

## SPECIFIC HEAT AND MAGNETIC ORDERING IN CuO SINGLE CRYSTALS

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### SUMMARY

We present measurements of the specific heat of single crystalline cupric oxide, CuO, in the temperature range 1.8 K to 1000 K and confirm the first order transition at  $T_1 = 213.8 \pm 0.3$  K and the second order anomaly (antiferromagnetic transition) at  $T_N = 229.8 \pm 0.3$  K, earlier found for powdered samples. Above 230 K, the specific heat contains significant magnetic contributions which decrease only above 700 K. Copper oxide displays the characteristic features of a one or two dimensional Heisenberg antiferromagnets. At low temperatures, the single crystal follows a  $T^3$ -law ( $\Theta_0 = 391 \pm 10$  K). The thermodynamic standard values at 298.16 K are given.

### INTRODUCTION

Among the monoxides of the 3d-transition elements, cupric oxide (natural tenorite) exhibits some unique structural and magnetic features. The lattice is built up of interleaved  $\text{Cu}_2\text{O}$  sheets with a characteristic square planar coordination of copper by oxygen (ref. 1), whereas the other oxides have octahedral coordination. The temperature dependence of the susceptibility follows neither a Curie-Weiss behaviour ( $\mu_{\text{eff}} = 0.6 \pm 0.1 \mu_B$ ) nor does it show a cusp at  $T_N$ , but, in the susceptibility, a broad hump was observed near 550 K (refs. 2,3). Although CuO has been investigated for nearly 50 years, its unusual magnetic properties are not yet fully understood. The recent development in high temperature superconductors, containing similar square planar coordinated  $\text{Cu}^{2+}$ , has generated new interest in this material.

In very early works on CuO by Millar et al. (ref.4) and Hu et al. (ref.5), poorly resolved anomalies were found in the specific heat near 230 K, and were attributed to the onset of antiferromagnetic (af) ordering. First neutron diffraction experiments by Brockhouse (ref.6) confirmed this suggestion. Recently, detailed neutron diffraction studies of single crystals by Forsyth et al. (ref.7) clarified the magnetic structure: an incommensurate af-structure forms between the Neel point at 230 K and a magnetic spin arrangement occurs at  $T_1 = 213$  K, below which CuO persists in a commensurate af-structure. Recently, Junod et al. (ref.8) and Loram et al. (ref.9) resolved both transitions in detail by specific heat measurements on powder samples. Both authors conclude that copper oxide behaves as one (1D) or two dimensional (2D) Heisenberg antiferromagnet (AF), for which a considerable part of short range magnetic order exists above  $T_N$  and a substantial amount of magnetic entropy (about 70%) is removed at higher temperatures. Nearly all known

structural, thermal and magnetic experiments and aspects of CuO have been summarized in the three latter papers (refs.7,8,9) and will not be recapitulated here.

We report on first experiments of the specific heat  $C_p$  of single crystalline CuO in the temperature range 1.8 K to 1000 K. The measured sample is identical to that investigated in ref.7. Our results, in the vicinity of the two magnetic transitions, essentially confirm  $C_p$ - data reported in refs.8,9, but we observe slightly higher transition temperatures and sharper transitions. Details on the low temperature data and on the measurements above 300 K are discussed only shortly and will be published elsewhere together with susceptibility data on single crystals (ref.10).

## EXPERIMENTS

The study was performed with two synthetic single crystals with total weight of 376.4 mg. The crystals were grown in a platinum crucible by the flux growth method as described by Wanklyn and Garrard (ref.11). Different types of calorimeters were used for the various temperature ranges: (i) a computer controlled adiabatic calorimeter below 80 K (ref.12), (ii) a low temperature, non-adiabatic, differential scanning calorimeter for the range between 60 K and room temperature (ref.13), and (iii) a commercial high temperature scanning calorimeter (ref.14) for temperatures above 320 K. The average total inaccuracies of the three calorimeters amount to .8% - 1.2%, 1% - 1.5% and 2% - 3%, respectively. The specific heat is shown in Fig.1 (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.

