Anomalous temperature dependence of the electric field gradient at the Y site in $In_{0.1}Y_{0.9}Ba_2Cu_3O_{9-\delta}$: Evidence for soft vibrational modes

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Perturbed angular correlation (PAC) spectroscopy has been used to measure a well-defined static electric quadrupole interaction in a superconducting ceramic, $In_{0.1}Y_{0.9}Ba_2Cu_3O_{9-\delta}$. Perturbation functions, Fourier transforms, and the derived PAC parameters are given for data taken at temperatures ranging from 77 to 1070 K. Indirect evidence is presented for the occupation of the Y site by the ^{111}In-^{111}Cd PAC probe. The derived electric field gradients were found to increase linearly with temperature. This result suggests the presence of soft, anisotropic vibrations in the structure. Additional evidence is presented to indicate that O^{2-}-ion or O-vacancy transport may not occur in the Y coordination sphere.

During recent months, many of the experimental[1] and theoretical[2] investigations of superconducting ternary-copper-oxide materials have focused on the roles of O vibrations and O vacancies. Perturbed angular correlation (PAC) spectroscopy may be a technique that is sensitive to these effects. The (zero-external-field) PAC experiment uses the nuclear electric quadrupole moments of the ^{111}In-^{111}Cd radioactive probe atoms (which are substituted into specific lattice sites) to measure extranuclear electric field gradients (efg). Since two recent studies of ionic-conducting ceramics have shown that the PAC technique is sensitive to vibrational degrees of freedom,[3,4] we decided to use the PAC technique to investigate the superconducting ceramic, $In_{0.1}Y_{0.9}Ba_2Cu_3O_{9-\delta}$.

The samples were prepared (with radioactive ^{111}In as $InCl_3$ in 0.05 M HCl) by a variety of techniques to be reported later.[5] These processes involved calcination in air at 1020 K. Then, pellets (9 mm in diameter and 3 mm thick) were pressed and sintered in a tube furnace at 1220 K under an O_2 atmosphere. A powder x-ray diffraction pattern confirmed the structure of the ceramic and indicated a single phase. Magnetic (ac) susceptibility and electrical resistance measurements indicated that the transition temperature for superconductivity was approximately 94 K. In addition, we obtained PAC results that we could not interpret from a variety of differently processed samples as well as the results presented below. Primarily, these uninterpretable results were characterized by inhomogeneously broadened lines that implied multiple chemical environments for the PAC probes. Also, some of the experiments indicated the formation of stable oxides such as $Ba_2In_2O_5$ during calcination and/or sintering.

Presently, direct evidence for In substitution into the Y site in this structure is not available. To obtain supporting evidence for In substitution into the Y site, we prepared (nonradioactive) sintered ceramic pellets having the compositions $(In_xY_{1-x})Ba_2Cu_3O_{9-\delta}$ and $YBa_2(Cu_{3-y}In_y)$-

$O_{9-\delta}$. The x-ray diffraction patterns showed no appreciable second phases for $x < 0.1$ and for $y < 0.3$. Thus, substitution of In into the Y site and into the Cu sites may be possible. These problems call into question the utility of using the ^{111}In-^{111}Cd probe to study the $YBa_2Cu_3O_{9-\delta}$ structure. Nonetheless, we present the measurement of and the analysis of a well-defined electric quadrupole interaction, and we give the corresponding case for the interaction having been at the Y site.

The PAC measurements were made using a four-CsF-detector apparatus (having a time resolution of 1 nsec FWHM) and the associated fast and slow coincidence method. Many of the details are described elsewhere.[3,5] Figure 1(a) presents the experimental perturbation functions, $A_{22}G_{22}(t)$, and the fitted curves. The perturbation functions were derived from eight concurrently measured correlation functions, $W_{ij}(\theta,t) = 1 + A_{22}G_{22}(t)P_2(\cos\theta) + \cdots$, in which the anisotropy factor, A_{22}, is time independent and $G_{22}(t)$ contains the time-dependent perturbation information. The one-site model for a polycrystalline source [based on the Abragam and Pound expression for $G_{22}(t)$[6]] is given by

$$A_{22}G_{22}(t) = A\left[S_0 + \sum_{k=1}^{3} S_k \exp(-\tfrac{1}{2}\delta\omega_k t)\cos(\omega_k t)\right],$$

