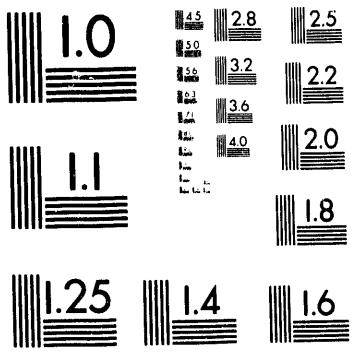
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Microscopic Study of Local Structure and Charge Distribution in Metallic $La_2CuO_{4+\delta}$

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Abstract

We employ NMR and NQR spectroscopy as probes of local structure and charge environments in metallic $La_2CuO_{4+\delta}$ (T_c=38 K). We discuss the effect of annealing the sample at various temperatures T_a ($T_c < T_a < 300K$) on the superconducting T_c. The dependence of T_c on annealing indicates that annealing allows the development of structural order with is important for T_c. The ^{139}La quadrupole frequency, ν_Q is smaller than in undoped materials. This is unexpected and may indicate a smaller charge on the apex oxygen in the doped material and thus a different distribution of charge between the La-O layer to the planes. The further, rapid decrease ν_Q just above T_c indicates that temperature dependent charge redistribution is occurring. The presence of doped holes induces a *distribution of displacements* of the apex oxygen off of the vertical La-Cu bond axis. These vary from zero to the value observed in lightly doped (antiferromagnetic) $La_2CuO_{4+\delta}$. These measurements demonstrate a striking degree of inhomogeneity in the crystal structure of the La-O layer. Copper NQR spectroscopy shows that there are *two distinct copper sites* in the CuO_2 planes and thus that either the structure or the charge distribution in the planes is inhomogeneous as well. These inhomogeneities are the intrinsic response of the crystal to doped holes; they are not the result of distortions of the lattice due to the presence of interstitial oxygen atoms.

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DISCLAIMER

1. Introduction

Structure is an underlying determinant of electronic behavior in all materials. A thorough understanding of structure of the high T_c cuprates is essential to unraveling the puzzle of the normal state electronic structure of these materials and thus superconductivity. It has been established that the superconductivity in some of the cuprates, if not all, is exceptionally sensitive to subtle details of the structure. It is becoming evident that the local structure of these materials deviates considerably from structures deduced from crystallographic determinations. There is growing recognition that these little understood structural properties may be at the root of the novel and potentially technologically important properties of these materials. We have undertaken an extensive *microscopic* study of local structural and charge environments with the goal of characterizing the nature of these local environments and gaining insight into the relationships between these and the novel electronic and magnetic behaviors observed in the cuprates.

For several reasons we have chosen to focus on metallic, oxygen-doped $La_2CuO_{4+\delta}$. A remarkably strong sensitivity of superconductivity to doping near x=0.125 has been observed in $La_{2-x}Ba_xCuO_{4+\delta}$ [1]. This has been attributed to a subtle change in structure from the LTO to the LTT structure [2]. There is recent evidence that the suppression of superconductivity may involve more than the simple structural transition [3]. Büchner et al. [4] have shown that superconductivity is suppressed in the LTT phase only when the octahedral tilt exceeds a critical angle. Such sensitivity of electronic properties to structure indicates that the lanthanum cuprates might be good place to begin a study of the effects of local inhomogeneities, be they structural or electronic. Of this class of materials, the oxygen-doped variety is attractive for magnetic resonance studies. The observed La NMR line does not exhibit the line shift nor the broadening which results from the oxygen displacements around an interstitial oxygen. This supports the result obtained earlier [5] that the structural distortion associated with the interstitial is very short range. The ^{139}La NMR lineshape is extremely sensitive to small structural changes in the majority of the

crystal which is not affected by the distortion around the interstitial oxygen. Samples with uniform doping of $0.01 < \delta < 0.06$ such as the one studied here undergo macroscopic phase separation [6-8]. Although this represents a complication for many probes, this is much less so for magnetic resonance techniques which readily distinguish the oxygen-rich and oxygen-poor phases [8].

We will address the question of oxygen mobility in $La_2CuO_{4+\delta}$ and show evidence that oxygen mobility is lost below 200 K, thus explaining the vertical phase lines in the phase diagram below this temperature. [8] Several experiments have shown there to be a dependence of the superconducting properties, including critical temperature T_c on the rate at which the sample is cooled from room temperature [10]. We will focus on the sensitivity of T_c to cooling rate and determine the temperature at which the sample must be annealed in order to achieve a higher T_c. Given the sensitivity of T_c to doping it is attractive to attribute the reduction in T_c to incomplete phase separation which would decrease the doping of the metallic phase. We have performed studies in which the sample is held at an annealing temperature T_a for varying times then quenched to low temperatures to measure T_c [12]. These experiments reveal the dependence of T_c on T_a and suggest that the reduction on T_c after quenching is not due to a reduction of the oxygen content of the metallic phase. Instead annealing may allow development of an optimum local structure or charge environment.

The remainder of the paper will be devoted to a microscopic study of local structure and charge environments by means of magnetic resonance techniques. These studies have shown that the addition of doped holes alters the local structure of $La_2CuO_{4+\delta}$.and that these changes are the intrinsic response of the crystal to the presence of doped holes--they are not manifestations of the distortion associated with the presence of the oxygen dopant. La NQR spectroscopy probes the electric field gradient at the La site, and this is determined by the location and charge of the neighbors. The unusual temperature dependence of the NQR frequency ν_Q and comparison of the experimental results with results

expected on the basis of point charge calculations suggests that there is temperature dependent redistribution of charge from the La-O layer to the planes.

2. Macroscopic phase separation

The phase diagram of oxygen doped $La_2CuO_{4+\delta}$ at doping levels in the phase separation regime shows some unusual features. Among these are the very rapid change in the doping of both phases at the phase separation temperature T_{PS} and the vertical sides of the phase diagram below about 200 K. In Fig 1 we show the temperature dependence of La $(T_1T)^{-1}$ as a function of temperature. Such a sharp peak as occurs at 210 K often occurs when the correlation time for oxygen motion relevant for La relaxation equals the Larmor frequency. We plan to confirm this hypothesis by determining the frequency dependence of $1/T_1$. The Larmor frequency is very low (~50 MHz) so oxygen motion is essentially frozen out at this temperature. This result is consistent with the observation that below this temperature the doping of both the oxygen-rich and oxygen-poor phases remains constant also showing the loss of oxygen motion.

