

^{63}Cu NMR study of conducting delafossites

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NMR data are presented for the conducting delafossites $\text{Y}_{0.99}\text{Ca}_{0.01}\text{CuO}_{2.65}$ and $\text{LaCuO}_{2.64}$. These materials exhibit a planar structure with triangular arrays of exchange-coupled $S = \frac{1}{2}$ (Cu^{2+}) spins. The two compounds examined show strikingly different quadrupole-broadened NMR powder patterns, which is evidence for different in-plane arrangements of O^{2-} ions. Their doped-hole carrier densities are comparable to those of the superconducting cuprates. In consequence, they have Korringa-like T_1 processes. We also find evidence for dynamic Jahn-Teller motion and *ferromagnetic* enhancement of the spin paramagnetism for $\text{Y}_{0.99}\text{Ca}_{0.01}\text{CuO}_{2.65}$. T_2 studies indicate that the strong antiferromagnetic fluctuation effects found in the superconducting cuprates are absent.

The delafossite compounds have recently been shown^{1,2} to offer an interesting opportunity to study the behavior of exchange-coupled $S = \frac{1}{2}$ (Cu^{2+}) moments on a two-dimensional (2D) triangular lattice. The host structures YCuO_2 and LaCuO_2 consist of layers of edge-sharing $\text{Y}(\text{La})\text{O}_6$ octahedra separated by triangular arrays of twofold coordinated Cu^+ bridging ions. On intercalating oxygen into the copper planes, the Cu^+ are converted to Cu^{2+} , exchange paths are provided which couple the resulting $S = \frac{1}{2}$ spin moments, and, for overdoping beyond $\text{O}_{2.5}$, mobile carriers are inserted into the planes as well.² The compound $\text{YCuO}_{2.5}$ is an exchange-coupled 2D magnetic insulator with interesting properties about which we shall report elsewhere.³ At higher doping levels one has a nonsuperconducting triangular analogue of the quadratic layer cuprate superconductors. These systems therefore offer an opportunity to study the evidently powerful influence of geometry on the behavior of copper oxide conductors.

In this paper we present $^{63,65}\text{Cu}$ NMR studies intended to examine the microscopic behavior of two weakly conducting delafossite compounds. We address structural questions as well as the nature of the metallic state, with a particular interest in contrasting their electronic properties with those of the quadratic layer cuprates. The two compounds investigated are $\text{Y}_{0.99}\text{Ca}_{0.01}\text{CuO}_{2.65}$ and $\text{LaCuO}_{2.64}$, which we refer to hereafter as the Y case and the La case, respectively. Synthesis of these materials as well as measurements of bulk properties are discussed elsewhere.^{1,2,4} Both samples exhibit paramagnetic susceptibilities with Curie-Weiss-like terms which dominate at low temperature,^{1,4} and specific heat anomalies which resemble metallic γT terms, but appear to have contributions from partially localized carriers as well.⁴ These effects have been discussed⁴ in terms of model theories which treat metals having strong disorder effects.⁵ Estimated from composition, the concentration of excess holes in these samples is ~ 0.3 per Cu^{2+} , comparable with that found in, e.g., $\text{YBa}_2\text{Cu}_3\text{O}_7$.⁶ The NMR dynamics exhibit grossly metallic behavior, where $T_1 T$ is found to be roughly constant. Beyond this, the two materials examined are evidently quite different, both structurally and in their detailed dynamical properties. In particu-

lar, the Y material has properties which indicate trigonal Cu-site symmetry. For this compound there is also evidence for ferromagnetic susceptibility enhancement, in contrast with the strong antiferromagnetic fluctuation effects which are the hallmark of the superconducting phases.⁷⁻⁹

Single-phase ceramic samples of the compositions noted above were ground and encapsulated for NMR spin echo studies. Efforts to achieve magnetic orientation of powdered sample material in the fashion employed for $\text{YBa}_2\text{Cu}_3\text{O}_7$, etc.,¹⁰ were unsuccessful. The spectra are therefore random powder patterns for the $\frac{1}{2} \leftrightarrow -\frac{1}{2}$ spin transition, with line shapes determined by the combined effects of anisotropic shifts and second-order quadrupolar splittings. Sample spectra for the two compounds studied are shown in Figs. 1 and 2, where we see immediately that they represent strikingly different cases. This difference in electric field gradient (EFG) tensors reflects a difference in the in-plane arrangement of oxygen ions. Such a difference is not unexpected, since the triangular lattice constant is very different for the Y (3.52 Å) and La (3.82 Å) cases.

