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On the low-temperature magnetic properties of CuO single crystals

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Abstract. The origin and magnitude of a paramagnetic contribution to the CuO susceptibility at $T < 150$ K are studied by analysing electron paramagnetic resonance and static magnetic susceptibility measurements carried out on a set of CuO single crystals. This has allowed us to confirm a previous supposition about the behaviour of the susceptibility for $T < 150$ K. The asymptotic finite value of the susceptibility in the antiferromagnetic phase is also discussed by means of a crystal-field calculation which seems to rule out contributions to the local magnetic moments from incompletely quenched orbital angular moments of the Cu^{2+} ions. Preliminary magnetization measurements suggest the presence of weak ferromagnetism, which may explain the unusual behaviour of the CuO susceptibility.

1. Introduction

The magnetic properties of cupric oxide show unusual features which have not yet been fully explained. A transition to an antiferromagnetic (AF) phase with long-range interactions has been identified at about 230 K, but experimental evidence exists to indicate the presence of strong interactions of low dimensionality [1–3] well above this temperature. In fact, for $T > 230$ K, the magnetic susceptibility χ does not follow the typical paramagnetic behaviour $\chi = C/(T - \vartheta)$, but it increases with increasing temperature, forming a very large maximum above 500 K [4]. The presence of short-range AF correlations at $T > 230$ K has been confirmed by neutron diffraction measurements which have not detected, on the other hand, any presence of the paramagnetic phase [5].

Below 230 K the available χ data were obtained mainly on powder samples [2, 4, 6–9]. Only recently, χ measurements [10, 11] and neutron diffraction studies [5] have been made on single crystals allowing one to determine the anisotropic features of the magnetic structure and the direction of the local magnetic moments which are oriented along the crystallographic b axis of the CuO monoclinic lattice.

At temperatures lower than 150 K, there are discrepancies in both the experimental behaviour of χ and its interpretation; some workers have observed a stabilization of χ on a finite value [4], while others have detected the enhancement of χ on decreasing T, following typical paramagnetic behaviour [2, 6, 11, 12] whose magnitude varies from sample to sample. The paramagnetic behaviour superimposed on the AF phase has been attributed in some cases to an extrinsic contribution due to impurities [2]. However, the dependence of the magnitude of this contribution upon

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annealing and quenching treatments [12] restricts the type of paramagnetic species to those of intrinsic origin, which may be derived from defects about oxygen vacancies or Cu^{3+} ions. The presence of Cu^{3+} ions as a possible cause has been eliminated by studying the effects of Li^+ doping of CuO, which does not result in an intensified paramagnetic feature [11]. Thus, it seems likely that the paramagnetic contribution to the low-temperature susceptibility arises from non-AF ordered Cu^{2+} ions, but it is not clear whether these ions are present in the material at defect sites near oxygen vacancies, where the exchange interactions with the other ions should be lower [11, 12], or in superficial fine particles whose dimensions and dispersion should not allow long-range AF order [4]. These ions seem to be responsible for the weak electron paramagnetic resonance (EPR) signal, with a g-factor of about 2, observed for sintered powders of CuO [12]. Unfortunately more detailed information from EPR measurements on single crystals is not available.

Knowledge of the nature of these paramagnetic species and their influence on the susceptibility is important to extrapolate the asymptotic behaviour for $T \rightarrow 0$ of the magnetic ordered phase from the experimental data on χ at low temperatures. It has already been proposed that, in the direction along which the magnetic moments are AF aligned, χ does not go to zero on decreasing T [4, 10]. This behaviour has been tentatively attributed in [4, 10] to an unusual contribution from an incompletely quenched orbital moment of the Cu^{2+} ion to the susceptibility [10].

2. Experimental details

The present study has been carried out on CuO single crystals grown by the flux method described by Wanklin and Garrard [13]. In order to obtain appropriate samples and to perform different measurements, numerous single crystals were prepared. The starting reagents for the flux were MoO_3, V_2O_3 and K_2CO_3, all laboratory reagent grade. The CuO, supplied by Aldrich, was 99.999% pure. Great care was taken to minimize the thermal gradient in the platinum crucible. Prismatic single crystals with a parallelogram-shaped base were selected. The crystalline c axis is along the long dimension, while the large natural faces lay in the (110) planes.

