# Correspondence between antiferromagnetic structure of $La_2CuO_{4-\delta}$ and NQR spectra of $^{139}La$

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The NQR spectra of $^{139}La$ in $La_2CuO_{4-\delta}$ correspond completely to the simple antiferromagnetic structure found for this oxide by neutron diffraction, despite the data of Kitaoka *et al.* [J. Phys. Soc. Jpn. **56**, 3024 (1987)] and Furo and Janossy [Jpn. J. Appl. Phys. **26**, L1307 (1987)].

Studying the NQR of $^{139}La$ in the high-$T_c$ superconductors $La_{2-x}(Sr, Ba)CuO_{4-\delta}$ has proved a valuable experimental method for observing antiferromagnetic order, for studying $(T, x)$ phase diagrams, and for studying deviations from stoichiometry in terms of oxygen. The nucleus $^{139}La$ ($I = 7/2$, $\gamma = 601.44$ Hz/Oe,

  

$Q = 0.21 \times 10^{-24}$ cm$^2$) is a probe which tells us whether there is a magnetic order in terms of the magnitude of the local magnetic field $\mathbf{H}_{loc}$ which is induced by the magnetically ordered, surrounding copper ions and also tells us about changes in the electron structure, by virtue of the magnitude of the electric field gradient (EFG) at the nucleus. Even in the earliest studies[1-3] of the NQR of $^{139}$La in pure $La_2CuO_{4-\delta}$ (space group *Cmca* with $a < c < b$), which is the basic compound for this series of high-$T_c$ superconductors, a contradiction was found between, on the one hand, the magnitude and (especially) the direction of $\mathbf{H}_{loc}$ in the crystal and, on the other, the antiferromagnetic structure reconstructed by magnetic neutron diffraction (Ref. 4, for example). At 1.3–4.2 K, several investigators[1-3] have experimentally determined an angle $\theta = 75$–$78°$ between $\mathbf{H}_{loc}$ and the principal axis of the EFG. According to the analysis of Refs. 1 and 3, in the case $\vec{\mu}_{Cu} \parallel c$ (a structure of this type, with a checkerboard alternation of directions of moments, was found in Ref. 4) the field $\mathbf{H}_{loc}$, of a dipole nature, is directed along the $c$ axis, while the principal axis of the nearly axial tensor of the EFG is directed along the $b$ axis, because the orthorhombic distortions are small. Consequently, the value of $\theta$ must be approximately 90°. For this reason, the presence of a significant component $H_{\parallel}$, parallel to the axis of the EFG, was explained on the basis that the actual magnetic structure of $La_2CuO_{4-\delta}$ is not what it has generally been thought to be. It was suggested in Ref. 1, for example, that the spin structure is modulated. It was suggested in Ref. 5, on the basis of symmetry considerations, that the reason for the appearance of an $H_{\parallel}$ is a tilting of the sublattices as a result of antisymmetric interactions.

We have now carried out accurate control measurements of the NQR frequencies of $^{139}$La at $T = 77$ K in a polycrystalline $La_2CuO_{4-\delta}$ sample with record-narrow resonance lines ($\Delta\nu = 20$–$40$ kHz, in comparison with the 150–200 kHz in Refs. 1 and 3) and with a value $T_N \approx 280$–$300$ K. The narrow resonance lines are evidence that the deviations from stoichiometry are small.[6] The particular temperature chosen for this study was dictated by the circumstance that uncontrollable magnetic impurities can affect the properties of $La_2CuO_{4-\delta}$ at liquid-helium temperatures.[7] We measured the following frequencies, $\nu_{1-8}$, of the NQR spectrum, which consists of four pairs of lines: 5354.5, 5705.8, 7623.5, 7975.2, 12 542.3, 12 779.7, 18 955.0, and 19 189.8 kHz. With $I = 7/2$, this NQR spectrum is explained in terms of a perturbing effect of $\mathbf{H}_{loc}$ (Ref. 6). Without going through a numerical diagonalization of the total nuclear Hamiltonian, we used approximate formulas found in first-order perturbation theory for an axisymmetric electric field gradient[6]:

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

Here $H_{\parallel}$ and $H_{\perp}$ are the components of $\mathbf{H}_{loc}$ in the directions parallel to and perpendicular to the principal axis of the EFG, and

$$\nu_{3/2 \leftrightarrow 1/2} = (1/2)\nu_{5/2 \leftrightarrow 3/2} = (1/3)\nu_{7/2 \leftrightarrow 5/2} = \nu_Q = (1/14h)eQ\vartheta_{zz} \quad (2)$$

Relations (1) hold for the $I4/mmm$ tetragonal structure, but because of the small values of $\eta$ expected in the $Cmca$ structure, we assumed that relations (1) hold if relations (2) are modified and are determined by series[8] in even powers of $\eta$.

The values $\nu_Q = 6.364$ MHz, $\eta = 0.097$, $\mathbf{H}_{\parallel} = 0.196$ kOe were determined from $\nu_{5-8}$, which have the smallest Zeeman perturbations. The component $H_{\perp} = 0.942$ kOe was determined from $\nu_{1-4}$. In this case we have $\mathbf{H}_{\rm loc} = 0.962$ kOe at 77 K, and this field makes an angle $\theta = 78.3°$ with the principal axis of the EFG. These results agree well with the data of Refs. 1–3 at 1.3–4.2 K.

