Magnetization fluctuations in the metal oxide $La_2CuO_{4-\delta}$

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Studies of the magnetic properties of polycrystalline $La_2CuO_{4-\delta}$ have revealed an unusual antiferromagnetic resonance, which occurs under conditions such that there is no long-range magnetic order.

There are now solid grounds for believing that the mechanism for high-temperature superconductivity[1,2] involves the unusual magnetic properties of perovskite structures of the $La_2CuO_{4-\delta}$ type.[3,4] This circumstance has stimulated increased interest in research on these properties.[5–9] It has been found[5] that the magnetic properties of these compounds depend strongly on δ, the deviation of the oxygen concentration from the stoichiometric value. For example, even a slight deviation (on the order of 0.03) of δ from 0 (or, according to other data, from a value between 0 and -0.03) leads to an increase in the Néel point of this compound from 0 to 290 K (Ref. 5). Our

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purposes in this study were to analyze the magnetic state of polycrystalline $La_2CuO_{4-\delta}$ compounds, to determine the nature of the magnetic fluctuations, and to determine how they depend on the presence of oxygen vacancies.

For the study we used two different values of δ of polycrystalline $La_2CuO_{4-\delta}$ samples, ground into powders. Some of the grains, oriented by a strong magnetic field, were fixed in paraffin. A special direction—the orientation axis—was thus created in the samples. We used x-ray diffraction to ensure that the crystals were of single phase and to determine their orientation. It was found that the *ac* basal planes of the various grains were oriented for the most part in the direction perpendicular to the orientation axis, while some made an angle of 60° with it, apparently because of crystal intergrowth. In the course of the studies we measured the magnetic susceptibility (in a field of 1.5 kG), and we recorded spectra of the magnetic-resonance spectra at the frequency of 9400 MHz.

In sample 1, with a stoichiometric oxygen concentration ($\delta \approx 0$), there was no transition to an antiferromagnetic state, according to the measurements of the magnetic susceptibility. The behavior of the susceptibility of sample 2, which was produced from sample 1 by annealing in air at 950 °C, and which had a value $\delta > 0$, contains a characteristic slope change, which corresponds to a Néel point of 250 K. We might add that the susceptibilities of both samples exhibit a Curie-like rise at $T < 50$ K with $T_C \sim 1$–3 K, which is evidence that there are localized magnetic moments in these compounds.

In the ESR measurements in sample 2 at temperatures below 90 K, we observed a resonant line whose width (380 G) remained essentially constant down to temperatures ~7 K (Fig. 1). During cooling below 35 K, the *g*-factor of this line, which does not depend on the orientation of the sample with respect to the static magnetic field H_0, shifts from $g = 2.14$ to $g = 2.16$. This line is always accompanied by a weak signal with $g \sim 4$. The integrated intensity of each signal varies in the same way as a function of the temperature. This behavior is consistent with the Curie-like region on the temperature dependence of the susceptibility. These signals probably correspond to a cou-

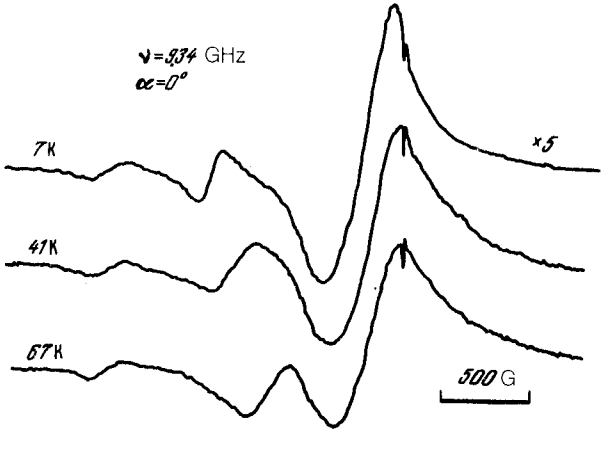

FIG. 1. Magnetic-resonance spectrum of sample 2 at $T < T_N$.

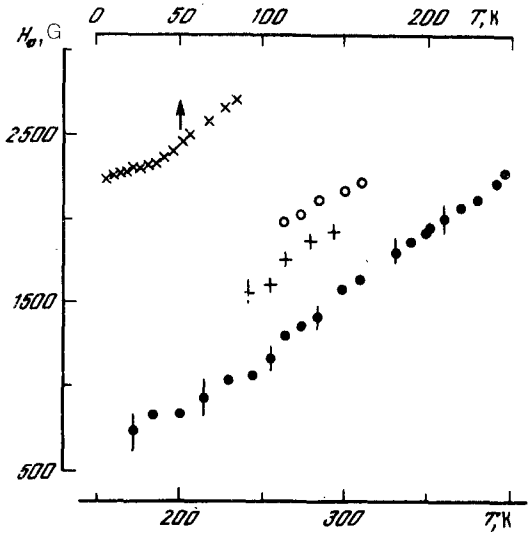

FIG. 2. Temperature dependence of the field values H_0 which correspond to (×) an antiferromagnetic resonance in sample 2, to (●,○) to the excitation of spin waves in sample 1, and (+) to the excitation of spin waves in sample 2.

pled ferromagnetic interaction of Cu^{2+} pairs which arise under conditions such that there is a frustration of antiferromagnetic bonds because of defects. Another possibility is that these lines correspond to high-spin copper localized in extended twinning boundaries with a tetragonal structure. In addition to these signals, we observe an absorption line (the central line in Fig. 1) in the same temperature interval. The position and intensity of this absorption line depend strongly on the temperature (Fig. 2) and the orientation of the static magnetic field. At $T = 24$ K, for example, this signal, with a width ~ 200 G, which can be identified as an antiferromagnetic resonance line, shifts 200 G up the field scale as the magnetic scale is rotated 60° around the orientation axis. At an angle of 90°, the signal disappears completely. As the temperature is raised, it shifts toward the $g = 2.14$ line, falling off in intensity, nearly to zero. In the interval $90\ \text{K} < T < 250$ K, we observe no lines, while above $T = 250$ K a wide signal (~ 300 G) appears, centered at $g \sim 2$. We also observe an additional line, which shifts up the field scale with increasing temperature (Fig. 2). Its intensity falls off as H_0 is rotated to a direction perpendicular to the orientation axis (the signal shifts up the field scale in this case), while its width is essentially constant at 340 G.