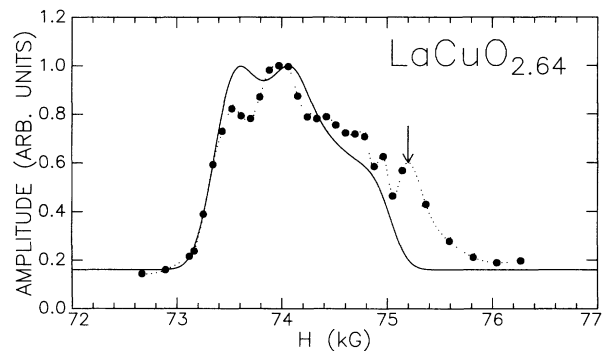


FIG. 1. ^{63}Cu NMR spectrum of $\text{LaCuO}_{2.64}$, taken at 83.5 MHz, is shown for $T = 293$ K. The dotted line is a spline fit to the data. The solid line is a calculated quadrupolar powder pattern with $\nu_Q = 15.5$ MHz, $\eta = 0.65$, $k_x = 0$, $k_y = 0.3\%$, and $k_z = 0.3\%$, with Gaussian smoothing. The arrow shows the position of a spurious ^{27}Al line from the NMR probe. The poor quality of the powder pattern fit may result from multiple Cu sites and/or disorder.

The spectrum in Fig. 1 is typical of a series taken from 8 K to room temperature, the double peak on the left being a persistent feature throughout. Only at room temperature does the splitting of these peaks collapse and the entire spectrum begins to narrow as with the onset of ionic motion. An approximate powder pattern spectrum is fitted to these data (solid line). The double peak is characteristic of an EFG asymmetry parameter η which is large, but not unity (see figure caption for parameter values). The shape is also affected by an anisotropic shift tensor. Note that the peak under the arrow (Fig. 1) is a spurious ^{27}Al line from the NMR probe. The fit shown is of course not satisfactory; the measured spectrum may have multiple sites or other complicating factors. Nonetheless, it gives a good idea of the quadrupolar parameters involved and suggests that the shifts are relatively small with a modest anisotropy. If there are multiple ^{63}Cu sites, their hyperfine parameters are evidently quite similar.

On the other hand, the spectrum for the Y sample in Fig. 2 shows clear evidence for multiple sites. The four major peaks in the ^{63}Cu spectrum have been numbered for the purpose of discussion. These peaks are also clearly identifiable in the ^{65}Cu spectrum. Their sharpness is characteristic of a nearly axial EFG tensor. Peaks 1 and 2 have been identified as belonging to a single site and have been fitted with a calculated powder pattern (solid line). The calculated fit employs a single quadrupolar splitting parameter ($\nu_Q = 27$ MHz), but uses independent distributions of shifts for the c axis and for the plane perpendicular to it (see caption, Fig. 2). The EFG

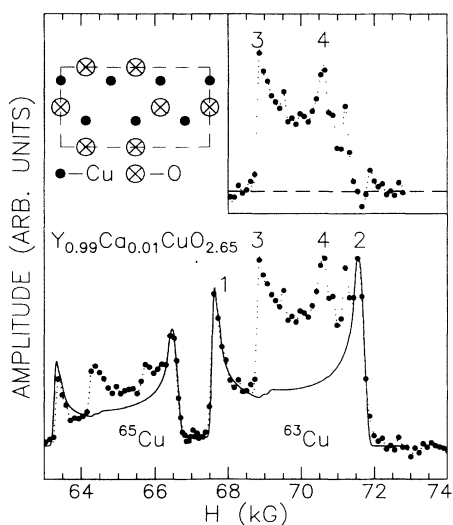


FIG. 2. ^{63}Cu and ^{65}Cu NMR spectra for $\text{Y}_{0.99}\text{Ca}_{0.01}\text{CuO}_{2.65}$, taken at 78.6 MHz, are shown for $T = 320$ K. The dotted lines are spline fits to the data. The solid line is a fit to both isotopes of a quadrupolar powder pattern with $\nu_Q = 27$ MHz (^{63}Cu), $\eta = 0.03$, and narrow distributions of shifts centered around $k_x = k_y = 0.66\%$ and $k_z = 0.90\%$. The spectrum of a second site is shown in the inset, where the solid line fit to the first site (peaks 1 and 2) has been subtracted from the raw data. The proposed hexagonal ordering of intercalated oxygen ions (Ref. 11) is shown as a unit cell on the upper left.

asymmetry parameter η is taken to be 0.03, but is actually indistinguishable from zero. The satisfactory fitting of both isotopes with a single set of parameters verifies that peaks 1 and 2 belong to a single major site.

