^{17}O NMR spectroscopy of magnetically ordered $YBa_2Cu_3O_{7-x}$ microcrystals

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We have obtained ^{17}O nuclear-magnetic-resonance spectra of powder samples of $YBa_2Cu_3O_{7-x}$ and $EuBa_2Cu_3O_{7-x}$, as well as magnetically ordered $YBa_2Cu_3O_{7-x}$. Two major features are observed in $YBa_2Cu_3O_{7-x}$: a sharp resonance at ≈ 1800 ppm (from external $H_2^{17}O$, International Union of Pure and Applied Chemistry δ scale) and a broader series of features centered at ≈ 400 ppm. The 1800-ppm feature undergoes a diamagnetic shift of ≈ 800 ppm on cooling to 77 K, and a similar magnitude shift on Eu substitution, suggesting assignment to the plane oxygens, $O(2,3)$. Measurements on magnetically ordered samples at 8.45 and 11.7 T give the magnitude of the diagonal terms of the electric-field-gradient tensor, which are 2.3, 3.5, and 5.8 MHz. For the column oxygen, $O(1)$, we find $e^2qQ/h = 7.7$ MHz, with a chemical shift anisotropy of ≈ 660 ppm.

All of the new high-T_c superconducting oxides[1-6] are, in principle, excellent candidates for study using ^{17}O nuclear-magnetic-resonance (NMR) spectroscopy. We show in this Rapid Communication that such studies are indeed possible, and by using magnetically aligned materials,[7,8] we are able to investigate both chain and plane sites in ^{17}O-labeled $YBa_2Cu_3O_{7-x}$. We observe large changes in the ^{17}O resonance frequency shifts (of the plane oxygens) upon formation of the superconducting state. Additionally, we have determined the nuclear quadrupole coupling constants (e^2qQ/h), electric-field-gradient tensor asymmetry parameters (η), and chemical shift anisotropies ($\Delta\delta$) for selected oxygen sites. Given the ubiquitous nature of oxygen in high-T_c superconductors, such atomic level probes of both magnetism and structure offer considerable hope for elucidating the details of superconductivity in these systems.

Unlabeled $YBa_2Cu_3O_{7-x}$ (and $EuBa_2Cu_3O_{7-x}$) was prepared from $Y_2O_3(Eu_2O_3)$, $BaCO_3$, and CuO (99.99%, Aldrich) using standard solid-state techniques. The finely ground mixture was initially fired in air (24 h at 950 °C then cooled at 50 °C/h to room temperature). The sample was then reground and refired in a flowing stream of $^{16}O_2$ gas (24 h at 950 °C, cooled at 50 °C/h to 450 °C, held for 24 h, then cooled at 50 °C/h to room temperature). Powder x-ray analysis (using a Rigaku D/Max diffractometer) indicated a monophasic material, identical with published data on $YBa_2Cu_3O_{7-x}$ (Ref. 9) ($EuBa_2Cu_3O_{7-x}$).

Labeling with ^{17}O was achieved by heating the sample under vacuum at 500 °C for 2 h, followed by annealing in a static 48% $^{17}O_2$ atmosphere (ICON, Summit, New Jersey) at 500 °C for 12 h. Powder x-ray analysis of the ^{17}O-enriched sample gave a pattern virtually identical to that of the unenriched sample. Magnetic-susceptibility measurement [using a SHE superconducting quantum interference device (SQUID) magnetometer] showed a sharp normal-to-superconducting transition with a T_c onset of 90 K for the $YBa_2Cu_3^{17}O_{7-x}$ sample. NMR spec-

tra were obtained at 8.45 or 11.7 T using a spin-echo sequence. The "solid" 90° pulse widths were typically 2 μsec. ^{17}O spectra are referenced with respect to water at 0 ppm, positive values corresponding to high-frequency, low-field, paramagnetic, or deshielded shifts (International Union of Pure and Applied Chemistry δ scale).

