La_2CuO_4 in the fluctuation region of the magnetic transition

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A first-order magnetic phase transition occurs in an La_2CuO_4 sample with $T_N \geqslant 315$ K according to measurements of the ^{139}La NQR. The possibility of a fluctuational cutoff of the continuous phase transition resulting in the formation of an abrupt transition, is discussed.

The antiferromagnetism of the compound La_2CuO_4—the precursor of the high-T_c superconductors—is the subject of considerable research interest because of its unique magnetic properties.[1] It has been established reliably that $La_2CuO_{4+\delta}$ is a layered antiferromagnet with a T_N value which is extremely sensitive to the oxygen

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content (T_N varies from 300 K to 0 as δ varies from 0 to 0.04; Refs. 2 and 3). A strong, isotropic, antiferromagnetic exchange interaction occurs between the moments of Cu^{2+} ions ($S=1/2$) with $J\simeq 1000$ K (Ref. 4) in CuO_2 planes. The interplanar exchange is $\sim 3.7\times 10^{-5}$ of the in-plane exchange.[5] The weak, symmetric, anisotropic exchange and the antisymmetric Dzyaloshinskiĭ exchange give rise to a noncollinear, "checkerboard," easy-plane antiferromagnetic structure, in which the spins are ordered along the c axis in the basal plane ($a<c<b$; orthorhombic structure; space group C_{mca}) with a slight skew ($\sim 0.17°$) in the bc plane.[6–8] Neutron diffraction has revealed strong two-dimensional spin antiferromagnetic correlations in CuO_2 planes far above T_N, but the long-range magnetic order at $T\leqslant T_N$ is three-dimensional.[1]

There have been only a few studies of the critical properties of La_2CuO_4 near T_N, and the results have been contradictory. For example, a study of the temperature dependence of the sublattice magnetization $M(T)$ by a high-precision nonperturbing method, involving nuclear quadrupole resonance (NQR),[9–13] has yielded contradictions even in the determination of the order of the phase transition. It was concluded in Refs. 9–11 (on the basis of the NQR of ^{139}La) that the variation of $M(T)$ is continuous (a second-order magnetic transition), but indirect evidence for a first-order transition has been found in some corresponding studies.[12,13] Further evidence in favor of a first-order transition comes from the slight hysteresis in the electrical conductivity near T_N (Refs. 14 and 15).

We have carried out a detailed study of the NQR spectra of ^{139}La in La_2CuO_4 near T_N for assistance in resolving the contradiction noted above and for unambiguously determining the order of the phase transition. Yet a further motivation was to learn about the critical behavior of La_2CuO_4. In a zero magnetic field, the $M(T)$ dependence can be reconstructed from the Zeeman splitting of the NQR spectra of a natural probe: ^{139}La nuclei ($I=7/2$). This splitting stems from the local magnetic field $\vec{H}$ (which is of a dipole and indirect hyperfine nature) induced at the nucleus by the magnetic moments of the surrounding Cu^{2+} ions. In the C_{mca} phase the field $\vec{H}$ makes an angle $\theta\simeq 78.5°$ with the z axis (the axis of the electric field gradient) at the nucleus, and the asymmetry factor of this field gradient is[11] $\eta\simeq 0.01$. Because of this small value of η, the field gradient can be regarded as axisymmetric. When we also make use of the circumstance that the Zeeman component, $\gamma H\simeq 0.6$ MHz ($T\to 0$), is small in comparison with the quadrupole coupling constant $\nu_Q=(1/14h)eQV_{zz}\simeq 6.4$ MHz, we find that the field gradient and $\vec{H}$ combine to produce the following NQR spectrum in first-order perturbation theory:[16]

$$\begin{aligned}
\nu_{1,2} &= \nu_{3/2\leftrightarrow 1/2} \mp (3/2)\gamma H_{\parallel} - (1/2)\gamma\sqrt{H_{\parallel}^2+(4H_{\perp})^2};\\
\nu_{3,4} &= \nu_{3/2\leftrightarrow 1/2} \mp (3/2)\gamma H_{\parallel} + (1/2)\gamma\sqrt{H_{\parallel}^2+(4H_{\perp})^2};\\
\nu_{5,6} &= \nu_{5/2\leftrightarrow 3/2} \mp \gamma H_{\parallel}; \quad \nu_{7,8} = \nu_{7/2\leftrightarrow 5/2} \mp \gamma H_{\parallel},
\end{aligned} \tag{1}$$

where $H_{\parallel}=H\cos\theta$ and $H_{\perp}=H\sin\theta$.