Several conclusions follow from the spectra in Fig. 2. First, there are at least two major sites in the lattice, with a second site corresponding to peaks 3 and 4. The spectral intensity of that site as well as any additional sites is shown in the inset, where the solid curve has been subtracted from the data in that region. There appears to be another site or sites corresponding to the peaks at 69.5 and 71.2 kG (see inset, Fig. 2). If so, their intensity is weak and they are not resolved in the ^{65}Cu spectrum. Consequently, their parameters are uncertain, and we have made no attempt to analyze them further. Second, the EFG tensors for both major sites have axial symmetry at this temperature, meaning that their site symmetries, which are apparently motionally averaged in some sense (see below), are trigonal or higher. The relative intensity of the spectra for these two sites is approximately 2:1. Both of these observations are in conflict with a preliminary Cu-plane crystal structure refinement, the unit cell of which is shown in the upper left corner of Fig. 2.¹¹ In this proposed structure there is only one kind of Cu site, and its symmetry is lower than trigonal. The only way to achieve trigonal "time-average" symmetry in such a structure is for the oxygen to be rapidly diffusing through the lattice. This scenario would, however, produce a single, sharply-defined ^{63}Cu powder pattern, contrary to our observations.

In Fig. 3 we show scans of the ^{63}Cu spectrum for $\text{Y}_{0.99}\text{Ca}_{0.01}\text{CuO}_{2.65}$ at a series of temperatures down to 10 K. One finds many changes occurring in the EFG ten-

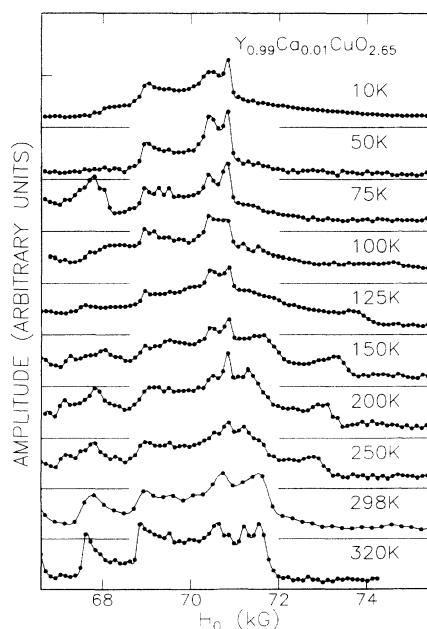


FIG. 3. ^{63}Cu NMR spectra on $\text{Y}_{0.99}\text{Ca}_{0.01}\text{CuO}_{2.65}$, taken at 78.6 MHz, are shown for a series of temperatures as indicated. The solid lines are spline fits to the data. The vertical dotted line shows the position of a spurious ^{27}Al line from the NMR probe, also noted in Fig. 1.

sor which (primarily) determines the frequency distribution in this spectrum, some occurring even at temperatures below 100 K. The sharply defined features observed at 320 K (Fig. 2) begin to blur immediately at room temperature, with peaks 1 and 2 vanishing entirely as temperature is lowered. At 10 K there is only a very broad smear of intensity remaining. This effect suggests that the site corresponding to peaks 1 and 2 is near the site, or possibly *is the site* of the partially localized magnetism in this system. In contrast, the spectrum of peaks 3 and 4 broadens slightly, then remains essentially unmodified all the way to 10 K. The corresponding site is evidently further from the disorder. Meanwhile, a new set of powder pattern extrema appear by 250 K (at 67 and 73 kG), then veer off the edges of the spectrum by 100 K or so. Another more bizarre feature appears on the left below 100 K, then abruptly disappears.¹² We are not yet in a position to analyze the foregoing effects in detail, but we can draw some general conclusions at this point. First, there is clearly ionic motion and perhaps phase changes of oxygen ordering over a wide range of temperatures. Yet, as argued above it seems unlikely that long-range diffusion is operating here. One possibility for local motion is the dynamic Jahn-Teller effect. We note that the Cu^{2+} ion in trigonal symmetry is a possible candidate for this, because the $d_{x^2-y^2}$ and d_{z^2} orbitals are degenerate.¹³ Activated motion between Jahn-Teller energy minima, setting in around room temperature, would then explain the sharpening of the axial quadrupolar extrema at $T = 320$ K (Figs. 2 and 3). It is important to note that peaks 1, 2, and 3 sharpen markedly at the same time, evidence that the two sites involved are not in different crystallites of a multiphase sample.