3. Cooling rate dependence of T_c

Many workers [10] have observed a cooling rate dependence of the superconducting properties in oxygen doped $La_2CuO_{4+\delta}$. In Fig 2 we have plotted the T_c which results when the sample is held for times as short as 20 minutes at various annealing temperatures T_a. We observe that T_c increases steadily with decreasing T_a down to approximately 200 K. Annealing below this temperature results in a low T_c similar to that achieved by rapid cooling from room temperature.

One possible explanation of this behavior is that rapidly cooling the sample leaves the metallic phase oxygen content δ_M at a lower value than is achieved by slow cooling and thus decreases T_c. While the magnitude of the change in T_c is consistent with this explanation[11], the weak dependence of T_c on $T_a$shown in Fig 2 is not. Studies of oxygen mobility in the cuprates find [12] a conventional Arrhenius behavior. In $La_{2-x}Sr_xCuO_4$ the activation energy U which falls in the range of 0.7 to 1.1 eV depending on x. In

$La_2CuO_{4+\delta}$ we find that a slow cooling rate R_s of about 1 K/minute is sufficient to produce a higher T_c; while a fast rate R_f of less than 4 K/minute will result in lower T_c. The difference in these rates is small compared to the several orders of magnitude change in oxygen mobility between 250 K and 200 K. Let us consider the possibility that the reduction in T_c is attributable to inadequate oxygen mobility which in turn causes the metallic phase to have reduced oxygen content. In this case this small change in cooling rate would not be expected to affect the low temperature value of δ_M and thus T_c outside a narrow range of annealing temperatures near a temperature T_f (~200 K) where oxygen mobility is lost. Assuming Arrhenius behavior $(U = 0.7\,\mathrm{eV})$ we estimate the width of this range to be $\Delta T \approx \left(T_f^2/U\right)\ln\left(R_f/R_s\right) \approx 7\,\mathrm{K}$. The result in Fig 2 is inconsistent with this scenario since T_c is changing with annealing temperature from room temperature down to 200 K. Thus the observed sensitivity of T_c to cooling rate is more complex. One possibility is that the oxygen mobility in the oxygen doped material has a very different temperature dependence than is observed in the Sr doped material. In order to explain the observed T_c dependence on annealing temperature the mobility would have remain nearly constant between room temperature and 200 K instead of decreasing with the strong activated behavior. This would imply that the kinetics of oxygen motion is very different in this material. This is not implausible if the interstitial oxygen plays a key role in determining oxygen mobility. Perhaps once the interstitial site is occupied the activation barrier for motion is greatly decreased leading to a much weaker temperature dependence. If the interstitial oxygen were then to become ordered in the lattice at 200 K this could reintroduce a (larger) activation barrier and thus initiate a strong temperature dependence to the oxygen mobility below this. A more likely possibility is that this is a conventional annealing effect and that the slow cooling allows the local structural environments to achieve a configuration more favorable for superconductivity. It has been proposed that the observation that T_c increases in $YBa_2Cu_3O_{7-y}$ with annealing [13] results from the optimization of the local configuration of oxygen in the chains which allows improved charge trans-

fer to the planes and thus increases T_c. As we will discuss shortly we have observed that the local structure of the La-O layer is quite temperature dependent, opening the possibility that an analogous effects may be important in the La-O layer. It may also be that residual local disorder is pair-breaking and that this can be reduced by annealing. [14]

4. Determination of local structure and local charge environments

We have employed NQR [15] and NMR [16] as local probes of the La-O layer and the CuO_2 planes. In both cases the key information we have obtained reflects the interaction of the nuclear quadrupole moment with the electric field gradient (EFG) at the nuclear site. The EFG is described by a symmetric traceless tensor[17]. In its principal axis frame this tensor is diagonal and can be described by two parameters: the quadrupole frequency ν_Q which specifies the magnitude of the largest component of the diagonal EFG tensor V_{zz}, and the asymmetry parameter η which specifies the degree of departure from axial symmetry. We determine both ν_Q and η from zero-field (NQR) measurements.

4.1 La NQR

Fig 3 depicts the temperature dependence of the La NQR spectrum. At high temperature ν_Q is the same for both the metallic and AF phases. However, below 200 K we observe the shift of the spectral weight associated with the metallic phase to lower frequency as well as substantial broadening of the spectrum. While the broadening is not unexpected in view of the distribution of structures we observe in NMR experiments (see below and [16]), the shift to lower frequency is. The addition of interstitial oxygen has the effect of compressing the lattice. The EFG at the nuclear site is the sum of the contributions from the distribution of charge on the ion as well as from the lattice of ions surrounding the site. In the case of a closed shell ion such as La, these two contributions are essentially proportional to one another and so ν_Q is proportional to the lattice contribution to V_{zz}. Thus $\nu_Q \propto \sum_i eq_i(3z_i^2 - r_i^2)/r_i^5$ where i labels the various ions having relative location r_i with respect to the La site and charge q_i. One expects that this compression should lead to an increase in ν_Q. We have used point charge calculations [18] to estimate

the EFG in the presence of the interstitial dopant oxygen. They confirm this picture and predict an *increase in* ν_Q of approximately 10% (for $\approx 50\%$ of the sites, roughly, another 10% of La sites will have $\Delta\nu_Q > 100\%$).

In order to understand the observed changes in the metallic phase spectrum we must assume that below 200 K there is a decrease in q_i with decreasing temperature. This would be consistent with a redistribution of charge from the La-O layer into the planes. It should be noted that this is a transfer of electrons, not holes, i.e. the magnitude of the (negative) oxygen valence is decreasing. The smaller value of ν_Q may be related to its unusual temperature dependence shown in Fig 3(b). The behavior of the average frequency observed in the AF phase is indicative of the behavior of ν_Q with temperature in $La_2CuO_{4.01}$. The contrast with the metallic phase is clear: the center of gravity of the La NQR resonance is non-monotonic in temperature, decreasing at low temperatures. The more rapid decrease just above T_c is interesting, indicating that charge redistribution accelerates in this temperature regime.