The $M(T)$ dependence was reconstructed from the frequencies of intense lines, $\nu_{7,8}$ or $\nu_{5,6}$, in Refs. 9–13. The splitting $(\nu_8-\nu_7)$ and $(\nu_6-\nu_5)$, however, results from the small component $H_\parallel \simeq 0.2H$, so measurements of $M(T) \sim H_\parallel(T)$ in the critical region are inaccurate. In the present study we measured the frequencies of weak lines, $\nu_{1\text{-}4}$ (such measurements constitute a far more complicated experimental problem). As a result, we were able to determine both the component $H_\parallel$ and the main component of the local field, $H_\perp \simeq 0.98H$, on the basis of the splitting

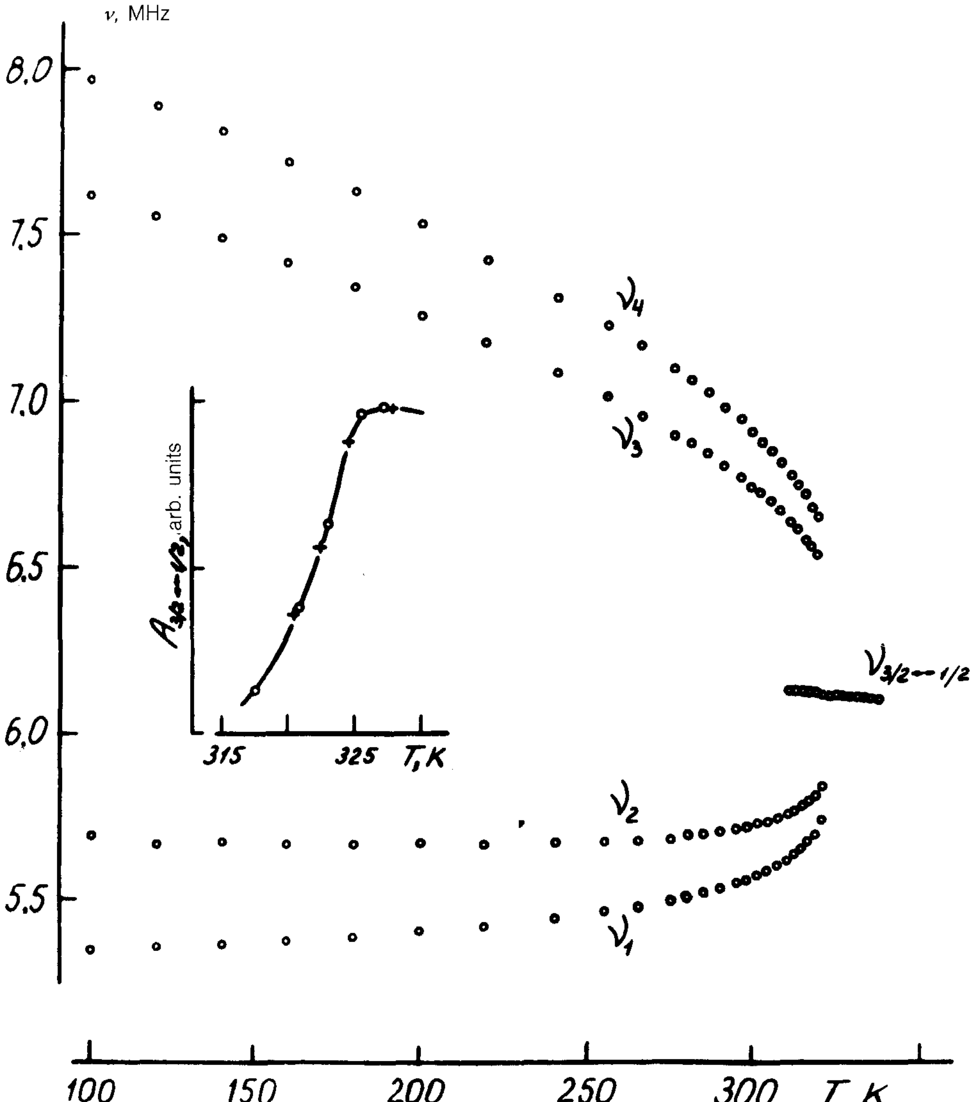

FIG. 1. Temperature dependence of the ^{139}La NQR frequencies of the lines ν_{1-4} of the antiferromagnetic phase of La_2CuO_4 and of the line $\nu_{3/2\leftrightarrow 1/2}$ of the paramagnetic phase. The inset shows the temperature dependence of the intensity $A_{3/2\leftrightarrow 1/2}$ of the NQR line of the paramagnetic phase as the sample is heated (+) and cooled (O).