Spin-lattice relaxation data, presented as $(T_1T)^{-1}$ vs T , are given for both compounds in Fig. 4. Apart from the peculiar maximum exhibited in the La case [Fig. 4(a)] below $T \sim 50$ K, these data show an approximately constant value of T_1T , which is characteristic of metallic behavior.¹⁴ Thus, these results corroborate the extraction of metallic γT terms from specific heat measurements⁴ on these materials. The detailed interpretations for the two cases are quite different. For the La case, T_1 data at all temperatures were taken at the position of the central maximum in the spectrum of Fig. 1. The T_1 relaxation curves were found to deviate somewhat from the expected form¹⁵ for a single saturation pulse applied to a $(\frac{1}{2} \leftrightarrow -\frac{1}{2})$ transition for $I = \frac{3}{2}$. This deviation was very nearly constant at all temperatures, however, consistent with its arising from anisotropy in the T_1 process. The T_1 anisotropy could arise here in a similar fashion to the case of Y-Ba-Cu-O (YBCO). The transferred hyperfine couplings might be weaker here than for YBCO (Refs. 7 and 16) on account of the long Cu-O-Cu bond length, leaving only the rather anisotropic local hyperfine tensor. The increase in $(T_1T)^{-1}$ below $T \sim 50$ K [Fig. 4(a)] is anomalous, and is not accompanied by any noticeable change in the NMR spectrum (Fig. 1), which only broadens gradually as T is lowered. One possible explanation for this effect is suggested by the high concentration of localized or partially localized moments in the La samples.^{1,4} These moments

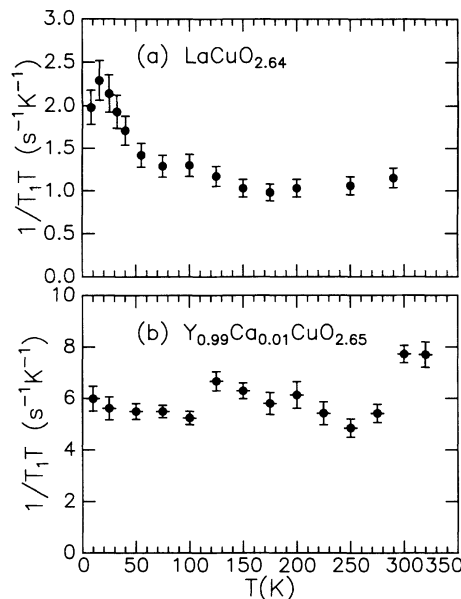


FIG. 4. Relaxation data for ^{63}Cu nuclear spins are plotted as $(T_1T)^{-1}$ vs T for (a) $\text{LaCuO}_{2.64}$ and (b) $\text{Y}_{0.99}\text{Ca}_{0.01}\text{CuO}_{2.65}$. Errors in the T_1 values extracted arise mainly from small deviations from the expected functional form of the decay (Ref. 15).

could induce additional nuclear relaxation at low temperatures where their fluctuations slow down, then weaken as the moments polarize in local fields or the applied field. What is remarkable is that the increased relaxation rate is found to be very uniform over the spins observed.

For the Y sample [Fig. 4(b)] the data for $(T_1T)^{-1}$ are more nearly constant, with a notable upturn at the highest temperatures. The latter effect is probably connected with the onset of motion, since T_2 also shortens by a factor of 2 between 293 and 320 K. The data shown were taken for peak 3 (Fig. 2), since it persists to low temperatures. At $T = 100$ K, peaks 1, 2, and 3 had similar relaxation rates, suggesting homogeneous and isotropic behavior in this phase. It is noteworthy that the relaxation process for the Y material is ~ 6 times stronger than for the La case. This fact is even more remarkable when one considers that the metallic density of states, as indicated by measured γ values,⁴ is ~ 4 times larger for the La material. This is consistent with the conclusion⁴ that there are substantial contributions to the measured γ from partially localized magnetism.

