Magnetic properties of La_2CuO_{4-y} with La^{3+} deficiency and with magnetic impurities

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In magnetic fields $H \approx 50$ kOe oriented along one of the twofold axes (a or c) of single crystals, a nonlinear increase in the magnetic moment of the sample with increasing H has been observed. This increase can be explained on the basis of a rotation of the antiferromagnetic vector **L** in antiferromagnetic crystals.

The magnetic properties of polycrystalline and single-crystal samples of the compound La_2CuO_{4-y} are at present the subject of active research. It has been shown[1,2] that, depending on the oxygen concentration and the concentrations of ions such as Sr which substitute for La, this compound may go into an antiferromagnetic state, a spin-glass state, or a superconducting state. It has been shown by neutron diffraction[3] that the magnetic moments of La_2CuO_{4-y} are oriented in Cu–O or a–c planes of the crystals, along one of the twofold axes. Figure 1 shows the unit cell of this compound.

Our purpose in the present study was to determine how the magnetic moments and magnetic susceptibilities of La_2CuO_{4-y} samples depend on the magnetic field and the temperature. Using a magnetometer with a vibrating sample which was capable of measuring the three mutually perpendicular components of the magnetic moments of the samples,[4] we studied the $M_{x,y,x}(H)$ dependence over the range of magnetic fields H up to 65 kOe at temperatures to 100 K. We used a Faraday balance to study the behavior of the magnetic susceptibilities of the samples in a magnetic field $H = 8$ kOe over the temperature range from 4.2 K to 300 K. The polycrystalline La_2CuO_{4-y} samples contained no additional impurities. The three La_2CuO_{4-y} single crystals had an approximately 0.1% concentration of other ions of various metals (primarily Fe^{3+}). Furthermore, a chemical analysis showed that in the single crystals which were studied the concentration of La^{3+} was lower, and that of oxygen higher, than the concentration which would be required stoichiometrically, and these single crystals can be described by the formula $La_{2-x}CuO_{4-y}$, where $x \approx 0.1$ and[3)] $y \approx -0.2$. These imperfections of the single crystals are attributed to difficulties in growing them.

The temperature of the phase transition of these samples to an antiferromagnetic state was found from the maximum on the temperature dependence of their magnetic susceptibility. Figure 1 shows the temperature dependence of the magnetic susceptibilities of the single crystals and polycrystalline samples of La_2CuO_{4-y}. In the measurements of $\chi(T)$ of the single crystals, the magnetic field was oriented along the twofold b axis (see the inset in Fig. 1). It can be seen from line 1 in Fig. 1 that at temperatures $T < T_N \approx 200$ K the magnetic susceptibility of the polycrystalline samples is essentially independent of the temperature, except at $T < 30$ K, where there is a slight paramag-

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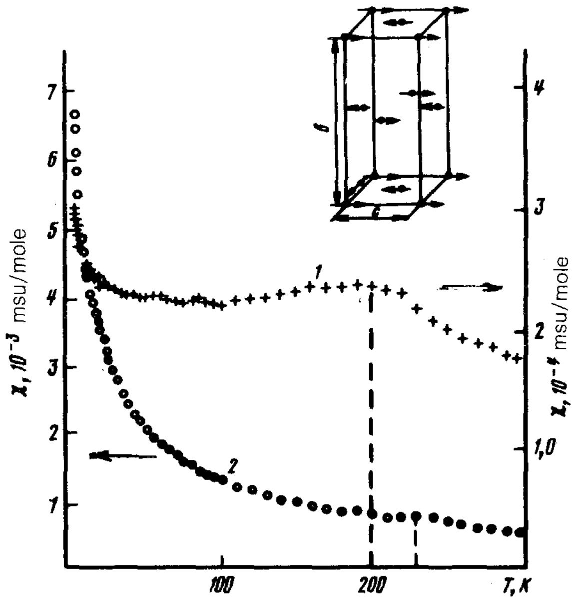

FIG. 1. Magnetic susceptibilities of (+) polycrystalline samples and (O) single-crystal samples versus the temperature.

netic increase in $\chi(T)$, related to a possible slight imperfection of the polycrystalline samples. Curve 2 in Fig. 1 shows the temperature dependence of the magnetic susceptibility of the single crystals. This dependence is markedly different from the $\chi(T)$ curve of the polycrystalline samples, in that the paramagnetic growth of the susceptibility is observed as early as $T < T_N$. At temperatures $T = T_n = 200$ K, we see a structural feature on the $\chi(T)$ curves of the single crystals, which indicates that they are in an antiferromagnetic state at $T < T_N$. The increase in the magnetic susceptibility below T_N can be described bv the expression $\chi(T) = \chi_0 + C/T$, where the susceptibility corresponds to an antiferromagnetic susceptibility of the single crystal which is independent of the temperature. The constant C determines a possible imperfection of the single crystals consisting of the presence of paramagnetic impurities or deviations from the stoichiometric relations in the crystals (which should amount to about 20% when scaled to spin of 1/2).