4.2 La NMR

In the NMR experiment we measure the quadrupole interaction at the La site in the presence of a large applied field. In this case the resonance frequency is sensitive to the orientation of the EFG principal axis frame with respect to the field which was applied along the c-axis (perpendicular to the planes) in our experiments. The shift $\nu^{(2)}$ of the $m = 1/2 \leftrightarrow -1/2$ transition frequency by an axially symmetric EFG depends on the angle θ between the applied magnetic field and V_{zz}. If we define $\mu \equiv \cos\theta$, then $\nu^{(2)} = (15/16)(\nu_Q^2/\nu_Z)(1-\mu^2)(1-9\mu^2)$ where the Zeeman frequency is $\nu_Z = (1+K)\gamma H_0$, K is the Knight shift, γ the ^{139}La gyromagnetic ratio and H_0 the magnitude of the applied magnetic field. The field dependence of the quadrupole shift ($\propto 1/H_0$) allows it to be easily distinguished from magnetic shifts ($\propto H_0$). Spectra were taken at 52.5900 MHz and 30.3629 MHz at all temperatures and occasionally at 39.1983 MHz as well to establish that the shifts were linear in $1/H_0$.

We have also modeled the relationship between the configuration of the oxygen ions surrounding the La and the orientation of V_{zz}. We find that this is primarily determined by the orientation of the bond between the La ion and the apex oxygen located vertically (along the c-axis) above it. Thus the development of a finite tilt of the EFG away from the c-axis reflects a lateral shift of the apex oxygen off the La-Cu bond axis. Point charge calculations indicate that, in fact, the tilt of the EFG exceeds the tilt of the La-O bond by about 60%. The tilts of the EFG we observe at the La site in the AF phase ($\approx 19°$) exceed the predictions of our simple point charge calculations ($\approx 7°$) by a factor of 2.5. This is not understood.

It is worth while to consider the effects of fluctuations of the EFG on the NMR spectrum. For small tilts we can make the approximation $\nu^{(2)} \propto \theta^2$. If these fluctuations are rapid compared to the Larmor frequency then $\nu^{(2)} \propto \langle\theta^2\rangle$ where $\langle f\rangle \equiv$ time average of $f(t)$. One might imagine a situation in which the EFG is tilted by a small angle away from the c-axis but rotating about it in such a way that $\langle\theta\rangle = 0$ on the NMR time scale. In this case $\langle\theta^2\rangle$ is not zero and $\langle\nu^{(2)}\rangle$ will not vanish, and the spectrum will be sharp whether the EFG is fluctuating or not. Another possibility is that the EFG at a given site is occasionally parallel to the field and occasionally tilted. If this fluctuation is slow (compared to the Larmor frequency) we will observe a broad line representing the distribution of tilts, while rapid fluctuations will produce a narrow line where the shift is given by $\langle\theta^2\rangle$. Thus, in this case rapid fluctuations can narrow the line, but they will not cause the shift to vanish.

We turn now to the results which we wish to emphasize: the determination of the off-axis displacement of the apex oxygen in the metallic phase and its description in terms of a distribution of orientations of the EFG at the La site. In Fig 4 we show that above and just below T_{PS} the ^{139}La NMR line is sharp and unshifted. Thus although we expect that the material is orthorhombic [6], there is no lateral displacement of the apex oxygen. That we observe a sharp, unshifted line observed at high temperature is also very interest-

ing because it shows that the La signal *we observe* is *not* affected by the structural distortion in the immediate vicinity of an interstitial oxygen. Note that oxygen motion cannot be responsible for the unshifted, narrow line. Our point charge modeling[18] confirms that the signal from the fraction (~10%) of La nuclei neighboring an interstitial oxygen is unobservable due to the very large values of ν_Q and large tilts. The behavior of the metallic phase should be compared with that of the oxygen-poor ($\delta \cong 0.01$) antiferromagnetic (AF) phase which displays a finite and well defined shift at all temperatures consistent with the tilt of the EFG (angle θ_{AF}) due to the off-axis displacement of the apex oxygen present in the orthorhombic phase.

With decreasing temperature the metallic ^{139}La NMR line becomes broadened as a distribution of apex oxygen off-axis displacements develop. We have [16] analyzed the lineshape as a function of temperature to obtain a distribution of tilts $P(\mu)$. In Fig. 4(b) we show $P(\mu)$ at four temperatures to indicate its the evolution with temperature. Note that there is never any spectral weight at shifts greater than are observed in the AF ($\delta \cong 0.01$) phase, thus, in the metallic phase, there is a cutoff in the tilt distribution at $\theta_{max} = \theta_{AF}$. At low temperature we find a simple but remarkable distribution of tilts: $P(\mu) \cong$ constant , i.e. the distribution is *uniform* (any point on the unit sphere with $\theta < \theta_{max}$ is occupied with equal probability). Note that the sharply peaked tilt distribution characteristic of the distortion associated with a point defect is *not* observed. Thus, even at low temperatures, NMR is unable to observe the signal from La atoms affected by the distortion due to the interstitial oxygen. We conclude that the distributed structure we observe is the intrinsic response of the crystal to the presence of doped holes. Note that for a low ($\delta \cong 0.01$) doping of the AF phase, there is a single, well-defined lateral displacement of the apex-oxygen at all temperatures. Thus there is some threshold doping necessary to induce the distributed structure. Unfortunately the macroscopic phase separation prevents one from varying the doping of the metallic phase in the region

$0.01 < \delta < 0.06$ in order to determine this threshold. It is tempting to speculate that it might coincide with the metal-insulator transition.

Recently neutron scattering measurements in powders and single crystals of electrochemically prepared $La_2CuO_{4+\delta}$ with sufficient oxygen content to be in the single phase region of the phase diagram have been performed [19]. They find the apex oxygen located directly above the copper (Fmmm structure) *on average*, however superstructure peaks indicate a long wavelength, commensurate modulation of the oxygen position. Given evidence of long range order, we conclude that the varying lateral displacements of the apex oxygens we observe locally are described by a long wavelength modulation commensurate with the lattice. Similar superlattices have been observed in BSSCO. Bianconi et al. have found [21] the superlattice structure to be associated with variations in the length of the Cu-apex oxygen bond and have hypothesized the existence of ordered polaron superlattice.

