Abrupt but Continuous Antiferromagnetic Transition in Nearly Stoichiometric $La_2CuO_{4+\delta}$

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(Received 4 October 1993)

Zero-field ^{139}La nuclear quadrupole resonance (NQR) has been used to characterize the antiferromagnetic transition in nearly stoichiometric single crystals of $La_2CuO_{4+\delta}$ (Néel temperatures T_N between 275 and 318 K). The onset of the NQR Zeeman splitting at T_N is abrupt but continuous, indicative of a second-order phase transition with either a crossover in critical behavior just below T_N or a very small critical exponent $\beta \lesssim 0.1$. The absence of any anomaly at T_N in the ^{139}La electric field gradient indicates no accompanying structural distortion.

PACS numbers: 74.72.Dn, 75.30.Kz, 76.60.Gv

The layered cuprate antiferromagnet $La_2CuO_{4+\delta}$ has been extensively studied for clues to the mechanism of high-temperature superconductivity in its hole-doped alloys. It has also emerged as an interesting material in its own right, with a rich variety of magnetic behavior: intraplanar XY and Dzyloshinskiĭ-Moriya anisotropy and a weak interplanar exchange interaction, in addition to isotropic intraplanar Heisenberg exchange between Cu^{2+} ions, lead to a complex antiferromagnetic (AFM) phase [1–3]. The Néel temperature T_N is very sensitive to the excess oxygen concentration δ [4–6]. Separation into an oxygen-poor AFM phase and an oxygen-rich superconducting phase at a temperature $T_{PS} \sim 250\,K$ has been observed for $\delta \gtrsim 0.03$ [3,7].

There has been considerable controversy over the nature of the phase transition to long-range AFM order at T_N. Neutron Bragg scattering [8], $\gamma\gamma$ perturbed angular correlation (PAC) [9], and early nuclear quadrupole resonance (NQR) experiments [10] have been interpreted in terms of a smooth second-order transition, whereas muon spin rotation (μSR) [11], ^{57}Fe Mössbauer-effect (ME) [12,13], and more recent NQR [14,15] studies found an apparently discontinuous onset of the AFM staggered magnetization below T_N. Consistent with these latter observations, the behavior of the metamagnetism in $La_2CuO_{4+\delta}$ [5,16] suggests a first-order transition. Neutron Bragg scattering in the 2D Ising antiferromagnet K_2NiF_4 [17] revealed an abrupt transition with an order-parameter critical exponent $\beta \simeq 0.14$. Theories of the AFM transition in $La_2CuO_{4+\delta}$ have appeared which treat the transition as continuous [8,18] and as first order [15]. Resolution of this question would shed light on the critical behavior of extremely anisotropic quantum magnetism.

This Letter describes measurements of the Zeeman splitting [19] of ^{139}La NQR in nearly stoichiometric single-crystal $La_2CuO_{4+\delta}$, which show that the onset of the AFM staggered magnetization M_s at T_N is abrupt but continuous. We describe below how the abrupt jump can be reconciled [13] with the considerably smoother temperature dependence of the neutron Bragg cross section [8]. Notwithstanding this abrupt behavior our data from a highly homogeneous sample show that the transition is continuous, and can be described in terms of either a crossover in critical behavior ~1 K below T_N or a very small value ($\lesssim 0.1$) of β. Matsuda *et al.* [20] and Keimer *et al.* [8] have noted that the AFM spin Hamiltonian of Thio *et al.* [2] leads to nearly coincident 2D-3D and Heisenberg-XY crossovers in $La_2CuO_{4+\delta}$, and crossover behavior is suggested by the Schwinger-boson mean-field theory of Ref. [8]. To our knowledge no specific *ab initio* prediction of an abrupt transition has appeared.

The single-crystal samples used in the present work were grown from a CuO flux melt and subsequently measured in the as-grown state ($T_N = 275\,K$) or after anneals at 650 °C under pure nitrogen ($T_N = 305\,K$) or vacuum ($T_N =$ 312–318 K). The samples contain few lattice defects, as evidenced by the fact that the observed NQR linewidths were an order of magnitude or more smaller than previously reported for ceramic powders. The good sample homogeneity implied by such narrow lines was essential for obtaining the results of this Letter. Even so, the continuous variation of Zeeman splitting discussed below was observed only in a particularly homogeneous single crystal; in less homogeneous samples the transition appeared discontinuous as in previous studies [14,15].