Static magnetic susceptibility and magnetization measurements were carried out in the temperature range between 70 K and room temperature, on a Faraday magnetic balance in fields of about 6 kOe on samples of dimensions restricted to a few millimetres. The instrumentation sensitivity, for a fixed magnetic field value, is determined by the sensitivity in the measurements of force, of the order of 10^{-3} dyn, which results in a minimum detectable χ of about 10^{-8} cm^3 g^{-1}. The accuracy of the χ data, depending upon the errors in the field gradient value and in the calibration of the balance, is estimated to be about 10% of the final value. The χ anisotropy has been studied by performing measurements along three orthogonal directions: along the c crystal axis, along the direction orthogonal to the large natural faces ((110) planes), and perpendicular to the natural small faces.

EPR measurements have been performed in the X band (about 9.13 GHz) in the temperature range between 130 K and room temperature, for different static magnetic field directions with respect to the crystal axis. The modulation field, the microwave power and the sample position in the resonant cavity have been assumed to be constant throughout all the measurements in order to allow correct comparison between the signal intensities from different samples. The relative populations of the paramagnetic centres were determined from the intensity of the first derivative of the EPR absorption, having observed the same linewidth and lineshape from sample to sample, while their absolute values were estimated by comparison of the signal area with a standard.

3. Results and discussion

A set of CuO samples was analysed in the form of single crystals characterized by mass values between about 20 and 80 mg with different surface-to-volume ratios and surface qualities. We present in the following the results of EPR, susceptibility and magnetization measurements.

3.1. EPR measurements

The EPR spectra of the samples, extending from 0 to 8 kG to include a wide interval of g-values, show the presence of only one type of signal. The mean g-value, about 2.095, and the asymmetric lineshape (figure 1), independent of the orientation of the CuO crystals in the magnetic field, are typical of the signal of Cu^{2+} ions in amorphous oxides [14, 15]. The lack of angular dependence of the signal strongly suggests an origin not associated with the crystalline features of the material; in effect, the low value of 0.79 for the correlation factor between the EPR signal intensities and the sample masses (figure 2) means that there is no significant link between the EPR centres and the bulk properties of the samples, in contrast with that suggested by others [12]. Also, we have noted that the dependence of the intensity of the EPR signal from sample to sample is consistent with the differences in the surface quality, since more intense signals are detected in samples which have shown more superficial irregularities on microscopic analysis. The number of paramagnetic ions in the smoother sample has been estimated to be of the order of 10^{17}, the dimensions of the crystal being about 1 mm × 1 mm × 5 mm.

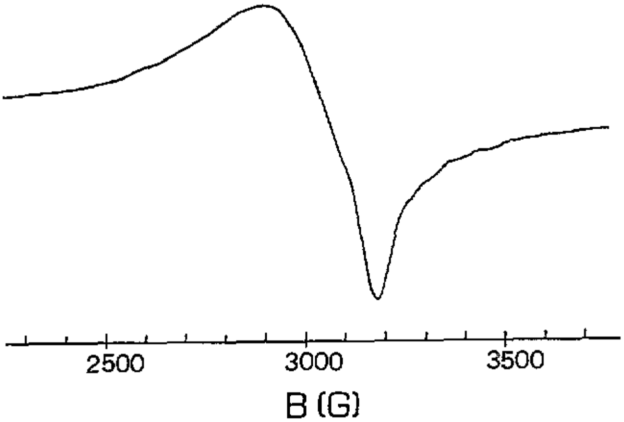

Figure 1. EPR derivative signal of a CuO single crystal irrespective of the orientation with respect to the magnetic field.

The temperature behaviour of the EPR signal intensity, proportional to the paramagnetic contribution χ_P to χ, arising from the EPR centres, shows a $1/T$-dependence (figure 3), as in the case of a perfect paramagnet with diluted magnetic moments without any evidence of magnetic correlations (as indicated by the intercept of the inverse EPR intensity curve). The weak anomaly in the thermal dependence of the EPR intensity that we detected in the region of the AF transition simply reflects the change in the Q-factor of the resonant cavity of the EPR spectrometer due to the change in the sample bulk properties.