4.3 Cu NQR

It is important to understand the effect this distribution of octahedral tilts has on the electronic properties of the CuO_2 planes, since this is the location of the itinerant holes which become superconducting at low temperature. Copper NQR is a local probe of the of the charge environment of the copper. In Fig. 5 we show the copper NQR spectrum obtained in oxygen-annealed $La_2CuO_{4+\delta}$ at 40 K (it is very little different at 250 K). The important feature of this spectrum is that when one takes into account the effect of the two copper isotopes, the appearance of three lines demonstrates unambiguously the existence of two distinct copper sites in the planes. Note that the signal from the antiferromagnetic oxygen-poor phase occurs at a frequency of approximately 100 MHz due the very large hyperfine field of the ordered copper moments in the Néel state. Thus all of the spectral features shown here arise from the metallic phase of the sample alone. It is natural to attribute the second site to the proximity of an interstitial oxygen. This explanation is rendered implausible by the fact that this spectrum is essentially identical to the

copper NQR spectrum observed in $La_{2-x}Sr_xCuO_4$. The dependence of this spectrum on doping has been extensively studied [21-24] and it has been found that the frequencies of the two ^{63}Cu spectral features depend on doping as shown in the inset to Fig. 5. Both features increase in frequency with doping, the minority feature increasing more slowly.

The magnetic susceptibility of most metallic cuprates including lanthanum cuprate is very sensitive to the level of hole doping in the planes. These measurements in metallic $La_2CuO_{4+\delta}$ have allowed a determination of the hole density arising from oxygen annealing [8,25]. In particular, the hole density in the metallic phase of phase separated $La_2CuO_{4+\delta}$ is approximately 0.09 holes/copper. When we compare (see inset to Fig 5) the frequencies of the ^{63}Cu features with those observed in $La_{2-x}Sr_xCuO_4$ at this doping we find that they both coincide perfectly.

The location of the dopant impurities in $La_2CuO_{4+\delta}$ and $La_{2-x}Sr_xCuO_4$ are very different: the excess oxygen is interstitial and located between the La-O planes at the center of four tetrahedrally coordinated La atoms whereas the strontium substitutes for a La atom. Furthermore the valence of the two dopants relative to the $La_2CuO_{4.0}$ background is different. The charge of the oxygen dopant is -1.4 to -2.0 while the charge of the strontium relative to the La it replaces is -1.0. It is quite implausible that these two very different lattice charge arrangements could be directly responsible for the two sets of spectral features having identical frequencies. Thus it is clear that the second copper site is not differentiated simply by the proximity of the dopant impurity. The agent which distinguishes the second site must be common to both systems and independent of the specific nature of the dopant. The most likely explanation is that the second site is a manifestation of the response of the system to the presence of doped holes themselves.

Identification of the specific origin of the second site is difficult. Ultimately, the quadrupole frequency ν_Q is determined by the distribution of charge surrounding the copper nucleus. Thus the larger value of ν_Q may be due either to a change in the local lattice structure around the copper site or due to a redistribution of charge in the lattice

surrounding the copper or within the copper ion itself: one possibility is a transfer of charge from the $d_{x^2-y^2}$ to the $d_{3z^2-r^2}$ orbital. It is important to point out that the feature which distinguishes the second site must be static on the time scale of at least the inverse of ν_Q. Thus whatever local variation in charge density is responsible for the second copper site must be essentially stationary or very slowly moving.

5. Interpretation and Discussion

At this point we would like to propose two mechanisms which might explain the inhomogeneous properties of the crystal structure and charge distribution. We must reconcile two seemingly inconsistent facts: the tilt of the oxygen octahedra are distributed *continuously* between zero tilt and the large tilt associated with very lightly doped material ($\delta \equiv 0.01$) whereas we observe *two distinct* charge environments in the CuO_2 planes.

If we focus first on the copper NQR results it is natural to think of a local region of increased hole density. The association of the feature at higher frequency with a region of increased hole density would be consistent with the fact that ν_Q increases with doping in $La_{2-x}Sr_xCuO_4$. The observation of two distinct sites would imply well defined regions having different hole densities. Thus this is, in effect, a *microscopic* phase separation of doped holes occurring within the metallic phase (which is unrelated to the macroscopic phase separation). The tilt of the oxygen octahedra decreases as hole density is increased so we might expect that the region of high hole density in the planes would produce a region of reduced tilts. In order to understand the observation of a continuous distribution of tilts, we might hypothesize that some feature of the cuprates prevents the magnitude of this tilt angle from changing rapidly with distance. If this were the case we might expect a suppression of the octahedral tilt at the location of the high hole density in the planes, and that this tilt would increase with distance from the hole-rich drop. The observation of superlattice points in the neutron scattering [19] would suggest that the locations of the hole rich regions in the planes exhibit long range order. One might imagine that in this case the interstitial oxygen would attempt to order as well.

On the other hand, the continuous distribution of octahedral tilts suggests a modulation of this tilt having a wavelength long compared to the lattice parameter. Such a modulation of local properties is reminiscent of materials which exhibit charge density waves (CDW). In $TaSe_2$ a CDW driven by Fermi surface nesting develops at low temperature [26]. This mechanism favors an incommensurate CDW because the nesting wave vector is incommensurate. However, lattice energies favor a commensurate CDW. The system resolves this competition by forming domains in which the CDW is commensurate. Phase slips in the domain walls allows the long range variation of the phase of the CDW to be incommensurate. If the tilt of the octahedra were correlated with the phase of the CDW a similar phenomenon could explain the observed distribution of tilts. In this scenario the interior of the domains and the domain walls could provide two distinct environments which would explain the two features in the copper NQR spectrum. The CDW and the domain structure would have to be static as previously mentioned, possibly pinned to the lattice by the presence of the interstitial oxygen atoms in the La-O layer.