Fourier-transform spectra were obtained from spin-echo ^{139}La NQR signals in a conventional manner, and the frequencies of the three pure NQR lines in the paramagnetic (PM) state and eight of the nine Zeeman-split

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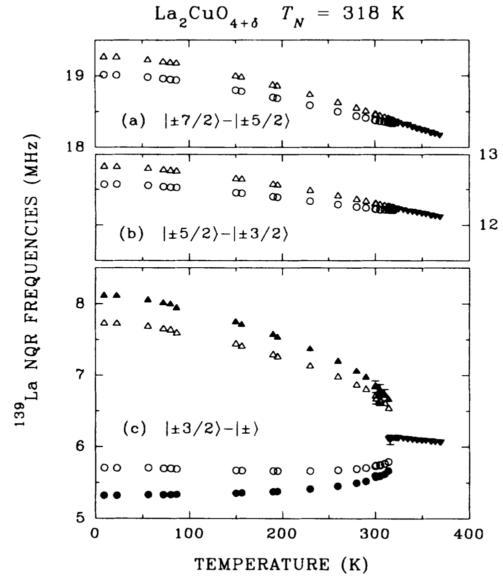

FIG. 1. Temperature dependence of ^{139}La Zeeman-split NQR frequencies in $La_2CuO_{4+\delta}$, T_N = 318 K. (a) Frequencies of transitions between |±7/2⟩ and |±5/2⟩ nuclear spin states. (b) |±5/2⟩ ↔ |±3/2⟩ transition frequencies. (c) |±3/2⟩ ↔ |±⟩ (see Ref. [21]) transition frequencies, where the effect of the jump at T_N is most evident. The ordinates of all three graphs have the same scale. The "error bars" give linewidths where larger than the symbol size.

NQR lines in the AFM state were determined. Figure 1 shows the temperature dependences of these frequencies for a sample with T_N = 318 K. The frequencies of the four transitions between |±3/2⟩ and |±⟩ nuclear spin states [21] show the abrupt onset of the AFM splitting most clearly and are crucial to its measurement [15]. Values of T_N obtained from the onset of the NQR splitting and from the peaks in the measured susceptibilities are in good agreement.

Coexisting unsplit and Zeeman-split NQR lines were observed within a narrow sample-dependent temperature range of width $\Delta T_N \sim$ 2–10 K, as was first reported by Borodin *et al.* [15]. With decreasing temperature in this region intensity is transferred smoothly from the unsplit PM-state line to the Zeeman-split AFM lines, indicating the presence of both AFM and PM phases due to inhomogeneity of T_N. In contrast to a recent ^{57}Fe ME study [13] the coexistence region in our samples is very narrow (relative width $\lesssim$ a few percent), with an upper bound of ~1% volume fraction on any untransformed phase outside this region. The spectra exhibited no thermal hysteresis, consistent with the results of Ref. [15]. Hysteresis has been observed in the zero-field resistivity of a sample with T_N = 260 K [22], but this is close to T_{PS} [3] and phase separation may have played a role in the hysteretic behavior.

The nuclear spin Hamiltonian which describes the NQR spectrum [21] is characterized by (1) the Zeeman frequency ν_Z, which sets the scale of the Zeeman splitting and is proportional to M_s [19]; (2) the quadrupole frequency ν_Q, which reflects the electric field gradient (EFG) at the nuclear site; and (3) the asymmetry parameter η, which measures the departure of the EFG from axial symmetry. The temperature dependences of these parameters were extracted from fits of the experimental transition frequencies to exact numerical diagonalizations of the nuclear spin Hamiltonian [14,21,23], and are given in Fig. 2 for the data of Fig. 1. It can be seen that the jump in ν_Z at T_N is ~30% of the zero-temperature value [Fig. 2(a)], as previously observed [15]. In contrast, there is no anomaly in ν_Q at T_N to within a few percent of the total variation between $T = 0$ and $T \gtrsim T_N$ [Fig. 2(b)] due to thermal expansion of the lattice. Neither is there an anomaly in η [Fig. 2(c)], although its error is considerably larger. There is therefore no NQR evidence for a structural distortion [24] at T_N, although a distortion usually accompanies a first-order magnetic phase transition [25]. This indicates that the transition is purely magnetic in origin and magnetoelastic coupling does not play an essential role.

