Magnetic properties of single-crystal and polycrystalline CuO

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The magnetic susceptibility of single crystals and polycrystalline samples of $CuO_{1-\delta}$ and $Cu_{0.99}Li_{0.01}O$ has been studied over a temperature range including $T_N \approx 230$ K. The anomalous behavior of $\chi(T)$ and the anisotropy which are observed are discussed in connection with a quasi-one-dimensional nature of the system and the possible formation of singlet Cu^{2+}–Cu^{2+} pairs.

In the CuO-based high-T_c compounds, Cu–O–Cu exchange interactions may play an important role in the formation of Cooper pairs,[1,2] so the magnetic properties of CuO are of substantial research interest. The present letter reports a study of the temperature dependence and anisotropy of the magnetic susceptibility of polycrystalline samples and single crystals of CuO of various degrees of defectiveness, in some cases doped with lithium, over the temperature range 56–600 K. There have been no previous reports of data on the magnetic properties of single crystals. The measurements were carried out on a Faraday magnetic balance in fields up to $H = 10^6$ A/m.

Single crystals of CuO with dimensions up to $3\times2\times8$ mm were grown from molten solutions. They were elongated parallelepipeds with c axis running along the long dimension. The large natural faces lay in the (110) plane. Polycrystalline samples of CuO and $Cu_{1-x}Li_xO$ were synthesized by annealing pressed tablets at 950° for 50 h and then at 500 °C in flowing O_2 for 20 h. An x-ray analysis revealed the CuO samples to have a monoclinic structure with the parameter values $a = 0.4706$ nm, $b = 0.3424$ nm, $c = 0.5117$ nm, and $\beta = 99°30'$.

Below $T_N \approx 230$ K, CuO is[3] a three-dimensional collinear antiferromagnet, but the behavior $\chi(T)$ is quite different from the behavior typical of Néel antiferromagnets. Specifically, above T_N, the susceptibility χ initially increases; it goes through a rounded maximum at ~ 550 K and then decreases. In the region $T \lesssim T_N$, there is an unexpected sharp increase in χ as T is lowered from ~ 65 K. This increase was attributed by O'Keeffe and Stone[4] to the presence of vacancies in the CuO cation sublattice and to a corresponding appearance of Cu^{3+} ions. If this explanation is valid, stoichiometric CuO should not exhibit this anomaly, and doping CuO with lithium ions should intensify it.

Figure 1 shows the behavior $\chi(T)$ at $H = 7.7\times10^5$ A/m for polycrystalline CuO (analytic purity) before and after annealing in flowing O_2 and for a $Cu_{0.99}Li_{0.01}O$ single crystal ($x \approx 0.01$: the solubility of Li in CuO). The CuO was annealed in order to reduce the concentration of oxygen vacancies. The temperature of the slope change on the $\chi(T)$ curve, which corresponds to T_N, shifts down the T scale in $Cu_{0.99}Li_{0.01}O$.

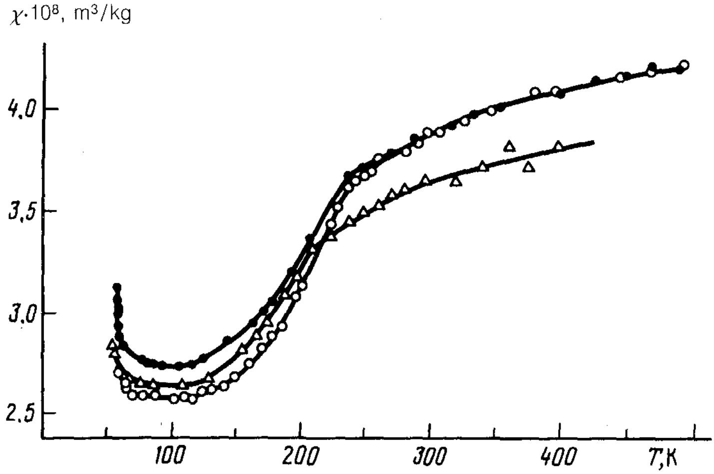

FIG. 1. Temperature dependence of the magnetic susceptibility of polycrystalline samples. ●—CuO before annealing; ○—CuO after annealing in flowing O_2; Δ—$Cu_{0.99}Li_{0.01}O$.

For all three samples we observe an increase in χ at $T < 65$ K. Annealing in O_2 results in a decrease in χ below T_N.

Zuo *et al.*[5] attribute the sharp increase in χ with decreasing T to the finely dispersed nature of the samples. If that explanation is valid, single crystals should not exhibit an increase in χ. We carried out measurements on several single crystals in the orientation $H \perp (110)$. For this H direction, the behavior $\chi(T)$ is similar to that found for the polycrystalline samples, but there are also several distinctive features. In the single crystals with a pronounced defectiveness, the maximum shifts down the temperature scale, $300 < T_{max} < 550$ K. In the region $T < T_N$ we see an anomalous growth of χ with decreasing T in all of the single crystals. This growth begins at higher temperatures, $T > 65$ K, than in the nonstoichiometric polycrystalline samples. The main reason for the increase in χ with decreasing T, in both the single crystals and the polycrystalline samples of CuO, appears to be a frustration of the exchange interaction between Cu^{2+} ions because of the defects.