The shorter T_1 values found for the Y compound are consistent with the rather large shifts found in this case for both orientations of applied field (Fig. 2, caption). The Korringa relation¹⁴ may be stated as $(K_s^2 T_1 T)^{-1} = 4\pi k_B \gamma_n^2 F_d / \hbar \gamma_e^2$, where F_d is the d -orbital degeneracy factor. Taking $F_d = 0.5$ (Ref. 17) gives $K_s = 0.7\%$ for $(T_1T)^{-1} = 6 \text{ sec}^{-1} \text{ K}^{-1}$ [Fig. 4(b)]. Although we cannot separate spin and orbital shift contributions using the present data, the conclusion of an essentially isotropic spin shift of 0.7% is compatible with the total shifts used to fit the spectra in Fig. 2. Such behavior stands in sharp contrast with that found, e.g., for YBCO, where both shift and relaxation of the planar ^{63}Cu are strongly

anisotropic.^{7,16,17} The implied shift $K_s = 0.7\%$ in the Y case is also more than twice that of YBCO, whereas the density of states implied by the measured $\gamma = 1.5$ mJ/mole K² (Ref. 4) is only $\sim 20\%$ of the estimated value for YBCO.⁹ It is very unlikely that the ⁶³Cu hyperfine constants for Y_{0.99}Ca_{0.01}CuO_{2.65} are an order of magnitude larger than those for YBCO. We therefore interpret these results as evidence for ferromagnetic exchange enhancement of both shift and relaxation. This is not an unlikely scenario, since part of the specimen has a clearly identified ferromagnetic instability.^{4,12} The corresponding Korringa relation shift for the La case (Fig. 4) is $K_s \sim 0.2\%$, also consistent with the shift values used to fit the spectrum (Fig. 1). Although the hyperfine constants may be somewhat smaller for the La case, the metallic density of states is evidently quite a bit smaller than that implied by the measured $\gamma = 6.5$ mJ/mole K². The measured γ must therefore be dominated by contributions from the partially localized magnetism in this compound.⁴

Another measurement on the Y sample which addresses the question of susceptibility enhancement is that of the relaxation time T_2 of the spin echo. As has been discussed extensively in the literature,^{18,19} there is a strong indirect nuclear spin-spin coupling in YBCO mediated by a large antiferromagnetic peak in $\chi'(\mathbf{q})$ in the vicinity of $\mathbf{q} = (\pi, \pi)$. Thus, the measured T_2 (~ 100 μ sec) for YBCO is substantially shortened from what one would estimate using dipolar spin-spin coupling alone. In the present case we have measured $T_2 = 0.248$ and 0.306 msec, respectively, for peaks 3 and 4 (Fig. 2) at $T = 100$ K. T_1 values for these peaks are found to be essentially the same [see Fig. 4(b)]. Correcting the measured T_2 's

for the T_1 contribution,²⁰ we find $T_2(\text{spin-spin}) = 0.53$ and 0.79 msec, respectively. The expected value from the calculated dipolar second moment is $T_2 = (2/(\Delta\omega^2))^{\frac{1}{2}} = 0.275$ μ sec. This estimate is a rough lower limit, since the T_2 process could be weakened by short-range inhomogeneous broadening. Nonetheless, there is clearly no evidence here for indirect spin-spin coupling. We conclude from this result that the antiferromagnetic enhancement effects found for YBCO are absent in the delafossite materials. The essentially q -independent ferromagnetic enhancement effects discussed in the previous paragraph would give rise to indirect spin-spin coupling which has a very short range and is therefore weak.

In conclusion, this initial survey of NMR effects in the conducting delafossites reveals that a simple hexagonal arrangement of the intercalated oxygen is not compatible with the number or symmetry of sites observed. Further, there are many peculiar temperature-dependent structural effects observed in the spectra which are suggestive of a Jahn-Teller ground state for the Cu²⁺ ion. T_1 studies reveal a sharp difference between the hyperfine fluctuations in LaCuO_{2.64} and Y_{0.99}Ca_{0.01}CuO_{2.65}, with evidence for ferromagnetic susceptibility enhancement in the latter case and a smaller metallic density of states for the La case than for the Y compound, contrary to the measured γ values. T_2 measurements for the Y compound give no evidence for indirect exchange coupling, consistent with the suggested modest ferromagnetic exchange enhancement.

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