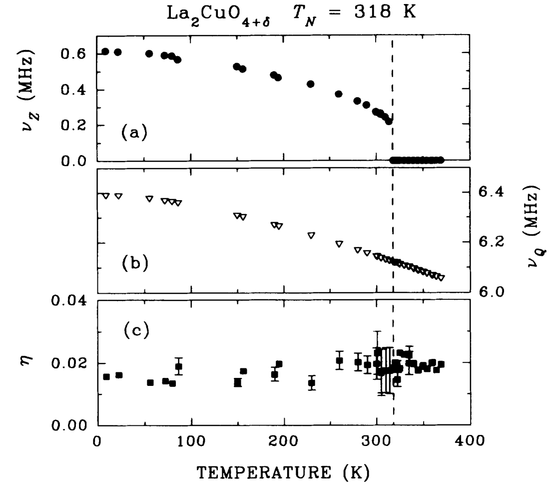

FIG. 2. Temperature dependence of ^{139}La NQR parameters in $La_2CuO_{4+\delta}$, T_N = 318 K, from fits to frequencies of Fig. 1 (see text). (a) Zeeman frequency ν_Z. (b) Quadrupole frequency ν_Q. (c) Asymmetry parameter η. Dashed line: T_N.

Figure 3 gives ^{139}La |±3/2⟩ ↔ |±⟩ spectra, obtained from a different sample of particularly high homogeneity, for temperatures in the vicinity of T_N. Only Zeeman-split lines with frequencies above that of the PM-state line at 6.13 MHz are shown; the low-frequency lines (Fig. 1) behave similarly. The split lines are broad, and their shapes do not reproduce well due to distortion by the spectrometer bandwidth. Coexistence with the unsplit line occurs only in the narrow temperature range 313–315 K, where the splittings are 2 to 3 times smaller than the minimum values reported previously [14,15] (see also Fig. 1). The Zeeman frequencies derived from these spectra tend smoothly to zero with increasing temperature, as shown in the inset to Fig. 3 where a "knee" at $\nu_Z \sim$ 0.2 MHz is evident. This smooth temperature dependence of ν_Z

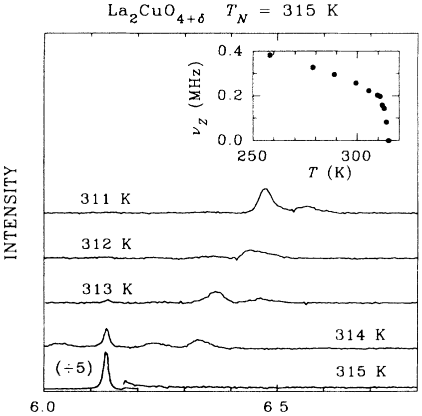

FIG. 3. ^{139}La $|\pm 3/2\rangle \leftrightarrow |\pm\rangle$ NQR Fourier-transform spectra from a homogeneous single crystal of $La_2CuO_{4+\delta}$ in the vicinity of $T_N = 315\,K$. Only frequencies above that of the unsplit PM-state line (6.13 MHz) are shown. Inset: Temperature dependence of ν_Z just below T_N.

is strong evidence that the jump at T_N is intrinsically continuous. Other salient features include the extremely small FWHM width ($\lesssim 10$ kHz) of the PM-state line, and the fact that the AFM-split lines are an order of magnitude broader. This indicates static disorder in the staggered magnetization, due presumably to hole doping by the residual excess oxygen.

An abrupt but continuous transition can be described phenomenologically by a small effective order-parameter exponent $\beta_{\rm eff}$, defined by $M_s \propto (T_N - T)^{\beta_{\rm eff}}$. It was not possible to extract $\beta_{\rm eff}$ from the data by fitting this expression to $\nu_Z(T)$, because the fit value depended on the range of data used [19,26]. An upper bound could, however, be obtained as follows: For an inhomogeneous sample, and for temperatures in and just below the coexistence region, nuclei in portions of the sample with T_N just above the temperature of measurement have low values of ν_Z. These nuclei give rise to a low-frequency "shoulder" in the distribution of ν_Z, and therefore to corresponding shoulders on the low-splitting side of each AFM-split line. Such nuclei have smaller splittings, and the shoulders are more pronounced, for a gradual transition (larger value of $\beta_{\rm eff}$) than for an abrupt one (smaller value of $\beta_{\rm eff}$). According to a rough estimate of this effect [27] a substantial shoulder would have been resolved for $\beta_{\rm eff} \gtrsim 0.1$; the fact that no shoulder is observed (Fig. 3) places an experimental upper bound of this order on $\beta_{\rm eff}$.