(1)

in which the S_i values are given by the original reference, A is the normalization, and δ is the line-shape parameter. The free parameters, ω_1, ω_2, A, and δ, were derived for each data set by nonlinear regression (with the constraint $\omega_1 + \omega_2 = \omega_3$). Figure 1(b) presents the corresponding Fourier transforms of the experimental data. Using the values of ω_1 and ω_2 obtained from each fit, the quadrupole frequency, ω_Q, and asymmetry parameter, η, were derived. The zz component of the efg in the principal axis
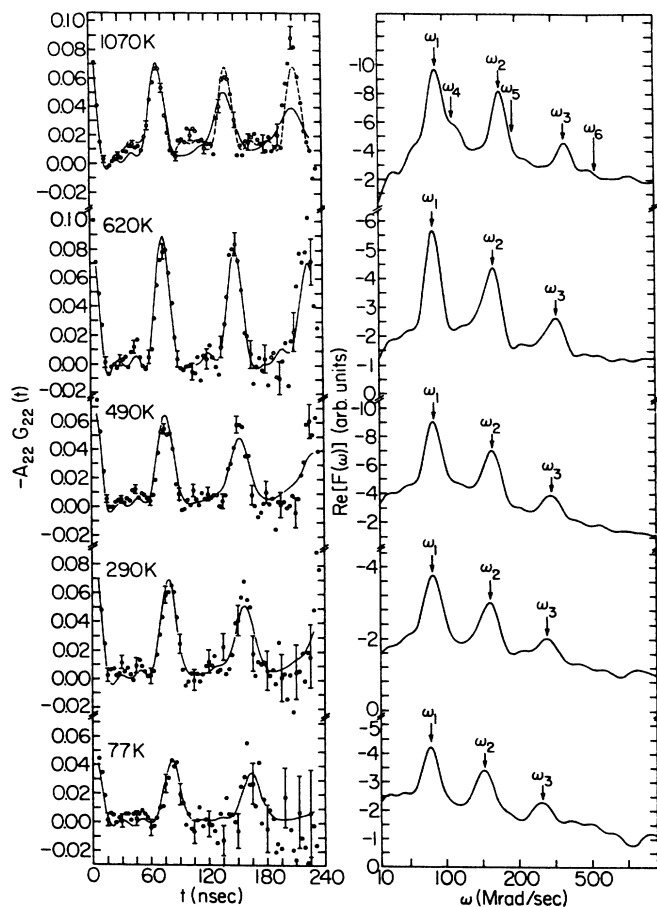
FIG. 1. (a) The perturbation functions and the associated one-site-model fitted curves are shown for the data collected at the indicated temperatures. For the 1070 K data, the solid curve indicates the one-site-model fit; and the broken curve indicates the two-site-model fit. (b) The real parts of the Fourier transforms of the corresponding data are on the left. The frequencies are indicated above the peaks. The real parts are displayed because the physical quantity $G_{22}(t)$ only involves cosine components. For the 1070 K data, the second-site frequencies are also indicated.

system, V_{zz} (in which the Y site was assumed to be at the origin in this case), was derived from the relation $\omega_Q = [eQV_{zz}/4I(2I-1)\hbar]$ and $\eta = (V_{xx} - V_{yy})/V_{zz}$. The frequencies, ω_i, indicated by the peaks in the transforms, agree to within 2% or less with the corresponding values derived from the fits. Thus, the derived frequencies and the asymmetry parameters for the primary interaction are unique. The values of the normalization A are less than the expected value, namely, $-A_{22} \cong 0.18$. At least some of this difference must be attributed to ^{111}In probe atoms in a collection of chemically inequivalent sites. We see evidence for a second site in the 1070 K data, as the one-site-model fit does not fully describe the data. The two-site-model fit [which consists of adding a second term to Eq. (1)] is also shown, and it better represents the data (giving $\omega_Q = 16.8 \pm 0.8$ Mrad/sec and $\eta = 0.35 \pm 0.15$). In addition, the peaks representing the second site (labeled ω_4, ω_5, and ω_6) are discernable in the Fourier trans-

form of the 1070 K data. (This transform shows yet additional peaks which may explain the small discrepancy in the fit to the third peak in the perturbation function.) Thus, increased temperature may be responsible for sharpening the broad lines associated with a second site. Figures 2(a), 2(b), and 2(c) present the derived quantities, V_{zz}, η, and δ, respectively. (The A parameters range in value from 0.06 to 0.09, and they differ primarily because the runs involved using different sample holders in which differences in γ-ray scattering occurred.)