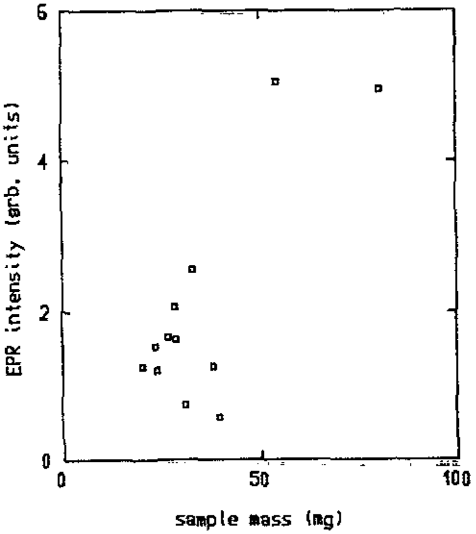

Figure 2. EPR signal intensities versus sample masses for different CuO single crystals.

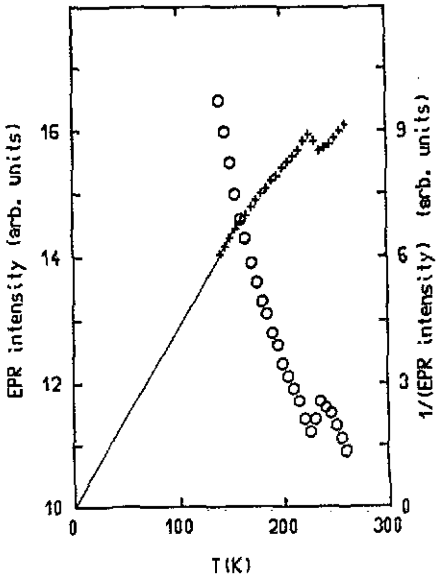

Figure 3. Temperature dependence of the EPR intensity (○) and its reciprocal (+).

3.2. *Low-T paramagnetism*

The susceptibility behaviour in one of the analysed crystals, along the three directions of the macroscopic dimensions is shown in figure 4. The χ anisotropy is of the same type as observed in [11], but we detected a weaker low-T paramagnetic feature. In order to subtract this χ_P contribution from χ, and to extract the true behaviour of the susceptibility χ_{AF} in the AF phase, it is necessary to make an independent estimate of the magnitude of the paramagnetic effect if previous knowledge of the AF behaviour is lacking. Therefore we have compared EPR data with χ curves, observing a more intense EPR signal, from non-AF ordered Cu^{2+} ions, in samples which show at $T < 150$ K a more pronounced paramagnetic behaviour. Figure 5 shows the χ curves for a sample whose EPR-active Cu^{2+} ion concentration is about 10^{21} cm^{-3}. This concentration should give rise to a paramagnetic contribution χ_P to the total χ of about 10^{-6} cm^3 g^{-1} at $T = 80$ K, as calculated from the Curie relation

$$\chi_P = n\mu^2 g^2 s(s+1)/3\rho kT \tag{1}$$

where $s = \frac{1}{2}$, n is the number of spins for unit volume, μ is the Bohr magneton, $g \simeq 2$, k is the Boltzmann constant and $\rho = 6.4$ g cm^{-3} is the density of the material. In figure 5 the corrected curves are also shown, after subtraction of the paramagnetic contributions calculated from the EPR signals. This result supports the previous supposition [10] that the $\chi_{\rm AF}$ in the direction of AF spin alignment tends to a finite value for $T < 100$ K.

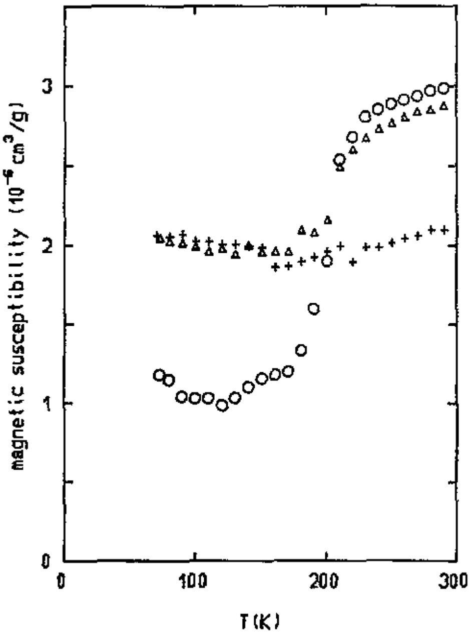

Figure 4. Magnetic susceptibility of CuO single crystals: +, $\boldsymbol{H}\|c$; ○, $\boldsymbol{H}$ orthogonal to the large natural {110} faces; △, $\boldsymbol{H}$ along the third orthogonal direction, perpendicular to the small natural faces.

