The CuO single crystal: anomalies in the thermal expansion and the magnetostriction

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Several anomalies have been observed in the thermal expansion and magnetostriction of CuO single crystals. These anomalies indicate a short-range magnetic order near $T_{N_1} \approx 230$ K and the existence of a new critical-behavior temperature, $T_0 \approx 203$ K. Near this temperature, field-induced magnetic phase transitions are observed. The low-temperature anomalies in $\Delta l/l$ and $\lambda(T)$ are linked with an involvement of copper–oxygen holes.

Copper (II) oxide, CuO, has attracted interest for two reasons. First, it is one of the simplest oxides of 3*d* elements. Second, it contains a structural element—the CuO_4 cluster—which is a basic structural element of a wide range of high-T_c superconductors based on copper oxides. For this reason, CuO can be thought of as a sort of model system for studying the semiconducting phase of the corresponding superconductors. The compound CuO has a monoclinic lattice C_{2h}^6. According to neutron diffraction,[1] it is an antiferromagnet with an intermediate helicoidal structure at $T_{N_2} \approx 213$ K $\leqslant T \leqslant T_{N_1} \approx 231$ K and a collinear structure at $T < T_{N_2}$. At high temperatures, $T > T_{N_1}$, CuO has reduced-dimensionality spin correlations.[1,2]

We measured the thermal expansion $\Delta l/l$ and the magnetostriction λ of a CuO single crystal in the temperature range 4.7–267 K with the help of a strain-gauge dilatometer (with a sensitivity no worse than 5×10^{-7}). The CuO single crystals, with dimensions up to $3 \times 2 \times 8$ mm, were grown from molten solution. They were long parallelepipeds with *c* axis running along the long edge. The large natural facets were in the (110) plane.

Curves of $\Delta l/l = f(T)$ and $\lambda(H)$ were recorded on an *x,y* chart recorder. The temperature was varied at a rate of 1 K/min. The thermal expansion and the magnetostriction were measured along the *c* axis of the crystal. The magnetic field was applied either along the *c* axis (this was the longitudinal geometry, $\lambda_\parallel$) or perpendicular to it (the transverse geometry, $\lambda_\perp$).

The temperature dependence of the thermal expansion $(\Delta l/l)_c$ is anomalous (Fig. 1), indicating a large magnetic component of exchange origin, with a characteristic structural feature over a broad temperature range near T_{N_1}. The absence of an anomaly in $\Delta l/l$ at T_{N_1} itself is evidence that a short-range magnetic order is dominating the temperature dependence of the thermal expansion.

Interestingly, the magnetic phase transition at $T = T_{N_2}$ from a helicoidal magnetic structure to a collinear magnetic structure is accompanied by essentially no

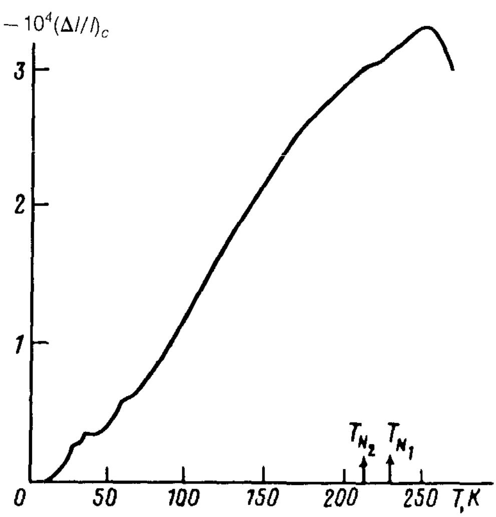

FIG. 1. Temperature dependence of the thermal expansion $(\Delta l/l)_c$ of a CuO single crystal.

distinct anomaly in the thermal expansion, if we ignore the small structural feature on the temperature dependence of $\Delta l/l$ over a fairly wide region ($\sim$200–220 K) near T_{N_2}.

The nonmonotonic temperature dependence of the thermal expansion below $T\sim 100$ K is probably analogous to the anomalies which have been observed in the low-temperature behavior of the magnetic susceptibility[2] of the same samples.

Holes in the copper–oxygen system, like the holes in the copper oxides $La_{2-x}Sr_xCuO_4$ and $YBa_2Cu_3O_{7-\delta}$ (the classic high-T_c superconducting systems), may be responsible for the structural features in the low-temperature behavior of the thermodynamic properties of CuO. Although their density is low ($\sim 10^{19}$ cm^{-3}), their contribution to the thermal expansion may be substantial in the case of the strong electron-vibrational interaction which is characteristic of holes in oxides of copper.

The magnetostriction of CuO is slight: Neither $\lambda_{\parallel}$ nor $\lambda_{\perp}$ exceeds $\sim(1–3)\times 10^{-6}$ in a field $H=43$ kOe.

