, nearly twice the value indicated for powdered material. The magnetic entropy removed below the onset of long range order, $\Delta S_m = 1.59 \text{ J/mol K}$ is unusually small, namely only 28% of the expected value of $\Delta S_m = R \ln 2 = 5.76 \text{ J/mol K}$. More than 70% of magnetic entropy is removed above the Néel point by short-range order processes. This fact is characteristic of low-dimensional magnetic systems for which a substantial part of short-range order persist above T_{N2} .

Some unusual aspects of $C_p(T)$ of CuO hint to strong magnetic contributions to the

specific heat above room temperature: (i) a substantially smaller $C(T_N)$ than usually seen at the long range ordering point for spin ($\frac{1}{2}$) systems; (ii) an unexpectedly small magnetic entropy below T_{N2} , much smaller than found for other oxide materials (only 28% of the theoretical value); (iii) an unrealistic shape of the Debye temperature above T_{N2} , and (iv) a decreasing heat capacity above 700 K which is in contrast to most other solids for which $C_p(T)$ increases linearly due to anharmonicity.

To calculate the magnetic specific heat C_m , we must (i) correct $C_p(T)$ for anharmonicity and (ii) reconstruct the harmonic lattice heat C_L . The first step is done by $(C_p - C_v) = A C_v^2 T$ with $A = 1.35 \text{ (J/mol)}^{-1}$ and results in the dashed curve in figure 3. The difference $C_p - C_v$ amounts to 1.6% at 300 K and 17% near 1000 K. To determine the lattice heat we employ the procedure used by Barron *et al* (1957) to separate harmonic and anharmonic phonon specific heat of the alkali halides. For more details on the procedure used and for the quantitative data we refer to recent publications (Loram *et al* 1989; Gmelin *et al* 1990). The pure phonon heat C_L , constructed in this way, is given in figure 3 as dash-dotted line (or dotted line in figure 2). The curve agrees within 2% with the lattice heat directly derived from phonon density of states measurements (Junod *et al* 1989). When C_L is subtracted from C_m , the magnetic contribution C_m is obtained.

In figure 4 (solid line), $C_m(T)$ is depicted. The C_m -contribution is significant between 200 K and 1000 K. The magnetic term constitutes between 2 to 3 J/mol K above 200 K; it amounts to about 5% of the total C_p between 300 K and 700 K. The maximum of C_m is located around 600 K, and coincides with the maximum of susceptibility (Parkin *et al* 1988). The magnetic entropy is calculated by integration of C_m/T (figure 4, solid line, labelled 'S'). The entropy loss ΔS_m below T_{N1} is only 28% and the major part of magnetic entropy is connected with short-range order. The magnetic entropy reaches 2.25 J/mol K (38.6%) at 300 K, 2.94 (51%) at 400 K, 4.08 (70%) at 500 K, and 5.67 J/mol K (97.5%) at 1000 K, respectively. Our analysis is in good agreement (see figure 4) with C_m values deduced from earlier C_p experiments below 300 K (Junod *et al* 1989; Loram *et al* 1989). Admittedly, the evaluation of C_m is based on assumptions which may introduce considerable absolute errors; we estimate the precision to be 50%. However, the fact that C_m tends to zero at high temperatures where the expected high

Figure 4. Magnet specific heat C_m and entropy (same scale as C_m and denoted 'S') of a CuO single crystal: and ——— this experiment; below 230 K our results are close to:----- results of Junod *et al* (1989) and ——— results of Loram *et al* (1989).

temperature value of S_m is reached gives support to our analysis. In addition, the total error of our analysis decreases with increasing temperature since the harmonic heat capacity approaches its high temperature limiting value and, therefore, becomes independent of the Debye temperature.

The temperature dependence of C_p and the related magnetic entropy unambiguously confirm the low dimensional character of magnetic interaction in the CuO spin system. Here we refer to the excellent review by de Jongh and Miedema (1974). A model of a linear spin- $\frac{1}{2}$ Heisenberg antiferromagnet ($H-af$), however, does not fit properly to our experimental results. In particular, the maximum value of magnetic specific heat, $C_m^{\max} = 2.8$ J/mol K, and its temperature, $T_{cp}^m = 600$ K, and the temperature of the susceptibility maximum, $T_x^{\max} = 600$ K, differ from the value predicted for a $H-af$, being: 3.48 J/mol K, 450 K and 600 K, respectively (Blöte 1974). A more satisfactory agreement is found for the XY -model (Katsura 1962) in which the spins are constrained to lie in one plane. This model requires $T_x^{\max} = T_{cp}^{\max} = 600$ K and $C_m^{\max} = 2.8$ J/mol K. The compound $\text{Co}(\text{N}_2\text{H}_5)_2 \text{SO}_4$ is an example which fits well to the calculated behaviour of the spin $\frac{1}{2}$ af XY linear chain model (Klaaijsen *et al* 1975). The above discussed susceptibility data (no critical behaviour along b -axis) is consistent with the XY -model. Szeto *et al* (1989) demonstrated that the magnetic properties of cupric oxide, the data of susceptibility and neutron scattering, can be explained best by the XY -model. In this picture T_{N1} is a minor effect which displays the tendency of the a - c plane to two-dimensional long-range ordering. On this two-dimensional background, a small out-of-plane coupling, which is superposed in any real system, may trigger the three-dimensional transition at T_{N2} and T_{N1} , respectively.

4. Conclusions

The anisotropy data for the susceptibility of a CuO single crystal below the Néel point suggest that the magnetic moments are oriented along the crystallographic b -axis. The calorimetric study ($1.5 \text{ K} < T < 1000 \text{ K}$) unambiguously demonstrates that more than 70% of the magnetic entropy is connected with short-range order processes, and that the ΔS_m -value, expected for a spin- $\frac{1}{2}$ system, is approached (97%) near 1000 K. The results favour the XY -model of magnetic interaction. We argue that some characteristic features of magnetic properties of CuO are displayed in HTSC; the magnetic interaction between Cu-ion sites in HTSC seems to be also low-dimensional and of short range, apparently a prerequisite for the occurrence of superconductivity.

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