The parameters derived from the perturbation functions strongly indicate that the probe ions primarily occupied one well-defined lattice site, where a single, static electric quadrupole interaction occurred. As mentioned above, this result is consistent with a single phase indicated by the x-ray pattern—to at least the 5% resolving level of the technique. Moreover, since the structure has two distinct
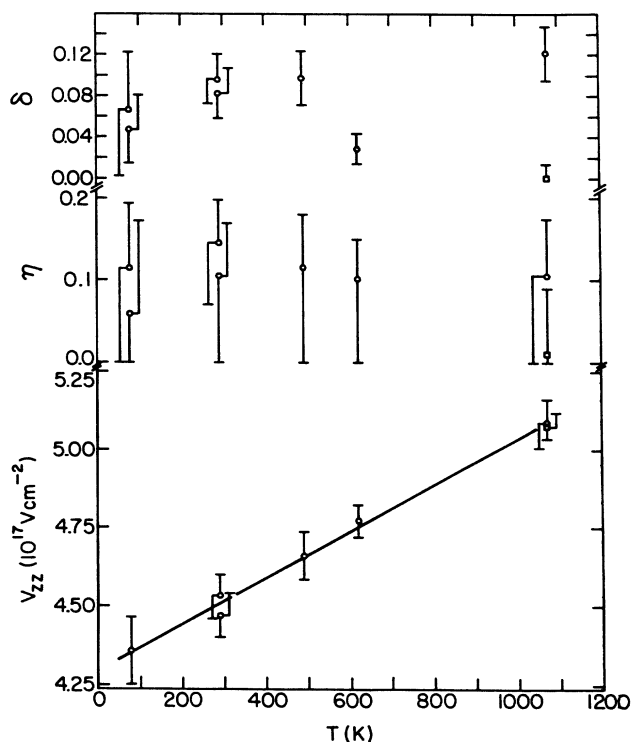

FIG. 2. (a) The zz component of the efg is given as a function of temperature. The value of the quadrupole moment Q (of the $5^+/2$ state in ^{111}Cd) used to derive V_{zz} from ω_Q is 77 b [Nucl. Data Sheets 27, 453 (1979)]. The line drawn through the data points represents a least-squares fit. The square indicates the value of V_{zz} for the major interaction derived from the two-site model. (b) The asymmetry parameters are shown as a function of temperature. The square indicates the η value derived from the two-site model. Although the experimental uncertainties are significant, the apparent decrease in value of η at 1070 K is consistent with the phase transition from the orthorhombic to the tetragonal structure which is reported (Ref. 10) to occur above 970 K. (c) The associated line-shape parameters. The square indicates the δ value derived from the two-site model. The linewidth decreases with temperature which may indicate motional narrowing. The large value of δ derived from the one-site-model fit to the 1070 K data is an artifact.

types of Cu sites, a single static interaction would not have been a likely consequence if the probe ions were to have occupied significant fractions of either of the Cu sites. The Ba site also was ruled out on chemical (valency and ionic radius) considerations. We note that the values of V_{zz} and η measured at 290 K are $4.50 \pm 0.11 \times 10^{17}$ V cm^{-2} and 0.12, respectively. But, for the Cu(1) and Cu(2) sites in YBa$_2$Cu$_3$O$_{7-\delta}$, Mali et al.[7] reported zero-field NQR frequencies and NMR-derived quadrupole coupling constants [corresponding to $V_{zz} \cong 7.7 \times 10^{17}$ and 12×10^{17} V cm^{-2} for the Cu(1) and Cu(2) sites, respectively] and asymmetry parameters ($\eta \cong 0.9$ and 0.14). For the In-substituted structure, the measured values of V_{zz} and η are not consistent with substitution of In into either one or both of the Cu sites. Hence, the substitution of In into the Y site appears as the most likely occurrence.

Although simplistic, the point-charge model has been used with some success in interpreting efg information for ionic crystals.[3,4] The model is given by ($eq = V_{zz}$)

$$eq = (1 - \gamma_\infty) \sum_{i=1}^{n} e\lambda_i (3z_i^2 - r_i^2)/r_i^5, \qquad (2)$$

in which e is the electronic charge, λ_i is the charge (usually taken as the formal charge) of the ith ion, $(1 - \gamma_\infty) = 30.3$ in the antishielding factor,[8] and $r_i^2 = x_i^2 + y_i^2 + z_i^2$ in the principal axis coordinate system. The sum runs over n ions which often are taken as the nearest-neighbor (NN) configuration around the probe ion. In this situation, we assumed that the ^{111}In-^{111}Cd probe ions occupy the Y sites.