6. Conclusions

We have found in $La_2CuO_{4+\delta}$ clear evidence that the addition of doped holes induces inhomogeneity into the octahedral tilt pattern and the charge environment of copper in the CuO_2 planes. We have argued that these inhomogeneities are not manifestations of the expected local distortion associated with the interstitial oxygen, but are, instead, the response of the material to the presence of doped holes. This observation is important in itself because it demonstrates a previously unrecognized tendency toward inhomogeneity in a cuprate when doped holes are added. The recognition that the inhomogeneity in the planes in both strontium- and oxygen-doped material is identical and therefore cannot be the direct result of the proximity of a dopant reinforces the belief that this is a general feature of doped lanthanum cuprate. The sensitivity of T_c to annealing suggests that these local structures play an important role in the superconductivity in these materials.

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Figures

Fig.1 Temperature dependence of the La relaxation rate divided by temperature is shown. Note the sharp peak in $(T_1T)^{-1}$ at 210 K. La nuclear spin relaxation is due to fluctuations of the EFG caused by motions of neighboring oxygen atoms. A likely interpretation of the peak is that at this temperature the frequency of fluctuations become equal to the nuclear Larmor frequency.

Fig. 2 The dependence of T_c on the temperature T_a at which the sample is annealed during cooldown is shown. T_c increases with decreasing anneal temperature from room temperature down to 200 K. It is unlikely that this phenomenon can be attributed simply to reduction in metallic phase oxygen content δ. Although one might expect rapid cooling to prevent full phase separation, the oxygen mobility changes by over four orders of magnitude between 250 and 200 K, much more than the factor of four difference between fast and slow cooling rates important for T_c.

Fig. 3 Temperature dependence of the NQR spectrum. Panel (a): the spectrum at 4 K. The two sharp peaks originate in the oxygen-poor phase, the splitting arising from the hyperfine field of the antiferromagnetically ordered copper moments. The broad line is from the metallic phase. The temperature dependence of the NQR frequencies is shown in panel b). The frequencies shown for the broad metallic line represent the center of gravity of the (asymmetric) line. The reduced value of ν_Q is unexpected as discussed in the text.

Fig. 4 Variation of the ^{139}La NMR spectrum with temperature. The broadening of the line at low temperatures results from a distribution of tilts of the oxygen octahedra which develop with decreasing temperature.

Fig. 5 Copper NQR spectrum in $La_2CuO_{4.06}$ is shown. The spectrum is the sum of spectra arising from ^{63}Cu and ^{65}Cu isotopes. The existence of three peaks unambiguously demonstrates that there are two distinct copper sites. The plot in the inset compares the frequencies of these peaks observed in oxygen doped material (present work) to those seen in Sr doped material. The frequencies are essentially identical. This clearly demonstrates that the second peak does not arise as a consequence of the proximity of the dopant impurity. Note that the copper signal arising from the oxygen-poor phase occurs at approximately 100 MHz due to the very large hyperfine field of the antiferromagnetically ordered copper moments, and so is not visible here.

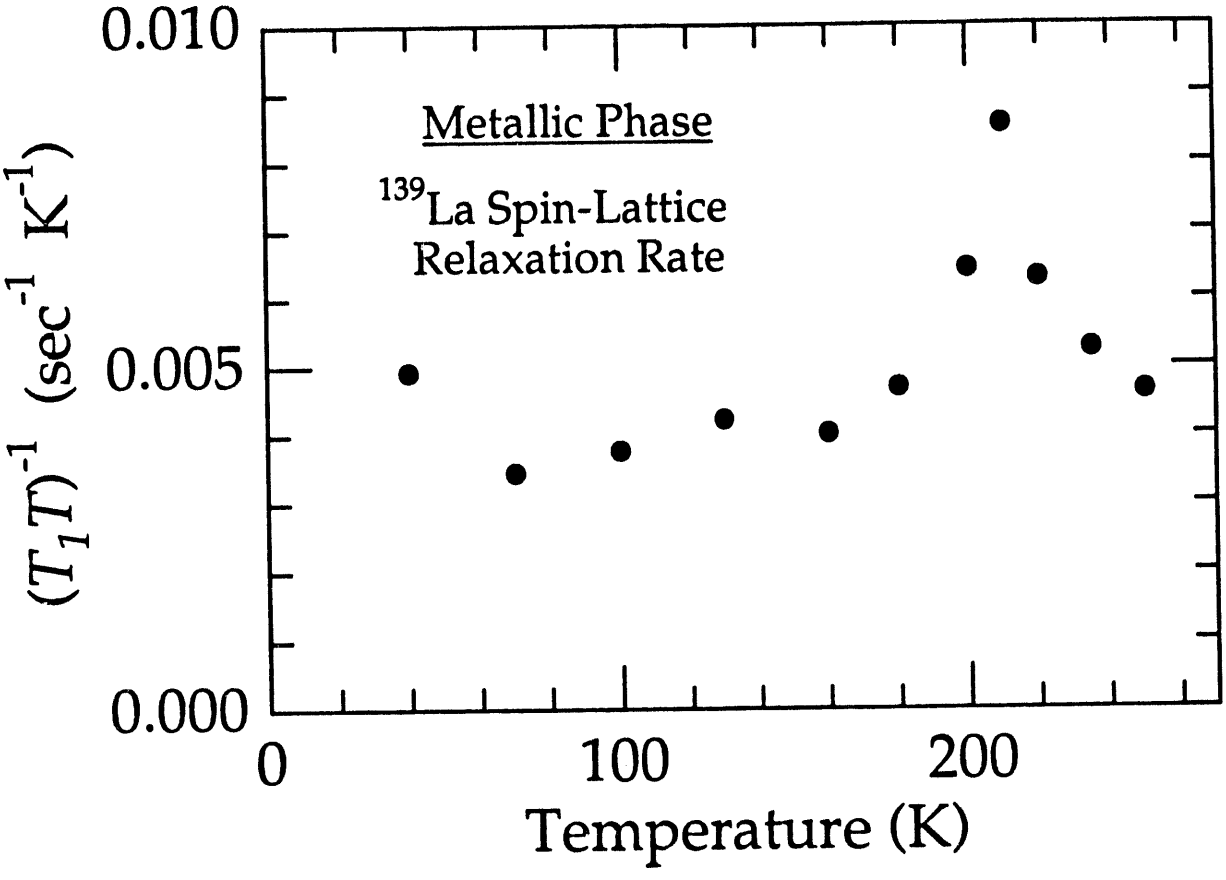

Fig 1.