Figure 2a shows the magnetic moment of a polycrystalline sample versus the applied magnetic field at $T = 60$ K. We observe a nonlinear increase in the magnetic moment with increasing magnetic field on the curves of $M(H)$ of the polycrystalline samples and in the magnetic-field interval $30 < H < 60$ kOe. The interval of magnetic fields in which this increase is observed is essentially independent of the temperature. A nonlinear growth of $M(H)$ of this sort might be explained in terms of a rotation of the antiferromagnetic vector $\mathbf{L}$ in polycrystalline antiferromagnets as H is increased.

We then turned our attention to the La_2CuO_{4-y} single crystals which were available.[4] Figure 3a shows the magnetic moments versus the magnetic field for various orientations with respect to the crystallographic directions.[5] It can be seen from the experiment represented by this figure that there is a fairly large difference between the

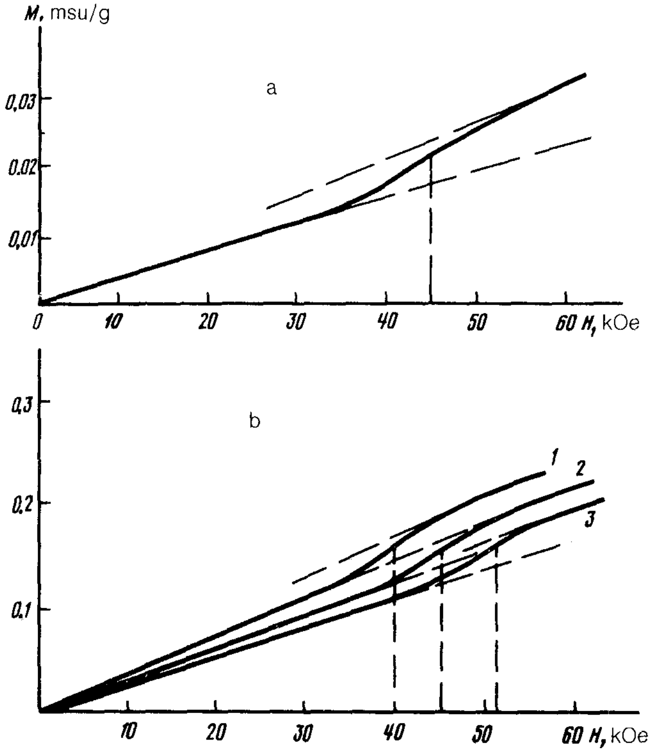

FIG. 2. a: Magnetic moments of polycrystalline samples versus the magnetic field at $T = 60$ K; b: Magnetic moments of single crystals at various temperatures. $\mathbf{H}\|c$. 1—$T = 10$ K; 2—$T = 20$ K; 3—$T = 30$ K.

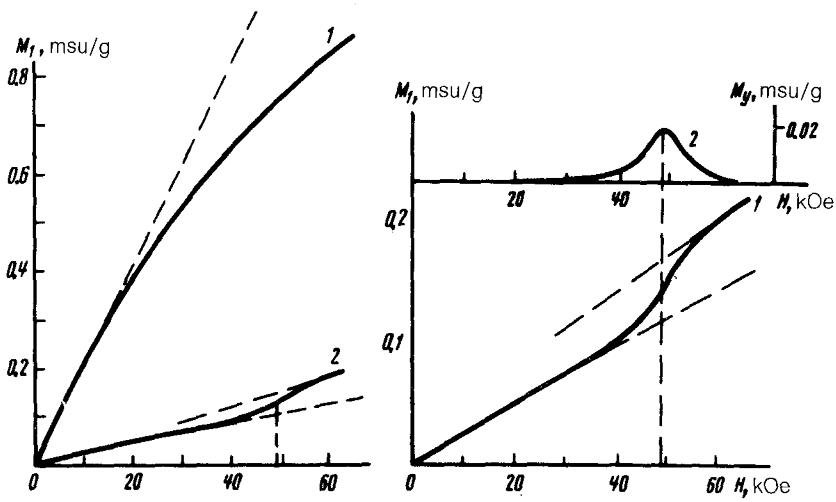

FIG. 3. a: Magnetic moments of the single crystals versus the magnetic field for various orientations of $\mathbf{H}$ with respect to the crystal axes. 1—$\mathbf{H}\|b$; 2—$\mathbf{H}\|c$. b: Magnetic moments of single crystals versus the magnetic field H. 2—M_y with $\mathbf{H}\|c$; 1—M_x with $\mathbf{H}\|c$.