Vacancies in the oxygen sublattice can lead to a strong exchange interaction between a defect and nearest Cu^{2+} ions and to their polarization, with the result that the magnetic moment of these ions deviates from the magnetization direction of the sublattice. The result should be the appearance of a net moment. The field dependence of the magnetization at $T < T_N$ indicates a slight ferromagnetic moment, similar to that[6] in the case of La_2CuO_4. At $T = 300$ K, the $\sigma(H)$ dependence is linear and extrapolates to the origin, but at $T = 56$ K we find $\sigma = \sigma_0 + \chi H$, where $\sigma_0 = 10^{-3}$ $A \cdot m^2/kg$.

A distinctive feature of three-dimensional antiferromagnetic single crystals is the pronounced anisotropy of χ along the principal magnetization directions at $T < T_N$, while there is no such anisotropy in the paramagnetic state. Figure 2 shows curves of

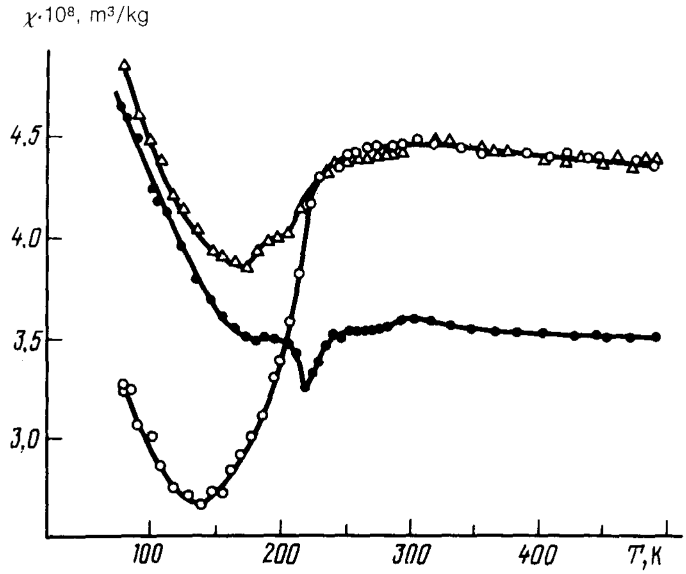

FIG. 2. Temperature dependence of the magnetic susceptibility of a CuO single crystal for various directions of H. ●—$H \| c$; ○—$H \perp (110)$ (large face); Δ—$H \perp (110)$ (small face).

$\chi(T)$ for a CuO single crystal annealed in flowing O_2 for the cases in which H was directed parallel to the c axis and perpendicular to the (110) faces. If the spin of the Cu^{2+} ions is directed along the b axis,[3] the measured value in the orientation $H \| c$ corresponds to $\chi_\perp$. For this direction of H, all of the single crystals exhibit a slight minimum in χ below T_N. This minimum appears to correspond to a second peak in the specific heat at $T = 212$ K (Ref. 8). For the two other directions of H, the susceptibility is determined by the sum of the components $\chi_\|$ and $\chi_\perp$.

In the paramagnetic region, the curves of $\chi(T)$ for the different orientations of the single crystal are again different. This result is evidence of a pronounced anisotropy of the magnetic properties not only at $T < T_N$ but also at $T > T_N$. The anomalous behavior of $\chi(T)$ above T_N may be a consequence of a competition between two tendencies: a decrease in χ in accordance with the Curie-Weiss law and an increase in χ due to excited triplet states of Cu^{2+} pairs.[5] In many compounds, Cu^{2+} ions form two-center complexes with $S = 0$ (a singlet state). The excitation energy of such a pair is comparatively low in CuO, and even at $T \approx 100$ K triplet pairs with $S = 1$ might appear. Their number would increase with increasing T, and χ would also increase. In the quasi-two-dimensional antiferromagnets La_2CuO_4 and $YBa_2Cu_3O_6$, χ decreases above T_N since the excitation energy is higher than that for CuO, and the number of triplet pairs which appear is insignificant.

Another reason for the anomalous behavior of χ might be a quasi-one-dimensional nature of the system. The magnetic structure of CuO may be described as chains of Cu^{2+} ions along the [101] direction with a strong antiferromagnetic coupling in the chain (I_1) and a weaker ferromagnetic exchange between chains (I_2). The interaction within a chain occurs through a Cu–O–Cu bond with an angle of 146°. The distance between nearest Cu^{2+} ions belonging to different chains is slightly smaller (0.289 nm) than the distance within a chain (0.328 nm), but the Cu–O–Cu angle is close to 90°. The relation between I_1 and I_2 is important. At high T, CuO behaves as if it were a one-dimensional system, while a lowering of T puts it in a three-dimensional antiferromagnetic state. The singlet state is the ground state for not only a pair but also a linear chain of spins.[7] The existence of a short-range order in CuO above 230 K is confirmed by data on magnetic neutron diffraction and on the specific heat.[3,8] Since an anisotropy of the susceptibility is observed above T_N, a description of the magnetic properties of CuO requires the incorporation of an Ising (anisotropic) term along with the Heisenberg term in the Hamiltonian. With increasing anisotropy, the $\chi(T)$ maximum should shift down the T scale, in agreement with data on the nonstoichiometric single crystals in the orientation $H\perp(110)$. We know that single pairs can form Cooper pairs if they are highly mobile.[2] In contrast with the situation in CuO-based high-T_c compounds, the mobility and concentration of free charge carriers in CuO, as in other oxides of $3d$ transition elements, are low, and pairs with $S=0$ are highly localized.

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