$(\nu_4 - \nu_3 + \nu_2 - \nu_1) = 6\gamma H_{\parallel}$ and $(\nu_4 + \nu_3 - \nu_2 - \nu_1) = 2\gamma\sqrt{H_{\parallel}^2 + (4H_{\perp})^2}$. There is a substantial improvement in resolution here. In the approximation $M(T) \sim H(T) = \sqrt{H_{\parallel}^2 + H_{\perp}^2}$, it is possible to eliminate the systematic errors which stem from the temperature dependence of θ as a result of the change in the extent to which the structure is orthorhombic.

We studied a polycrystalline La_2CuO_4 sample with $T_N \geqslant 315$ K and narrow NQR lines (30 kHz); these properties are evidence of a close adherence to oxygen stoichiometry. After synthesis, the sample was heat treated in a vacuum $\sim 10^{-2}$ Torr for 12 h at 900 °C, ground, and stabilized with paraffin. The ^{139}La NQR spectra were record-

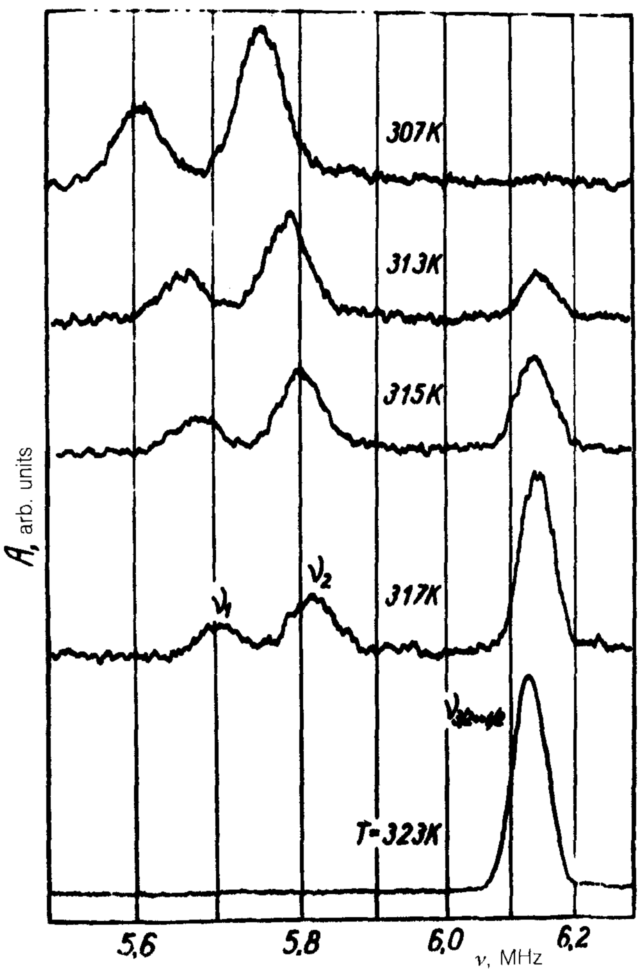

FIG. 2. Part of the NQR spectrum of ^{139}La in La_2CuO_4 near T_N. The lines at the frequencies $\nu_{3,4}$ are not shown; the temperature dependence of their intensity is similar to that of the lines $\nu_{1,2}$. The spectrum for $T = 323$ K was recorded at a spectrometer gain reduced by 12 dB.

ed by the Hahn echo method with a boxcar integrator.