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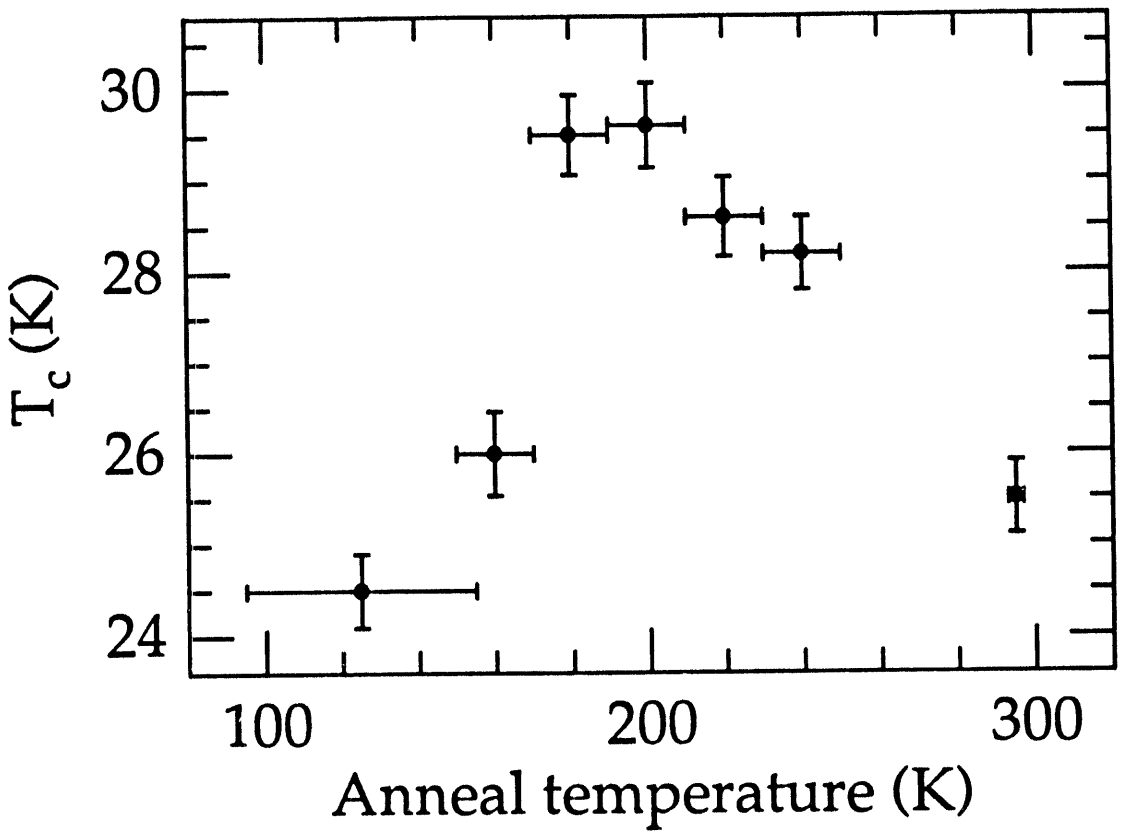

Fig 2

Hammel et al., "Microscopic Study of Local Structure..."

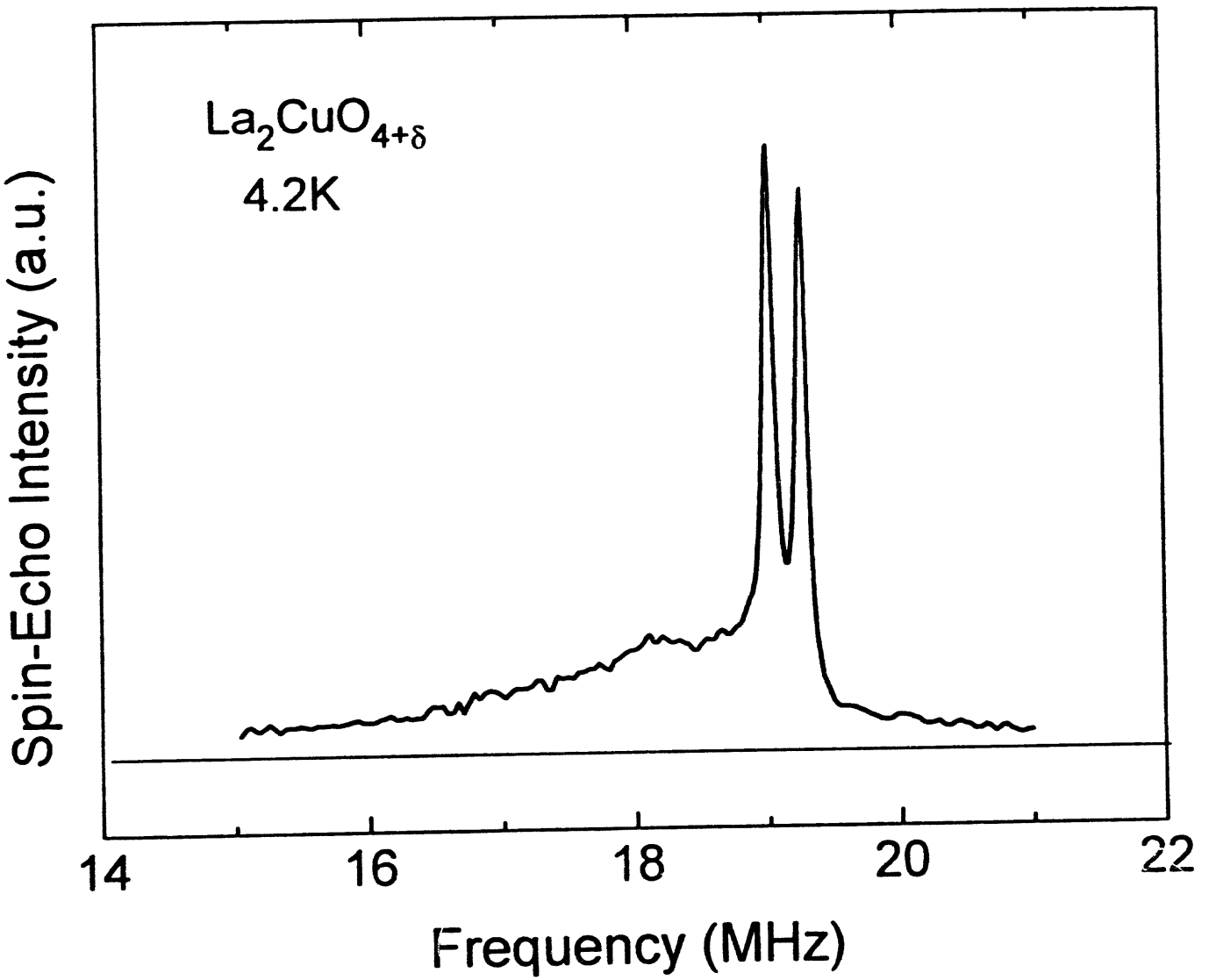

Fig 3(b)

