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LETTER TO THE EDITOR

Magnetic transitions in cupric oxide: the effect of oxygen defects

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Abstract. The magnetic moment of high purity CuO powder was measured in the range 5 K–400 K using a SQUID magnetometer. T_N was determined to be $\simeq$230 K. A clear cusp is observed in the magnetic moment versus temperature curve at T_N, in contrast to reports in the literature which merely note a change in the slope of the curve at that temperature. We attribute this feature to the formation of oxygen defects in cupric oxide.

Cupric oxide has been subjected to a number of investigations in recent years because of its intimate relationship with high-T_c superconducting cuprates. CuO is an essential constituent of almost all the high-T_c systems discovered so far. There are reports of striking similarities in the magnetic properties of CuO and other cuprates like $YBa_2Cu_3O_x$ [1]. Both order antiferromagnetically at relatively high temperatures and show ordered magnetic moments of $\simeq 0.65\mu_B$, lower than what is expected of Cu^{2+}. Besides, as in the case of high T_c systems, oxygen stoichiometry is known to play an important role in influencing the magnetic properties of CuO [2]. Therefore, a study of this material, revealing the magnetic iterations between Cu and O, is of direct relevance to the understanding of high-T_c phenomena in cuprates.

The crystal structure of CuO is monoclinic and known to undergo a paramagnetic-to-incommensurate antiferromagnetic transition at a temperature $T_N \simeq 230$ K. This is followed by a incommensurate -to- commensurate antiferromagnetic transition at about $\simeq 213$ K [3]. The occurrence of the antiferromagnetic transition is explained in terms of spin coupling between two copper ions via an intervening oxygen ion along the $[\bar{1}01]$ direction. A number of previous investigations have shown that the susceptibility of CuO follows neither a Curie–Weiss behaviour, nor shows a cusp at T_N. Instead, it continues to rise above T_N showing a broad hump near 550 K [1]. Only a change of slope is noticed at T_N in the otherwise increasing χ against T curve. In order to account for the hump above T_N, it was argued that in addition to antiferromagnetic coupling, there is a formation of a singlet–triplet system (with two neighbouring Cu^{2+} ions of $3d^9$ configuration forming a singlet $S = 0$ ground state and a higher lying triplet $S = 1$ state) [4]. However, based upon diffuse neutron-scattering studies [5], it was suggested that the peak in susceptibility arises out of one-dimensional correlations along the Cu–O–Cu chains. This point of view was corroborated by magnetic susceptibility measurements on a single crystal of CuO [6]. It is believed that strong, oxygen-atom mediated, low-dimensional magnetic couplings are present in CuO until, at lower temperatures, the interactions along the remaining space directions are strong enough to drive the system into three-dimensional magnetic ordering. If this picture were valid, creation of oxygen defects should disrupt these low-dimensional magnetic couplings and it should be possible to see a Curie–Weiss behaviour above T_N. It is this feature that we address to in the present communication. Our results show that a clear cusp appears in the magnetic moment versus temperature curve at $T_N \simeq 230$ K and Curie–Weiss behaviour for $T > T_N$, when oxygen vacancies are presumably created in a sample of powder CuO, due to prolonged exposure to helium atmosphere having zero partial pressure of oxygen. It may be noted that oxygen deficiency is reported to have led to the breaking of magnetic correlations in quenched CuO pellets [2].

We have measured the temperature dependence of the magnetic moment of a high-purity cupric oxide powder (MERCK, 99%) using a SQUID magnetometer (Quantum Design, Model MPMS). Prior to the measurement, the powder was annealed in flowing oxygen at 600 °C for about 12 hours and slowly cooled to room temperature under the same atmosphere. This was to eliminate the possibility of any hydrated oxide being present and to have as near a stoichiometric compound as possible. The powder sample was first cooled to 5 K, a magnetic field of 2000 Oe applied and the magnetic moment of the sample measured as a function of temperature in the warming run. It was noted that the nature of the m against T curve of the annealed sample was similar to that of the unannealed sample, both being unexposed to the helium atmosphere during the measurement. To prevent the exposure, powder samples were wrapped up in thin PTFE tape. For subsequent runs, a fresh sample of CuO powder was taken in a quartz ampoule open at the top, resulting in exposure to helium environment throughout the measurement, running into hours.

The figure depicts the results of the SQUID measurements in the temperature range 5 K–400 K. The salient features that emerge from the figure are as follows.

(i) A clear cusp is evident at $\simeq 230$ K characterizing the paramagnetic–incommensurate antiferromagnetic transition. Incommensurate–commensurate antiferromagnetic transition may be noted on all the curves, as a change of slope, at $\simeq 212$ K (please refer to the inset). This is against the conclusion of an earlier susceptibility study [5] which rules out the possibility of this latter transition being seen in powder samples.

(ii) For a given temperature, the normalized magnetic moment increases with greater exposure to helium. Magnetic moment above T_N shows a greater tendency to fall off with temperature, while the moment for temperature region below $\simeq 180$ K tends to increase. The fall above T_N can be understood in terms of disruption of low-dimensional Cu–O magnetic correlations discussed above. The increase for the temperature range below $\simeq 180$ K can also be accounted by an identical argument. Vacancies in the oxygen sublattice lead to polarized Cu^{2+} ions whose magnetic moment deviates from the magnetization of the sublattice. This results in an appearance of a net moment [7].

(iii) Curie–Weiss behaviour is followed in the region 230 K–250 K, just above T_N. By plotting the inverse of magnetic moment against temperature for this region, we have calculated the effective magnetic moment on the copper ion. It increases from $0.66\mu_B$ for curve B to $0.73\mu_B$ for curve C and $0.75\mu_B$ for curve D.