The temperature dependence $\lambda(T)$ is very unusual (Fig. 2). Instead of the essentially constant temperature-independent magnetostriction in the region of saturation of the magnetic subsystem, there are sharp changes in $\lambda_{\parallel}$ and $\lambda_{\perp}$ below $T\sim 60$ K in CuO. The magnetostriction in fact changes sign at $T\sim 10$ K. There is also a nearly hyperbolic increase in their absolute value as the temperature is lowered further. This behavior of the CuO magnetostriction agrees with the anomalous increase[2] in $\chi(T)$ as the temperature is lowered below $T\sim 60$ K. This behavior may be due to copper–oxygen holes and magnetic centers which they form.

The field dependence $\lambda(H)$ is the characteristic quadratic dependence in essentially the entire temperature range studied, except in a narrow region near $T_0\approx 203$ K. At $T\sim T_0$, there are some clearly defined anomalous regions on the magnetostriction isotherms (Fig. 3, a and b). These anomalous regions are characteristic of field-

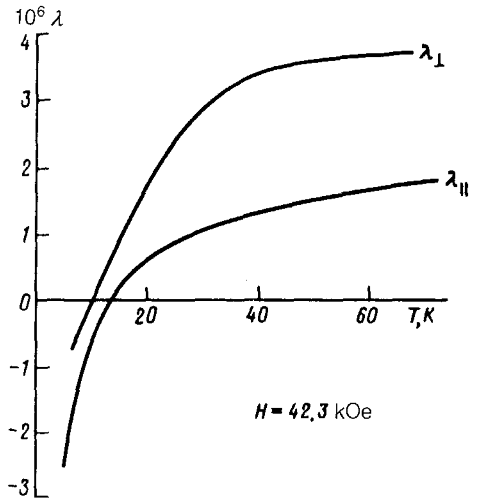

FIG. 2. Temperature dependence of the magnetostriction $\lambda_\parallel$ and $\lambda_\perp$ of a CuO single crystal.

induced spin–flip transitions in several antiferromagnets (e.g.,[3] $DyFeO_3$), with a hysteresis and a possible manifestation of an antiferromagnetic domain structure.

Interestingly, the temperature $T_0 \approx 203$ K is also the temperature at which the curves of the magnetic susceptibilities as a function of the temperature "cross"[4] χ_b and χ_c ($\chi_b = \chi_c$ at $T = T_0$). This fact is indirect evidence of a sort of "softening" of the magnetic subsystem of CuO near T_0. Further research will be required in order to find

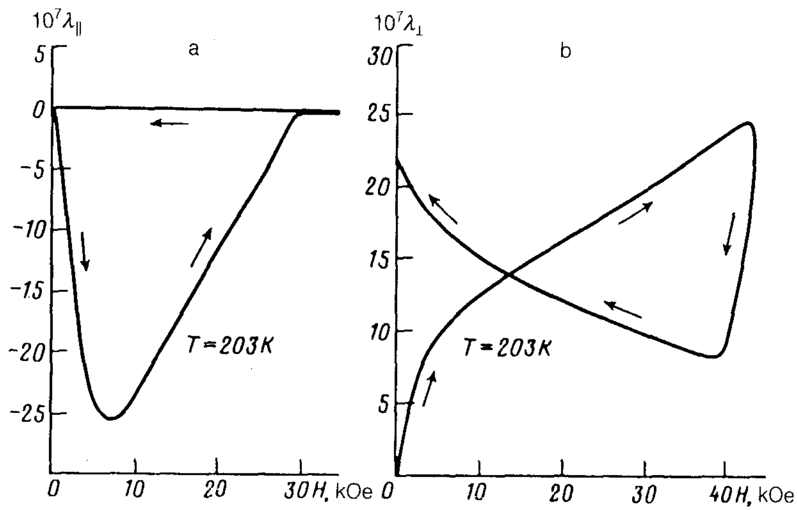

FIG. 3. Field dependence of the magnetostriction of a CuO single crystal at $T = 203$ K. a—$\lambda_\parallel$; b—$\lambda_\perp$.

a correct interpretation of the phase transition, induced by an external magnetic field, which we have observed.

[1] J. B. Forsyth, P. J. Brown, and B. M. Wanklyn, J. Phys. C **21**, 2917 (1988).
[2] T. I. Arbuzova, A. A. Samokhvalov, I. B. Smolyak *et al.*, Pis'ma Zh. Eksp. Teor. Fiz. **50**, 29 (1989) [JETP Lett. **50**, 34 (1989)].
[3] A. K. Zvezdin, I. A. Zorin, A. M. Kadomtseva *et al.*, Zh. Eksp. Teor. Fiz. **88**, 1098 (1985) [Sov. Phys. JETP **61**, 645 (1985)].
[4] U. Köbler and T. Chattopadhyay, Z. Phys. B **82**, 383 (1991).

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