Let us examine the behavior of the intensities and frequencies of the NQR lines as the temperature is varied. Figure 1 shows the temperature dependence of the frequencies. The intensities of lines ν_{1-4} vary roughly as $1/T$ (a Boltzmann factor) in the interval $100 < T < 310$ K. Beginning at 310 K, the intensities fall of anomalously sharply, with the signals disappearing at 320 K. Also at 310 K, an additional line appears, with a frequency close to $\nu_{3/2\leftrightarrow 1/2} = (\nu_1 + \nu_2 + \nu_3 + \nu_4)/4$. The intensity of this line, $A_{3/2\leftrightarrow 1/2}$, increases rapidly with the temperature (see the inset in Fig. 1), but at 326 K saturation sets in. We see essentially no thermal hysteresis of the intensity $A_{3/2\leftrightarrow 1/2}$. This additional line undoubtedly corresponds to the transition $3/2\leftrightarrow 1/2$ in the paramagnetic phase of La_2CuO_4 in the absence of a magnetic perturbation of the quadrupole levels.

We are thus observing a coexistence of antiferromagnetic and paramagnetic phases in the temperature interval ~310–320 K, with a smooth redistribution of the volumes of these phases. We also see a jump in the local field. This behavior is characteristic of a first-order phase transition which has been smeared over a certain temperature interval. The most likely cause of the smearing, in our opinion, might be nonuniformities of the oxygen distribution, which would have a substantial effect on T_N, although deoxygenated samples have an approximately stoichiometric composition according to Ref. 3. If the transition were continuous but smeared, we would have observed a broadening (smearing) of the lines ν_{1-4} over the entire frequency interval from ν_1 to ν_4 in the phase coexistence region, because of the spatial distribution of the sublattice magnetization and thus of the local field H. However, what occurs in the coexistence region is a "pumping" of the line intensity of the antiferromagnetic and

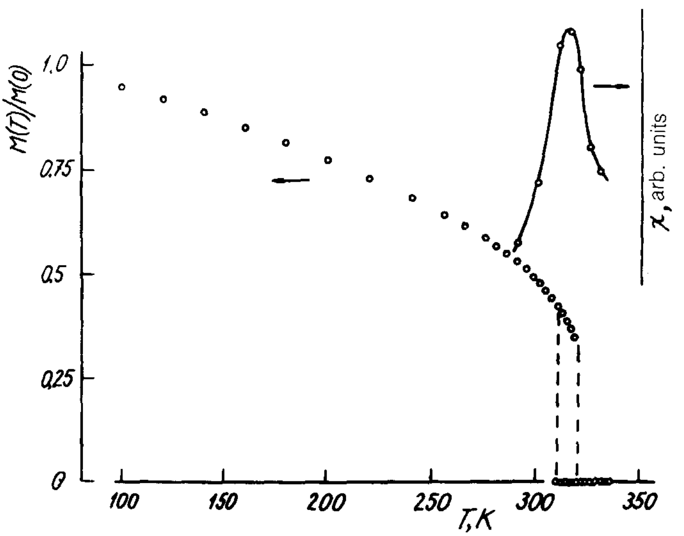

FIG. 3. Temperature dependence of the reduced sublattice magnetization $M(T)/M(0)$ of La_2CuO_4 according to data on the NQR of ^{139}La, along with the temperature dependence of the static susceptibility near T_N. The dashed lines show the region in which the antiferromagnetic and paramagnetic phases coexists.

paramagnetic phases, without any significant line broadening, as is clear from Fig. 2.

Figure 3 shows the temperature dependence of the reduced sublattice magnetization, $M(T)/M(0)$, along with the dependence of the static magnetic susceptibility, $\chi(T)$. The temperature at which $\chi(T)$ reaches its maximum, $T_m = 315$ K, is seen to correspond approximately to the midpoint of the region in which the antiferromagnetic and paramagnetic phases coexist. The jump in the magnetization at 315 K is $\sim 30\%$. In an effort to determine the critical exponent β, we approximated the high-temperature part of the $M(T)$ curve—the part preceding the first-order transition—by a power law characteristic of second-order transitions: $M(T) \sim (1 - T/T_N)^\beta$. In the temperature interval 300–318 K we found the values $\beta \simeq 0.3$ and $T_N = 327$ K.