(iv) The peak at T_N becomes broader and broader while the kink at $\simeq 212$ K more and more prominent. The ratio of the magnetic moments, m (212 K)/m (230 K), at the two temperatures increases with exposure to helium. This observation suggests that cupric oxide may directly undergo paramagnetic–commensurate antiferromagnetic transition around 212 K, provided sufficient number of oxygen vacancies are created.

(v) On the basis of the present study, *it can be clearly identified that the low temperature ($<\simeq 40$ K) rise in the magnetic moment is due to formation of oxygen vacancies*. This feature is barely seen in curve A and becomes more and more prominent from curve B to C. This report thus settles the controversy regarding the origin of this low-temperature feature, which defied agreement between various researchers [1]. However, further investigations

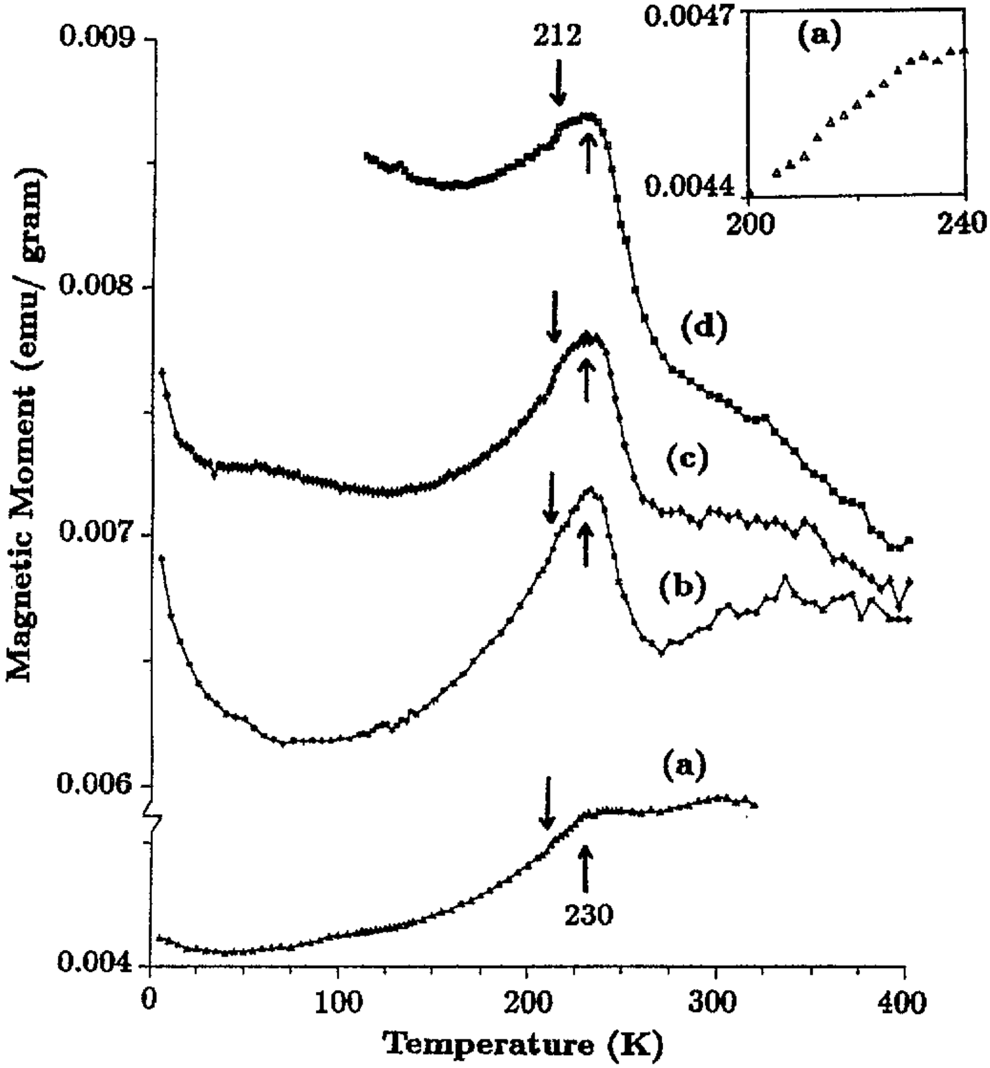

Figure 1. Temperature dependence of the magnetic moment of CuO powder exposed to a helium atmosphere for different durations. The duration t is the (approximate) time in hours for which the powder was exposed to the helium atmosphere before hitting a target temperature of $\simeq$ 230 K during the measurement. Curve A, unexposed; B, $t = 9$ hours; C, $t = 100$ hours; D, $t = 200$ hours. Magnetic field used for the measurement was 1000 Oe for curve A and 2000 Oe for others. In the case of curve D the measurement was carried out as the sample was cooling under the field. In all other cases the powder was first cooled to 5 K, magnetic field switched on and the measurement carried out as the sample warms up. Inset: a portion of curve A, showing the magnetic transitions at $\simeq$ 212 K and $\simeq$ 230 K.

are necessary to unravel the nature of magnetic interactions which give rise to the unusual increase of magnetic moment.

Finally, it must be emphasized that the features connected with oxygen deficiency reported here would not have shown up as conspicuously if, instead of a powder sample exposed to helium gas, other arrangements were used, such as wrapping the sample in

PTFE tape or encapsulating it or using a pellet etc. As regards to the studies on quenched CuO pellets reported in [2], it is possible that quenching has resulted in isolated oxygen vacancies, while regions of Cu–O–Cu chains are intact, so that the nature of m against T curve is similar to that of the untreated pellet.

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