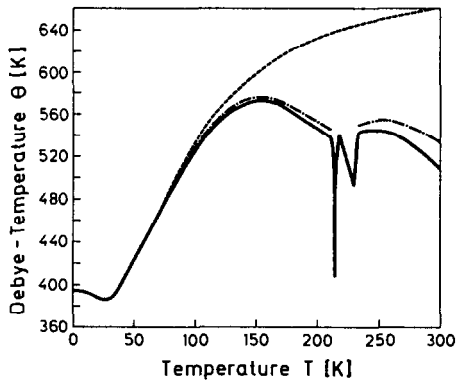


Fig.1 Debye temperature  $\Theta$  vs. T for single crystalline CuO, as calculated  
 — from the specific heat  $C_p - \gamma T$   
 - - - according to equ.1 from  $C_p - \gamma T$   
 . . . extrapolated from harmonic part according to a fit to equ.3

## RESULTS

### Experimental data

From the low temperature specific heat we deduce a nearly zero electronic term,  $\gamma = 0.1 \text{ J/mole K}^2$ , and a limiting Debye temperature,  $\Theta_0(0) = 391 \pm 10 \text{ K}$ . These results are in excellent agreement with the values indicated by Junod et al. (ref.8):  $\gamma < 0.05 \text{ mJ/mole K}^2$  and  $\Theta_0(0) = 390 \pm 0 \text{ K}$ , and those given by Loram et al. (ref.9):  $\gamma = 0.26 \text{ mJ/mole K}^2$  and  $\Theta_0(0) = 396 \text{ K}$ . In Fig. 2, our  $C_p$ -data near the two magnetic transitions are shown. For comparison, the data of refs.4,8,9 are also plotted (shifted  $C_p$  scale). The peak at  $T_1 = 213.8 \pm 0.3 \text{ K}$  marks a first order incommensurate /

commensurate phase transition and the anomaly at  $T_N = 229.8 \pm 0.5$  K (midpoint) is the onset of af-ordering, the Néel point. For the single crystals, both transitions are located at slightly higher in temperature ( $T_1 = 212.6 \pm 0.5$  K and  $T_N = 229.5 \pm 0.5$  K in ref.8, and 212 K and 230 K in ref.9, respectively) and the anomalies are higher and narrower than the earlier reported ones. The latent heat for the peak at  $T_1$  was determined to be:  $\Delta H = 7.96 \pm 0.25$  J/mole or  $0.00415 RT_1$  (R denotes the gas constant); for comparison  $\Delta H = 4.5$  J/mole and  $\Delta H = 4.8$  J/mole were reported in refs.8,9. The magnetic entropy removed below the Neel point is unusually small, namely only 33.2 % of the expected value of  $\Delta S = R \ln 2 = 5.96$  J/mole K.

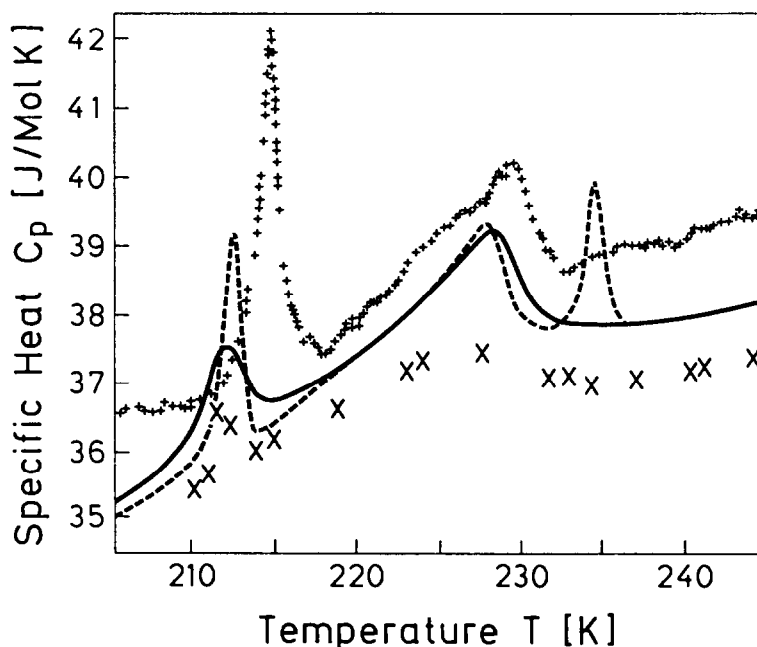


Fig. 2 Specific heat  $C_p$  vs.  $T$  in the vicinity of the magnetic transitions:  
 +++++ single crystal, present data  
 ——— results of ref.9 and - - - of ref.8, shifted in scale by  $-1$  J/mole K  
 xxxxx results of ref.4, shifted in scale by  $-2$  J/mole K

The results for the high temperature specific heat which are preliminary data up to 1000 K indicate a rather constant  $C_p$  above 350 K and display a small and broad maximum between 600 K and 700 K. Above 750 K,  $C_p(T)$  decreases until about 1000 K; at higher temperatures the sample starts to decompose into  $Cu_2O$ .