We believe that the observed properties of the magnetic phase transition in La_2CuO_4—the substantial jump in the magnetization with a small thermal hysteresis and the realization, over a wide temperature range, of a value of the critical exponent β which is characteristic of a three-dimensional magnetic material during a second-order transition—are evidence for a fluctuational cutoff of a second-order transition, i.e., the effect which is observed in (for example) the cubic antiferromagnet MnO (Ref. 17).

The presence of an orthorhombic distortion of the lattice and of a magnetic interaction between CuO_2 layers differing in nature makes it a rather complicated matter to theoretically analyze the fluctuational cutoff of the phase transition in La_2CuO_4. However, when we note that the corresponding distortion of the lattice is small ($\sim 10^{-2}$), we can, as a simple approximation, examine the situation in a tetragonal crystal (whose cell becomes the same as the orthorhombic cell in the case $a = c$) with two antiferromagnetically ordered subsystems of CuO_2 layers. The distortion can then be dealt with in the standard way, as a perturbation in the form of a (quadratic) field which disrupts the symmetry.[18] The free-energy functional takes the following form in this case:

$$\mathcal{H} = \frac{1}{8}\int d^d r \Big[\sum_{i=1}^{2}[\tau(\varphi_i^2+\eta_i^2)+(\nabla\varphi_i)^2+(\nabla\eta_i)^2+u_1(\varphi_i^4+\eta_i^4)] + 2u_3\varphi^2\eta^2 + 2u_2(\varphi_1^2\varphi_2^2+\eta_1^2\eta_2^2)\Big], \tag{2}$$

where the vectors $\vec{\varphi} = (\varphi_1, \varphi_2)$ and $\vec{\eta} = (\eta_1, \eta_2)$ describe the ordering in the two types of CuO_2 layers, respectively. Functional (2) has a ditetragonal symmetry.[19] The system of renormalization-group equations describing the evolution of the parameters of this functional in the fluctuation region can be written as follows:

$$\dot{u}_1 = u_1 - \frac{9}{2}u_1^2 - \frac{1}{2}u_2^2 - u_3^2; \quad \dot{u}_2 = u_2 - 3u_1u_2 - 2u_2^2 - u_3^2;$$

$$\dot{u}_3 = u_3(1 - 3u_1 - 2u_3 - u_2). \tag{3}$$

One of the fixed points in (3) (an isotropic point) has an intermediate stability in lowest order in ϵ (this circumstance is quite natural in the case $n = 4$; Ref. 20). In second order in ϵ, this point splits[19] in such a way that one of the points which results is stable.

The presence of a stable fixed point is extremely important, since it makes the answer to the question of the nature of the transition a matter of whether the physical seed parameters of functional (2) belong to the region of attraction to this point. We should stress, however, that (at any rate) a first-order transition induced by fluctuations would be possible in this case. Since the interaction between planes is weak, the conditions $u_3 \ll u_1$, u_2 hold. Near the $u_3 = 0$ plane, the system of renormalization-group equations degenerates to a system of equations for a cubically anisotropic medium (with $n_1 = n_2 = 2$), for which we know quite well that there are regions in which phase trajectories go beyond the stability boundaries. The nature of the phase transition is thus determined primarily by the relation between the seeds u_1 and u_2. Also noting that the first-order phase transition is expressed only poorly (in particular, the hysteresis is very slight) when induced by fluctuations, we might suggest that the procedure by which the specific sample is prepared is crucial to the occurrence of this transition. This circumstance might explain the observed differences in the data on the nature of the phase transition[9-13] in samples differing in oxygen content. This question requires further study.

Strictly speaking, a symmetry analysis permits an invariant $u_4(\vec{\varphi}\cdot\vec{n})^2$ in the functional. From the standpoint of fluctuation theory, this invariant would strengthen the tendency toward a cutoff of the transition, causing an abrupt transition, since there is no stable fixed point for this system with u_4 (Ref. 19). However, the interaction containing the scalar product of the magnetic moments of the two subsystems is weak ($u_4 \ll u_3$) for the particular type of antiferromagnetic structure which forms in La_2CuO_4, and its effect on the critical behavior should be negligible.[21]

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