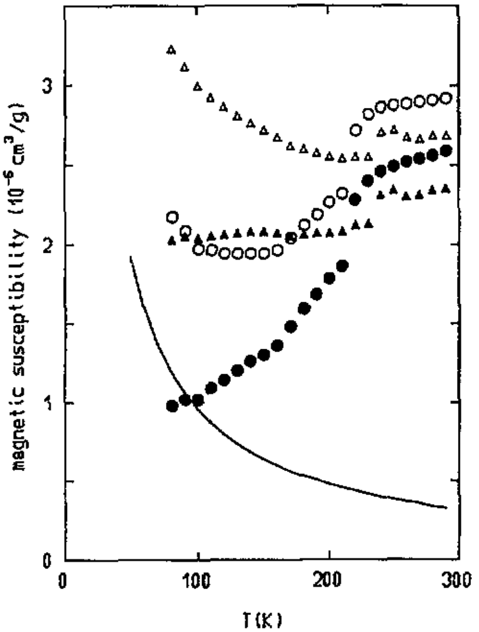

Figure 5. Magnetic susceptibility: ○, ●, $\boldsymbol{H}$ orthogonal to the large {110} faces; △, ▲, $\boldsymbol{H}$ orthogonal to the small faces; ○, △, before subtraction of the paramagnetic contribution from EPR data; ●, ▲, after subtraction of the paramagnetic contribution from EPR data; ——, paramagnetic contribution.

3.3. AF *susceptibility*

The low-temperature $\chi_{\rm AF}$ in the direction along which the moments are aligned does not show the usual AF behaviour which consists in susceptibility which decreases to zero for $T = 0$. The finite value of $\chi_{\rm AF}$ for $T < 100$ K has been tentatively interpreted [10] as due to a contribution from the incompletely quenched orbital moment of the $\rm Cu^{2+}$ ion to the magnetic moments. As these moments are not pure spins, they do not result in compensation of the magnetizations of the AF sublattices by decreasing the temperature to zero. This proposal has been made in analogy with the case of CoO which shows the same unusual low-T features of $\chi_{\rm AF}$. However, it should be noted that in CoO the orbital contribution to the magnetic moments arises from the presence of a triple orbitally degenerate ground state [16] which would be quite unexpected in $\rm Cu^{2+}$ ions. On the other hand, electronic configurations with an orbital singlet in the ground state must have a zero expectation value of the orbital moment in the direction of the magnetic field [17], while orbital doublets would be split by the Jahn–Teller effect, also resulting in a non-degenerate ground state.

Starting from the parameters of the lattice structure of CuO [18], we have carried out a crystal-field calculation in order to determine, almost as a first approximation, the probable energy level structure of the Cu^{2+} ion in CuO. Owing to the highly distorted local configuration of the copper ion with respect to the regular octahedral configuration, we have avoided the weak-perturbation formalism and we have calculated *ab initio* both crystal-field effects and spin–orbit coupling. The spin–orbit constant is taken to be equal to $-710\ \mathrm{cm}^{-1}$ including a reduction factor due to covalency [17]. The Hamiltonian is expressed in terms of the Stevens equivalent operator $\mathcal{O}_{nm}$ in the form [19]

$$\mathcal{H}_{nm} = (-e) \sum_{nm} F_{nm} \mathcal{O}_{nm}$$

with

$$F_{nm} = a_{nm} c_{nm} \vartheta_n \langle r^n \rangle \tag{2}$$

where the terms $c_{nm} = \sum_j [4\pi/(2n+1)] q_j Z_{nm}(r_j)/R_j^{n+1}$ have been calculated as a function of the anionic coordinates R_j and in terms of the tesseral harmonics by which the crystal-field potential has been expressed while a_{nm} are the numerical factors which multiply the Cartesian functions f_{nm} in the expression of the tesseral harmonics $Z_{nm} = a_{nm} f_{nm}(x, y, z)/r^n$, ϑ_n are the Stevens multiplicative factors and $\langle r^n \rangle$ is the expectation value of r^n for the wavefunction of the Cu^{2+} $3d^9$ electron. In table 1 the wavefunctions of the 3d manifold are listed with their energies. At the ground state there is a Kramers doublet consisting of an orbital singlet of the type $\alpha|2\rangle + \beta|-2\rangle$, 0.37 eV lower than the first excited state. It should be noted that the small temperature changes in the cell parameters of the crystal structure between low temperatures [5] and room temperature [18] are negligible in the adopted approximation. Such an energy level structure does not match the proposed mechanism of orbital contribution to the magnetic moment of Cu^{2+} ions invoked to explain the unexpected low-T behaviour of χ_{AF}.