#### Thermodynamic.. calculations

The thermodynamic standard values at 298.15 K, as derived from our measurement, are listed in Tab.1, together with the values indicated in refs. 5 and 8. As our values agree, in particular, with the data of Hu et al. ( ref.5 ) within 1.5 %, we

note that the check of the third law of thermodynamics, the free energies of formation and the standard entropy of copper oxide, as calculated in detail in ref.2, are based on correct  $C_p$  - values.

TABLE 1

Thermodynamic functions at 298.16 K for cupric oxide (Molar weight: 79.55 g). All values are given in J/mole K

Specific heat $C_p$	Entropy $S^0$	Enthalpy $(H^0 - H_0^0) / T$	Ref.
	43.5	23.8	4
42.32	42.7	23.82	5
41.80	42.03	23.68	8
42.18	42.54	23.71	present data

### MAGNETIC SPECIFIC HEAT

Some unusual aspects of  $C_p(T)$  of CuO become obvious from figs. 1 and 2:

- (i) a substantially smaller  $\Delta C(T_N)$  than usually detected at the long range ordering point of spin-(1/2) systems,.
- (ii) an unexpected, small magnetic entropy below  $T_N$ , much smaller than found for other oxide materials, it amounts to 33.2% of the theoretically expected value.
- (iii) an unrealistic shape of the Debye temperature,  $\Theta(T)$  above  $T_N$ , and
- (iv) a decreasing heat capacity above about 700 K, which is in contrast to most other solids where  $C_p$  increases linearly due to anharmonicity.

Conclusions i) and ii) has yet been drawn in refs. 8, 9. In order to determine the magnetic specific heat,  $C_m$ , above  $T_N$ , we have to separate harmonic and anharmonic contributions of the phonons and so must construct the harmonic lattice heat,  $C_l$ . To this end, we employ the procedure developed for alkali halides by Barron et al. ( ref. 15). This procedure has been applied to many other materials ( see for example refs. 9, 16). Loram et al. (ref.9) analyse their  $C_p$  - data of CuO in the same way and give a very detailed description of the procedure. We refer to this paper for details. Briefly the steps in the calculation are as follows:

- Calculation of the effective Debye temperature  $\Theta_p(T)$  from measured  $C_p(T) - \gamma T$ , see fig.1, continuous line.

- Correction for anharmonicity:  $(C_p - C_v) = A C_v T$  ( 1 )

with  $A=1.35 (J/mole)^{-1}$  which, for reason of consistency, is the same value as estimated by Loram et al. ( ref. 9 ); this correction amounts to 1.6 % and the resulting  $\Theta_v(T)$  - curve is plotted in fig.1 as interrupted line.

Recalculate  $C_l$  by:  $C_l = C_v - \gamma T - C_m$  ( 2 )

where  $C_v$  at higher temperatures ( $T > T_N$ ) is calculated by extrapolation of  $\Theta_v(T)$  from the harmonic part at low temperatures to higher temperatures, using:

$$(\Theta_v)^{-2} = (\Theta_l)^{-2} * ( 1 + a (\Theta_l/T)^2 + b * (\Theta_l/T)^4 + \dots ) \quad ( 3 )$$

The continuous line in fig.3 shows a best fit for  $\Theta_1 = 691$  K,  $a = 0.0156$  and  $b = -3.66 \cdot 10^{-3}$  in the temperature range 57 K to 198 K with the assumption of a trial form for  $C_m = \beta T^3$  (with  $\beta = 1.85 \cdot 10^{-7}$  J/moleK<sup>4</sup>) in equ. (2) for  $T < 200$  K, as predicted and observed for 3D AF, sufficiently below  $T_N$ . The extrapolated  $\Theta_1(T)$  curve is displayed as dotted line in fig.1

- Convert  $\Theta_1$  into  $C_1$  and determine  $C_m (T > T_N)$  from equ. (1).