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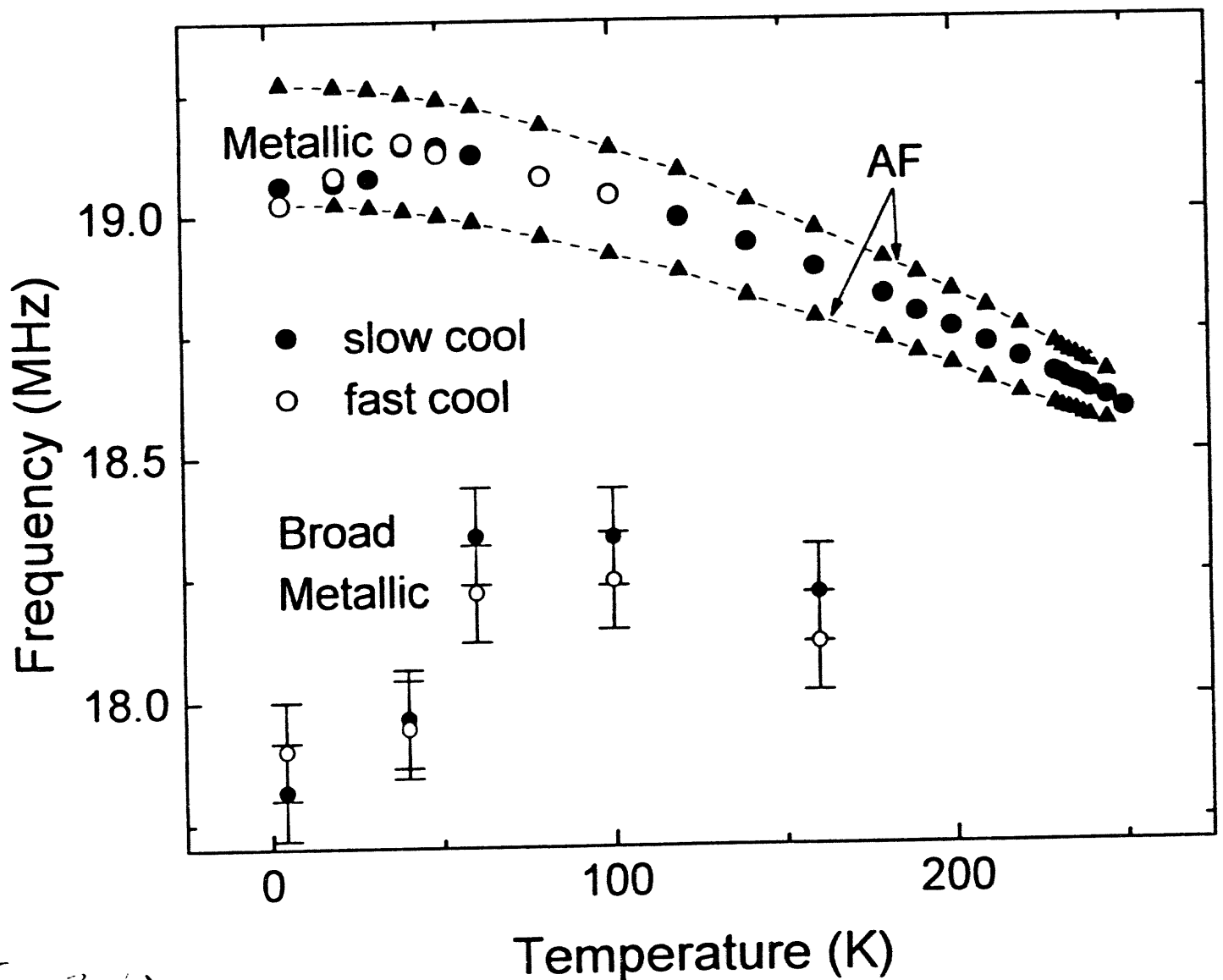

Fig 3(b)