This analysis has the advantage that it is sensitive only to $\nu_Z(T)$ very near T_N, but the upper bound is crude and we have no evidence that $\beta_{\rm eff}$ should considered a true critical exponent. Accurate determination of the asymptotic behavior of $\nu_Z(T)$ requires reduced temperatures $1 - T/T_N$ of the order of 10^{-3} or smaller [19,26], which is not possible in $La_2CuO_{4+\delta}$ at present due to the remaining inhomogeneity of T_N; a more accurate determination of $\beta_{\rm eff}$ will require samples with ΔT_N considerably less than 1 K. This upper limit, like the value $\beta \simeq 0.14$ found by neutron Bragg scattering in the established Ising system K_2NiF_4 [17], is close to the Ising value of 1/8, but the temperature dependence of $M_s(T)$ in $La_2CuO_{4+\delta}$ (Figs. 2 and 3) does not in fact resemble the corresponding data of Ref. [17].

The observation that the AFM transition in $La_2CuO_{4+\delta}$ is abrupt conflicts with the results of some previous studies. Saylor *et al.* [9] concluded from PAC measurements that the transition in a nearly stoichiometric sample was smooth and exhibited S=1/2 mean-field behavior. A sizable jump in hyperfine splitting at T_N has, however, been observed in μSR [11] and ^{57}Fe ME [12,13] studies of $La_2CuO_{4+\delta}$. The scaled hyperfine data from these measurements (see, e.g., Ref. [18]) lie close to those of Fig. 2(a). It should be noted, however, that some of these studies used samples with low values of T_N, for which phase separation might have played a role as mentioned above. Furthermore, in hyperfine techniques other than NMR or NQR the implanted probe (PAC or ME ion, muon) might perturb its surroundings (see, e.g., Ref. [28]).

Keimer *et al.* [8] reported a gradual onset of the AFM neutron Bragg scattering cross section σ_B below T_N in nearly stoichiometric $La_2CuO_{4+\delta}$. We note that σ_B varies as M_s^2 whereas $\nu_Z \propto M_s$, so that a ~30% jump in ν_Z at T_N corresponds to a smaller effect (~10%) in σ_B. Even at this level, however, the neutron data show no sign of a jump [8]. This discrepancy can be explained by the inhomogeneity in T_N described above: The AFM Bragg intensity increases smoothly as the temperature is decreased through the transition not because the transition itself is smooth, but because the AFM fraction of the sample is increasing smoothly. Imbert *et al.* [13] pointed out that this difference between "local-probe" and "sample-average" techniques can play an important role in $La_2CuO_{4+\delta}$; we emphasize that it can explain the discrepancy between neutron and NQR results even in the most homogeneous samples. Apart from the lack of a jump, $M_s(T)$ from Ref. [8] scales well with $\nu_Z(T)$ from the present measurements.

The absence of anomalies at T_N in ν_Q and η and in the thermal expansion [29] indicate that the abrupt AFM transition is not accompanied by a structural distortion. This result, together with the lack of thermal hysteresis noted above, argue against a conventional first-order AFM transition in $La_2CuO_{4+\delta}$. Borodin *et al.* [15] explained their apparently discontinuous jump in ν_Z at T_N as a fluctuation-induced first-order transition [30], the purely magnetic character of which does not require an accompanying structural distortion. We reiterate, however, that the continuous onset of the Zeeman splitting below T_N (inset to Fig. 3) shows that the transition is second order.

These results do not answer the question of whether the abrupt behavior signals a crossover between critical regimes, or if the transition should be described by a very small value of the critical exponent $\beta = \beta_{\rm eff}$. A second-order transition with a value of $\beta \sim 0.1$ might indicate Ising-like behavior of the transition. We may be observing the crossover suggested by a Schwinger-boson mean-field calculation of the staggered magnetization [8], but that this gives an abrupt transition remains to be demonstrated. A satisfactory understanding of the antiferromagnetic transition in $La_2CuO_{4+\delta}$ awaits resolution of these issues.

We wish to thank G. Aeppli, F. Borsa, R. H. Heffner, D. C. Johnston, D. Mandrus, R. L. Orbach, J. Saylor, and F. Steglich for helpful discussions, and T. Bell for assistance in sample preparation. This work was supported in part by the U.S. NSF, Grants No. DMR-8814783 and No. DMR-9114911, by the University of California, Riverside, Academic Senate Committee on Research, and by the Netherlands FOM and NWO, and was performed in part under the auspices of the U.S. DOE.

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