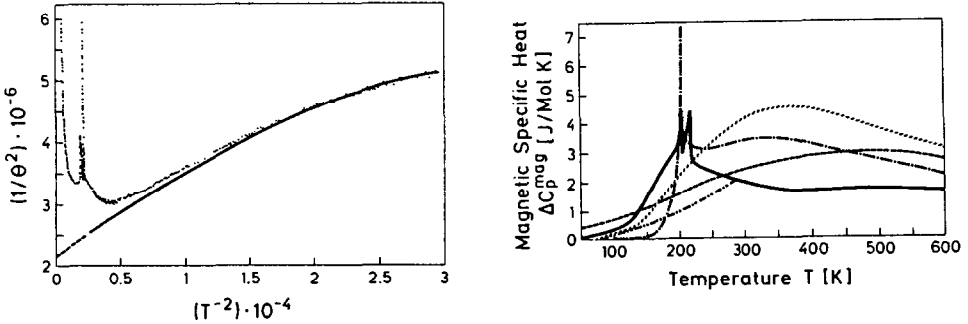


Fig.3 (left) Plot of  $1/\Theta^2$  vs.  $1/T^2$  for extrapolation of  $\Theta(T)$  from below  $T_N$ :  
 .....  $\Theta^v$  as calculated from  $C_v$   
 ———  $\Theta^v$  assuming a magnetic heat of  $C = \beta T^3$  below  $T$   
 - - - -  $\Theta_1$  extrapolation to above  $T_N$  by use of equ. 3

Fig.4 (right) Magnetic specific heat of CuO single crystals and theoretical values:  
 ——— experimental values as derived by the described analysis  
 - - - - 1D ( $S=1/2$ ) Heisenberg antiferromagnet (ref.17) for  $J/k=460$  K  
 - · - · 2D spin wave term (ref.18) for  $J/k=306$  K  
 · · · · 2D (square planar,  $S=1/2$ ) Ising model  
 · · · · · Schotky contribution calculated in the Cu cluster model (ref.4)

The magnetic specific heat, deduced by the above procedure, is plotted in fig.4 (continuous line). The present analysis agrees fairly well (50%) with the  $C_m(T)$  reported in refs. 8 and 9, where  $C_m$  was calculated either by using the density of states of phonons (ref. 8) or the same procedure, outlined above (ref.9). However, great care must be taken in interpretation of the absolute values of  $C_m$ . Note that the uncertainty of  $C_m$  becomes  $\pm 0.7$  J/mole K (at 300 K) which means nearly 50% error. The evaluation of  $C_m$  is strongly dependent on the fitting procedure, in particular the chosen temperature range for the harmonic part of  $C_v$ . Therefore, the differences between the  $C_m(T)$  values, given in refs. 8, 9 ( $C_m(300\text{ K}) = 1.9$  J/mole K and 2.5 J/mole K) and our data ( $C_m = 1.5$  J/mole K) are not surprising. According to our analysis the magnetic entropy at 300 K and 600 K amounts to  $\Delta S(300) = 2.62$  J/mole K and  $\Delta S(600) = 3.92$  J/mole K.

The existence of  $C_m$  - contribution above  $T_N$ , and up to 700 K seems to be well established. As it has been pointed out in refs. 8, 9, low dimensional magnetic coupling, in particular 1D or 2D Heisenberg AF (refs. 17,18) can explain the temperature dependence of  $C_m$  and  $\chi$ . Similar behaviour has been observed for some transition metal tatalates (ref. 20). For CuO the susceptibility  $\chi$  can be fitted

between 300 K and 1000 K to the theoretical curve of Bonner and Fischer (ref.17) for an ( $S=1/2$ ) 1D Heisenberg AF with  $J/k=460$  K and  $g = 2.21$ , or equally well to the high temperature series expansion of de Jongh and Miedema (ref.18) for a ( $S=1/2$ ) 2D (quadratic lattice) AF with  $J/k=306$  K. For reason of consistency, we have chosen the same values as used in ref.9. The corresponding magnetic heat capacities using the above  $J$ -values are plotted in fig. 4; the maximum heat capacity of  $C_m = 2.91$  J/mole K occurs near 440 K and 470 K, respectively. At present, we cannot discriminate between the 1D and 2D case. In addition, our preliminary  $C_p$ -data above 300 K locate the maximum of  $C_m$  at temperatures higher than expected from  $\chi$ -experiments, namely near 700 K to 800 K.

#### CONCLUSION

In conclusion, the study of the specific heat of CuO single crystals shows that there is no substantial difference with respect to powdered material. The magnetic transitions, near 214 K and 230 K, are slightly higher in their transition temperatures and more pronounced. New specific heat and entropy data above 300 K strongly favour the suggestion that CuO behave like a low dimensional (1D or 2D) ( $S=1/2$ ) Heisenberg antiferromagnet. More precise heat capacity measurements at higher temperatures are required and are being currently done.

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