Using the structural data of Siegrist et al.,[9] we considered three cases: (1) the eight-coordinate NN configuration of O^{2-} ions, (2) the NN configuration of O^{2-} and Cu^{2+} ions, and (3) the NN configuration of O^{2-} and Cu^{1+} ions. The results are $V_{zz} = (-2, -6,$ and $-4) \times 10^{17}$ V cm^{-2}, respectively; and $\eta = 0.25, 0.05,$ and 0.10, respectively. The magnitudes of the results from the third case are closest to the measured values given above. But the accuracy of this model is not expected to be better than 20%–50%, and the uncertainties arise in part because covalent bonding is not taken into account and because the antishielding factor may be inaccurate. Although the results of the point-charge calculations are consistent with In substitution into the Y site, the model is too simplistic to allow the assignment of the In^{3+} ion to the Y site.

Additionally, the continuous, linear increase in the efg with temperature suggests that the NN O^{2-} ions or O vacancies are not mobile species in the structure. By mobile species, we mean the O^{2-} ions or O vacancies that participate in the observed changes in oxygen composition with temperature.[10] If the O^{2-} ions or O vacancies were sufficiently mobile at elevated temperatures, we would expect to observe nuclear-spin relaxation, which would result from O^{2-} ions or O vacancies jumping from site to site. Similarly, if O transport involving NN O vacancies were to occur slowly (compared to the PAC time scale), we would expect to observe inhomogenous line broadening (of the primary interaction). The absence of evidence for either spin relaxation or line broadening in the perturbation functions suggests that the NN O^{2-} ions are immo-

bile and that the NN vacancies are not involved in O^{2-} ion transport.

Figure 2(a) shows the anomalous, linear increase of the efg with temperature over the range of measurement 77 to 1070 K. This result is in contradistinction to the information that both Coey and Donnelly[11] and Freimuth et al.[12] derived from the Mössbauer measurements on EuBa$_2$-Cu$_3$O$_7$, namely, that the strength of the nuclear quadrupole interaction at the Y site decreases with temperature. Moreover, this increase is unlike the near-universal decrease of the efg with temperature exhibited by metals[13] $eq(T) = eq(0)(1 - aT^{3/2})$. Also, several measurements on ionic crystals show nonlinear decreases of the efg's with temperature, which have been attributed to vibrational anharmonicity.[3,4] Very few PAC measurements have been made on semiconductors, and increases as well as decreases of the efg's with temperature have been reported.[14] Currently, no theory is available to explain these phenomena.

We can consider one possibility, however. Thompson et al.[15] and Das and Schmidt[13] separate the contributions to the efg from lattice vibrations into two categories, anharmonic and anisotropic. The former causes changes in the lattice parameters with temperature; the latter arises in noncubic lattices. Both of these contributions affect the temperature dependence of the efg. For example, their calculations for Cd metal and Zn metal show that the anharmonic contribution to the efg decreases and the anisotropic contribution increases with temperature. At temperatures below the orthorhombic-to-tetragonal phase transition in YBa$_2$Cu$_3$O$_{9-\delta}$, Gallagher, O'Brian, Sunshine, and Murphy[10] reported that the lattice parameters increase approximately linearly, but at the phase-transition temperature, a discontinuity appears in these data. Using these data[10] and the point-charge approximation, we found that (1) the calculated efg increases slightly with temperature (below the phase transition) for the sum over only O^{2-} ions, and (2) the calculated efg decreases slowly for the sum over O^{2-} ions and Cu^{1+} (or Cu^{2+}) ions. Even for the sum over only O^{2-} ions, the rate of increase is insufficient ($< 50\%$) to account for the measured effect. Therefore, we attribute the rise in the magnitude of the efg with temperature to primarily an anisotropic O vibrational mode(s). The sensitivity of this mode(s) to temperature may indicate a softening of the O vibrations.

In conclusion, we measured a well-defined static electric quadrupole interaction which is consistent with the probe having occupied the Y site. This conclusion is based on the self-consistency of the efg measurements, i.e., a single site and reasonable agreement with the model values as well as disagreement with the efg's reported for the Cu sites. The absence of nulcear-spin relaxation and the reasonably narrow lines especially at elevated temperatures, suggest that neither the NN O^{2-} ions nor the O vacancies participate in O transport. The efg anomalously increases with temperature. This effect is unusual and may indicate anisotropic O vibrations. Moreover, the effect is not in agreement with the results of the Mössbauer measurements[11,12] on the Eu-substituted structure, which may result from differences in the respec-

tive materials. In the Mössbauer case the information about the quadrupole interaction is often obtained indirectly, i.e., by analyzing the effects of line broadening. Whereas, the PAC experiment provides the information directly. Consequently, the PAC technique may be more sensitive to the effects of anisotropic vibrations in this structure than either Mössbauer spectroscopy or perhaps other techniques.

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