Table 1. Energy levels and wavefunctions for the 3d multiplet of Cu^{2+} in the sixfold-coordinated configuration of the Cu sites in CuO with spin–orbit coupling $\lambda = -0.088$ eV.

E (eV)	Eigenstates
$+0.42$	$0.72\vert -1, \frac{1}{2}\rangle - 0.69\vert 0, -\frac{1}{2}\rangle$ $-0.69\vert 0, \frac{1}{2}\rangle + 0.72\vert 1, -\frac{1}{2}\rangle$
$+0.25$	$0.99\vert 1, \frac{1}{2}\rangle - 0.16\vert 2, -\frac{1}{2}\rangle$ $-0.16\vert -2, \frac{1}{2}\rangle + 0.99\vert -1, -\frac{1}{2}\rangle$
$+0.21$	$-0.69\vert -1, \frac{1}{2}\rangle - 0.72\vert 0, -\frac{1}{2}\rangle$ $-0.72\vert 0, \frac{1}{2}\rangle - 0.69\vert 1, -\frac{1}{2}\rangle$
-0.25	$-0.52\vert -2, -\frac{1}{2}\rangle + 0.15\vert 1, \frac{1}{2}\rangle + 0.84\vert 2, -\frac{1}{2}\rangle$ $-0.84\vert -2, \frac{1}{2}\rangle - 0.15\vert -1, -\frac{1}{2}\rangle + 0.52\vert 2, \frac{1}{2}\rangle$
-0.62	$0.85\vert -2, -\frac{1}{2}\rangle + 0.52\vert 2, -\frac{1}{2}\rangle$ $0.52\vert -2, \frac{1}{2}\rangle + 0.85\vert 2, \frac{1}{2}\rangle$

Really, the finite low-T value of χ_{AF} may be accounted for by the presence of weak ferromagnetism due to spin canting, as is often observed in AF compounds with a large anisotropy, e.g. CuO and in particular rare-earth copper oxides [20]. In order to verify the presence of such an effect, we have performed magnetization measurements along the monoclinic a axis. We have found a non-linear dependence in the initial magnetization, followed by a linear behaviour at magnetic fields higher than about 1 kOe, with a negative intercept on the magnetic field axis of about 540 Oe (figure 6). This value, obtained by extrapolating the linear behaviour of the magnetization back to zero local magnetic moment, represents an internal field which shows possible weak ferromagnetism. This may arise from spin-canted AF domains whose orientation is achieved by a very small external magnetic field. In fact our data do not show any clear evidence of hysteresis but such an effect may be masked in the experimental error. This agrees with the fact that other cupric oxides seem to be characterized by very weak coercivity effects [20].

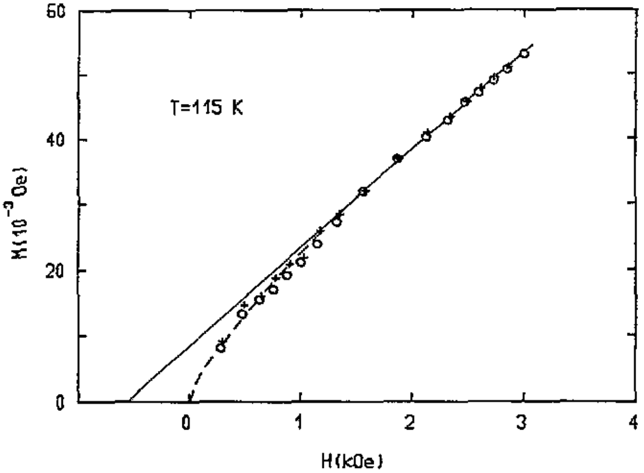

Figure 6. Magnetization of a CuO single crystal in the (100) direction with increasing (○) and decreasing (+) magnetic field.

Our preliminary experimental evidence of weak ferromagnetism in CuO may then explain the low-T behaviour of χ_{AF}, even if further confirmation is needed, especially from other spectroscopic techniques.

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