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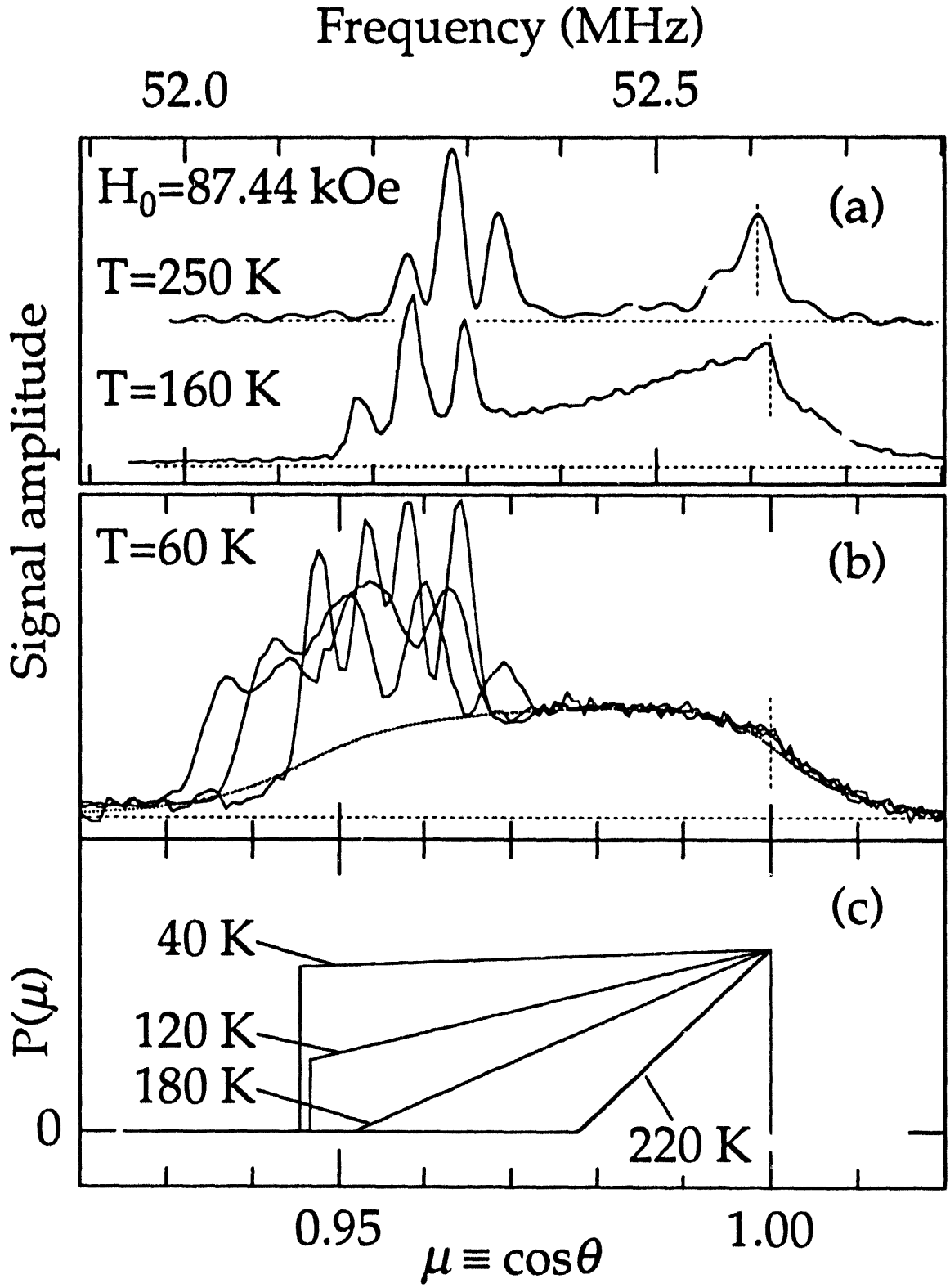

Fig 4

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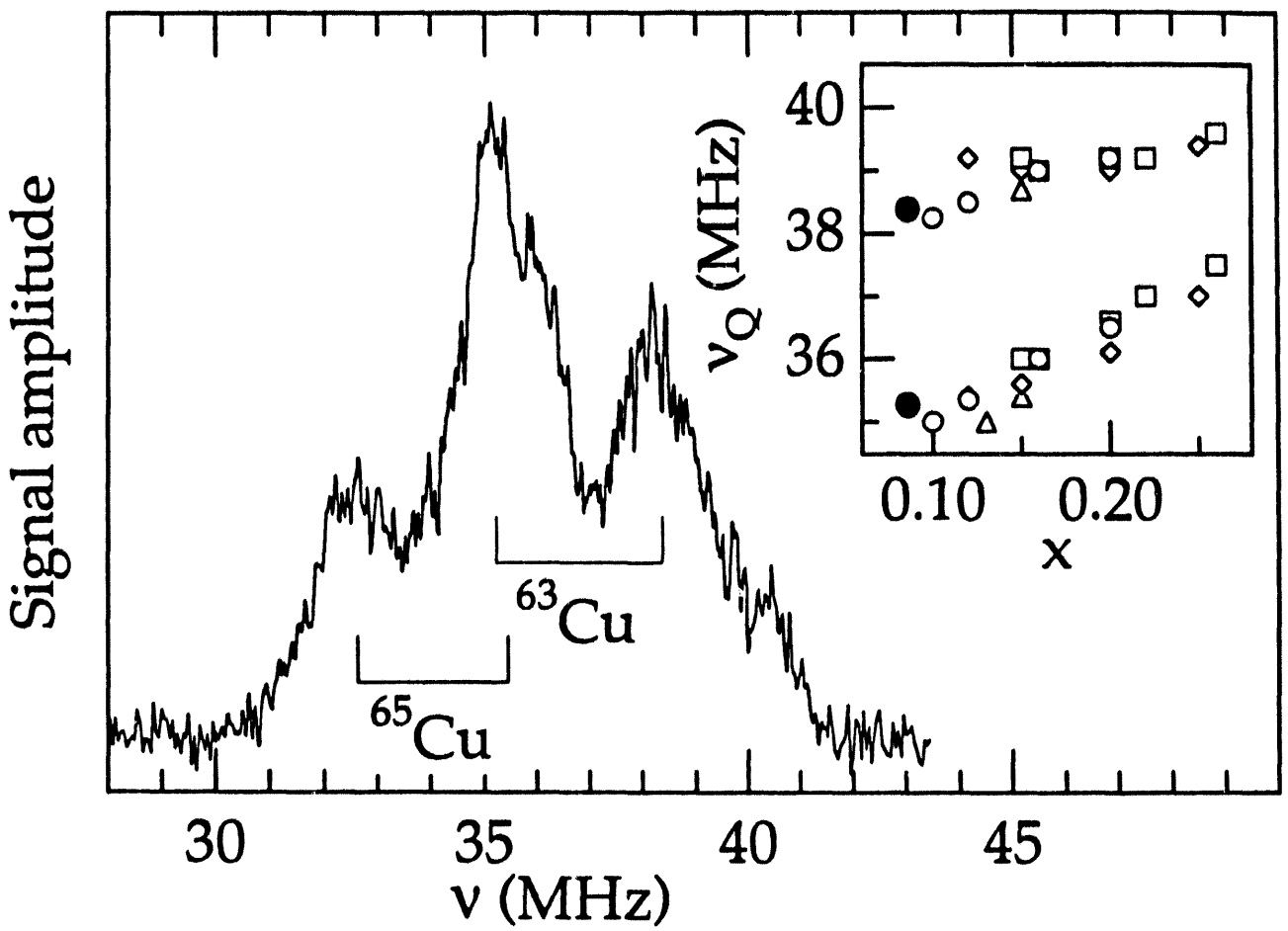

Fig 5

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