The ESR spectra of sample 1 at low temperatures also contains signals with $g \sim 2$ and $g \sim 4$, but the former has a more pronounced increase in g-factor with a decreasing temperature. At $90\ \text{K} < T < 170$ K, we do not observe resonance signals; beginning at 180 K, two absorption lines with a width ~ 300 G appear. As the temperature is raised, they shift up the field scale (Figs. 2 and 3). When the field deviates from the orientation axis, these lines shift in the same direction and fall off sharply in intensity. In experiments on samples which were not oriented by a magnetic field, we did not observe signals of this sort. In addition to them, we observe a very broad and weak signal near $g \sim 2$ at high temperatures.

An important point for reaching an explanation of the results is that the magnetic

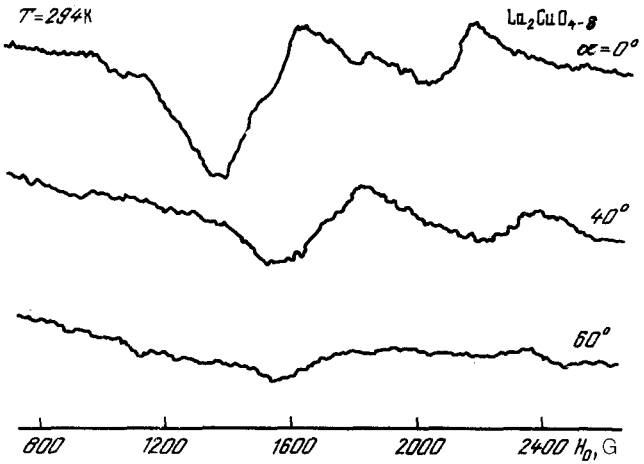

FIG. 3. Orientation dependence of the absorption signals during the excitation of spin waves in sample 1. Here α is the angle between the magnetic field and the orientation of the axis.

moments of the Cu^{2+} ions ($S = 1/2$) in the Cu–O_2 planes are coupled by a nearly isotropic Heisenberg antiferromagnetic exchange.[6-9] Accordingly, a long-range antiferromagnetic order is possible only if there is a coupling between the planes; such a coupling arises if there is a deviation from stoichiometry. If $\delta > 0$, there is an antiferromagnetic state with a slight anisotropy in the ac plane and a more pronounced anisotropy along the b axis. The temperature dependence (Figs. 1 and 2) and the orientation dependence of the antiferromagnetic resonance line imply that the picture seen here is similar to an easy-plane situation. The resonant frequency is approximated by[10]

$$\omega_0 = \gamma \sqrt{2H_E |H_A(T)| + H_0^2}, \qquad (1)$$

where H_E and H_A are respectively the exchange and anisotropy fields along the b axis, and γ is the gyromagnetic ratio. At $T = 7$ K, for example, setting $H_E \sim (k_B T_N/\gamma\hbar) \sim 1.95 \times 10^6$ G, we find the anisotropy field along the b axis from the dependence $\omega_0(T)$: $|H_A| = 12.2$ G.

In the case $d = 0$, and also for $d > 0$ at $T > T_N$, a long-range order would be impossible; nevertheless, the isotropic exchange J leads to the formation of antiferromagnetically correlated fluctuation regions in the Cu–O_2 planes.[7] The size of these regions is greater than the lattice constant a_0 by a factor of[6] $\exp(2\pi J\rho_S/T)$. Over distances on the order of the average size of the individual grains, L ($\sim 6 \times 10^4$ Å), we can ignore the fluctuational renormalization of the spin rigidity ρ_S which appears here; we can therefore assume that the sizes of these antiferromagnetic regions are on the order of L. A uniform rf field excites spin waves with a wave vector $k \sim 1/L$ in each such region. If all the grains are oriented identically, the result will be a resonant absorption of the rf field (Fig. 3), which is determined by the extreme dimensions of the antiferromagnetic regions. The frequency of the spin-wave resonances, ω_k, can be

found by assuming that the magnetization of the sublattices is close to saturation in the fluctuationally correlated regions. In this case ω_k is given by an expression like (1), with $|H_A| \to |H_A| + Dk^2$, where $D = Ja_0^2/\gamma\hbar$, but with different values of H_E and $H_A(T)$, which corresponds to the high-temperature curves in Fig. 2. An analysis of this behavior yields the exchange integral, $J \sim 10^3$ K, in agreement with the results of Ref. 8. This agreement is evidence in favor of the validity of our estimate of the correlated regions.

In summary, the unusual resonant properties of $La_2CuO_{4-\delta}$ stem from the circumstance that there are fairly large fluctuational regions with a two-dimensional antiferromagnetism in this compound. This circumstance may be of considerable importance in the development of magnetic models for high-temperature superconductivity.

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