Since $\theta$ is the angle between the principal axis of the electric field gradient and $\mathbf{H}_{\rm loc}$, in order to explain their relative orientation, we need to separately examine the mechanisms for the induction of $\mathbf{H}_{\rm loc}$ and the EFG in the orthorhombic coordinate system of the $La_2CuO_{4-\delta}$ cell.[1)]

A calculation of the dipole magnetic fields induced at the $^{139}$La nuclei by $\vec{\mu}_{\rm Cu}$ has been carried out in the model of point dipoles, with allowance for the coordinates of the ions[9] and for $\vec{\mu}_{\rm Cu} \parallel c$ (i.e., for a collinear antiferromagnetic structure). A calculation of the dipole lattice sums in a sphere $r \leqslant 4a$ leads to the values (in kiloersteds)

$$H_{a\,\rm dip} \equiv 0; \qquad H_{c\,\rm dip} = 0.916 n_{\rm Cu}; \qquad H_{b\,\rm dip} = 0.0382 n_{\rm Cu}, \quad (3)$$

where $n_{\rm Cu}$ is the localized moment, in Bohr magnetons. The values in (3) show that the local field makes an angle $\sim 2.4°$ with the $c$ axis in the $bc$ plane, and with the value $\vec{\mu}_{\rm Cu} = 0.6\vec{\mu}_{\rm B}$, which is characteristic[10] of crystals with $T_N \approx 300$ K, the dipole component of $\mathbf{H}_{\rm loc}$ is $\sim 60\%$. The rest of $\mathbf{H}_{\rm loc}$ is apparently due to indirect hyperfine interactions, since there is no direct mixing of the $La^{3+}$ and $Cu^{2+}$ orbitals in $La_2CuO_{4-\delta}$ (Ref. 11). Since the indirect hyperfine field is parallel to $\vec{\mu}_{\rm Cu}$, there is a change in primarily the component $H_c$. As a result, the angle between $\mathbf{H}_{\rm loc}$ and the $c$ axis decreases fo $\sim 1.4°$. Incorporating a tilting $\sim 0.17°$ of the sublattices[12] in the calculations has no effect on the results in (3).

The components of the EFG tensor have been calculated in the point-charge model with the nominal ion charges and coordinates of Ref. 9. The lattice sums were calculated in a sphere $r \leqslant 4a$. It turns out that the $O^{2-}$ ions in (8e) make the dominant contribution. Taking the Sternheimer antiscreening factor of $La^{3+}$ into account, $\gamma_\infty = -65.8$, we find the following components of the EFG tensor (in units of $10^{14}$ esu):

$$\vartheta_{aa} = 27.67; \qquad \vartheta_{cc} = 20.20; \qquad \vartheta_{bb} = -47.87; \qquad \vartheta_{cb} = 10.99, \quad (4)$$

These figures correspond to a rotation of the principal axis ($z$) of the tensor through an unexpectedly large angle $\sim 9°$ from the $b$ axis in the $bc$ plane. The monopole contribution to the EFG which we calculated ($\vartheta_{zz} = -49.60$, $\nu_Q = 5.39$ MHz, $\eta = 0.116$) describes nearly completely (85%) the experimental value $\nu_Q = 6.36$ MHz. It also agrees with the experimental value $\eta = 0.097$. An important result of this calculation is the fact that in a $Cmca$ structure the principle ($z$) axis of the EFG tensor deviates from the $b$ axis by a significant angle. As a result, the calculated angle

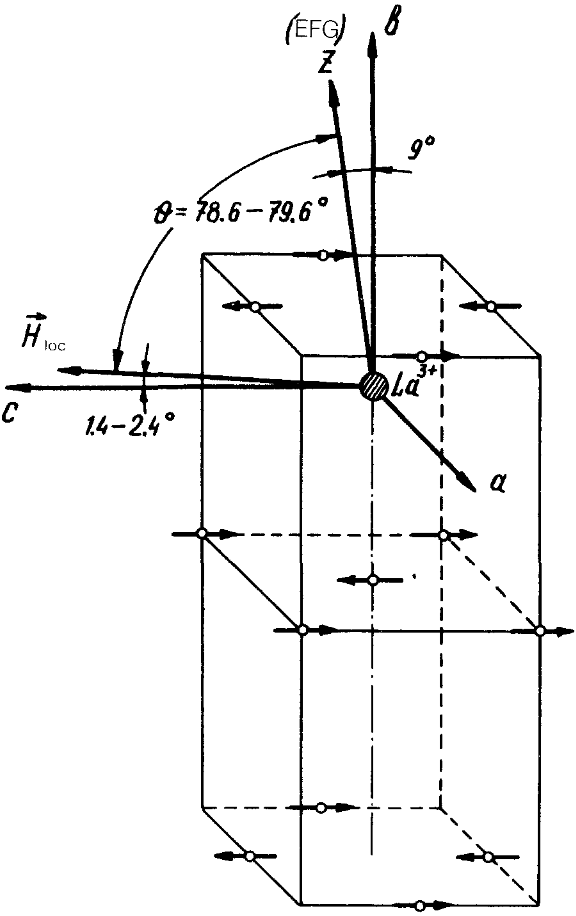


FIG. 1. Magnetic structure of $La_2CuO_{4-\delta}$ according to neutron diffraction[4]; orientation of $\mathbf{H}_{loc}$ and of the principal ($z$) axis of the tensor of the electric field gradient. (The displacement of the $La^{3+}$ ion and the tilting of the sublattices are not shown.)

between $\mathbf{H}_{loc}$ and the $z$ axis of the EFG (Fig. 1) is 78.6–79.6°, in excellent agreement with the experimental value of 78.3°. The magnetic structure found by neutron diffraction for $La_2CuO_{4-\delta}$ thus agrees completely with the NQR spectra of $^{139}La$ when the directions of $\mathbf{H}_{loc}$ and of the principal axis of the EFG tensor are taken into account correctly.

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[1)] Unfortunately, it is difficult to determine the orientation experimentally, since a high-quality single crystal of large dimensions would be necessary, and there might be uncertainties due to twinning.

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