$M(H)$ dependences corresponding to orientations of **H** along various crystal axes. When the applied magnetic field is along one of the twofold axes in the *a–c* plane of the crystal (Fig. 1), we observe a nonlinear increase in $M(H)$ at fields $H \approx 48$–50 kOe. This increase is similar to the increase observed in $M(H)$ in the polycrystalline samples. When **H** is oriented along another axis, this increase is not observed. In a study of various La_2CuO_{4-y} single crystals, we observed a nonlinear increase in $M(H)$ with increasing H in certain crystals even in the $H \| c$ orientation in the *a–c* plane of the crystal. This increase, however, was associated with a breakup of the single crystal into crystallographic domains, with *a* axes rotated 90° from each other and oriented perpendicular to the *b* axis (Fig. 1).

Since the antiferromagnetic vector **L** in La_2CuO_{4-y} is oriented along the twofold *c* axis, according to neutron-diffraction data,[3] it can be suggested that the increase in $M(H)$ with increasing $\mathbf{H} \| c$ is associated with a rotation of the antiferromagnetic vector **L** in the crystal.

To determine the particular plane in which **L** rotates in the single crystal, we studied the $M(H)$ dependence with **H** along the twofold *c* axis, measuring the three mutually perpendicular components of the magnetic moment $M_{x,y,z}(H)$. Line 2 in Fig. 3b shows the dependence of M_y. The dependence $M_y(H)$ which is observed, and which is characteristic of the rotation of the antiferromagnetic vector **L**, combined with the absence of a dependence $M_z(H)$, provides evidence that the rotation of the antiferromagnetic vector **L** in magnetic fields $H \approx 50$ kOe occurs in the *a–c* plane of the crystal.

Figure 2b shows the dependence of the magnetic moments of the single crystals studied ($T_N = 200$ K) on the magnetic field in experiments in which **H** was oriented along the twofold *c* axis at various temperatures. We see that the magnetic field of the phase transition, $H_c(T)$ increases with increasing temperature. A study of the $M(H,T)$ dependence for $\mathbf{H} \| c$ of the La_2CuO_{4-y} single crystals at low temperatures, $T \leqslant 10$ K (Fig. 3b), shows that at these temperatures the dependence $M(H)$ at $H > 50$ kOe can be described by the expression $M(H) = M^* + \chi H$, where M^* is the nonzero value found through an extrapolation of $M(H)$ at $H > 50$ kOe to $H = 0$. The value M^* depends strongly on the temperature, and at $T > 20$ K (Fig. 2b) M^* is essentially zero. It is possible that this $M(H,T)$ behavior is associated with a saturation of the paramagnetic moments of impurities in magnetic fields $H > 50$ kOe at low temperatures.

In summary, this study has shown that in the La_2CuO_{4-y} samples studied we observe a nonlinear increase in the magnetic moment of the sample below the temperature of the transition to the antiferromagnetic state when **H** is oriented along one of the twofold axes in the Cu–O plane. In magnetic fields $H \approx 50$ kOe, we observe a nonlinear increase in the magnetic moment of the sample, which can be explained on the basis of a rotation of the antiferromagnetic vector **L** in the crystal with increasing magnetic field. The rotation of **L** occurs in the *a–c* plane of the crystal. The samples which we studied differ from those which were studied in Ref. 5 in that the magnetic susceptibility was highly anisotropic at low temperatures.

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[4)]The La_2CuO_{4-y} single crystals were synthesized at the G. A. Emel'chenko Institute of Solid State Physics, Academy of Sciences of the USSR. We wish to thank G. A. Emel'chenko for graciously furnishing the crystals.
[5)]The orientation of the axes of the single crystals was determined by Yu. M. Orekhov at the Institute of Physical Problems, Academy of Sciences of the USSR. We wish to thank U. M. Orekhov for carrying out this work.

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