We show in Fig. 1 the 48.8 MHz (8.45 T) ^{17}O NMR spectra of a powder sample of $YBa_2Cu_3^{17}O_{7-x}$ at 300 K and at 77 K, Figs. 1(a) and 1(b).
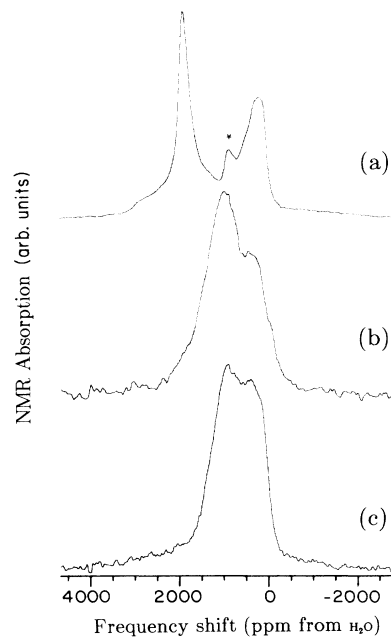
There are clearly two main features in the 300 K spec-

FIG. 1. 48.8 MHz (8.45 T) ^{17}O NMR spectra of (a) $YBa_2Cu_3^{17}O_{7-x}$ powder, 300 K. Asterisked peak originates from aligned crystallites. (b) $YBa_2Cu_3^{17}O_{7-x}$ powder, 77 K. (c) $EuBa_2Cu_3^{17}O_{7-x}$ powder, 300 K.

trum: an intense peak at $\simeq 1800$ ppm, and a weaker set of peaks at $\simeq 400$ ppm. On cooling to 77 K, the intense feature undergoes a diamagnetic shift of $\simeq 800$ ppm, while the less intense features remain at approximately the same resonance frequency. Taken together, these intensity and shift results lead to the tentative assignment of the intense feature to the plane sites [4 oxygens, O(2) and O(3)], while the weaker features, which shift much less with temperature, can be assigned to the other sites [3 oxygens, one O(4), and two O(1)]. This assignment is supported by the result on EuBa$_2$Cu$_3$^{17}O$_{7-x}$, Fig. 1(c), in which the intense feature appears to be shifted by the magnetic Eu^{3+} ion, which replaces Y^{3+} near the Cu-O planes, while a second peak, at $\simeq 400$ ppm, assigned to the other sites, O(1,4), is only slightly shifted. Due to the proximity of the plane oxygens to the europium site, they are expected to be most affected by replacing Y^{3+} with Eu^{3+}, strongly supporting our tentative assignment of the 1800 ppm feature to O(2,3).

In order to obtain enhanced resolution, we have investigated magnetically ordered samples[7,8] of YBa$_2$Cu$_3$-^{17}O$_{7-x}$. Finely powdered YBa$_2$Cu$_3$^{17}O$_{7-x}$ was mixed with Duro-TM epoxy and rapidly transferred to a Teflon cylinder and magnetically aligned at 8.45 T for 15 min.[7] This causes the c axis to align along the field direction, leaving the a,b plane rotationally disordered. SQUID results on our sample, after completion of the NMR experiments, are shown in Fig 2(a), and appear satisfactory. In order to verify orientation we show in Fig. 2(b) the ^{63}Cu

NMR spectrum of our ^{17}O-labeled sample. In contrast to the results of Cu NMR studies of powder samples,[10–12] we obtain two rather sharp peaks, whose frequency shifts are well predicted from the results of Pennington *et al.*,[13] on a hand-oriented microcrystalline array of YBa$_2$Cu$_3$O$_{7-x}$. Our samples also show excellent ordering via x-ray diffraction technique (XRD) (data not shown).

We recorded ^{17}O NMR spectra (at 8.45 and 11.7 T) on our magnetically ordered sample, as a function of rotation about an axis perpendicular to the ordering (c) axis. For most sites, complex powder patterns are generated as the sample is rotated about the a-b plane. However, for any axially symmetric site whose principal electric-field-gradient tensor axis (V_{zz}) and chemical (or Knight) shift tensor axis (δ_{zz}) is aligned *along c*, a sharp line is expected, as a function of rotation angle. Based on previous calculations,[14] and on symmetry and structure arguments,[15] the columnar oxygen, O(1), appears most likely to fulfill at least the axially symmetric field gradient requirement ($\eta \sim 0.27$, V_{zz} along c). As may be seen from Figs. 2(c) and 2(d), one peak does clearly shift as a function of θ.

The expression for the frequency shift as a function of θ for a single crystal rotated about an axis perpendicular to the principle axis is

$$\delta(\theta) = \delta_i + \frac{\Delta\delta}{3}(3\cos^2\theta - 1) - \frac{9}{800}\left[\frac{e^2qQ}{v_0h}\right]^2$$
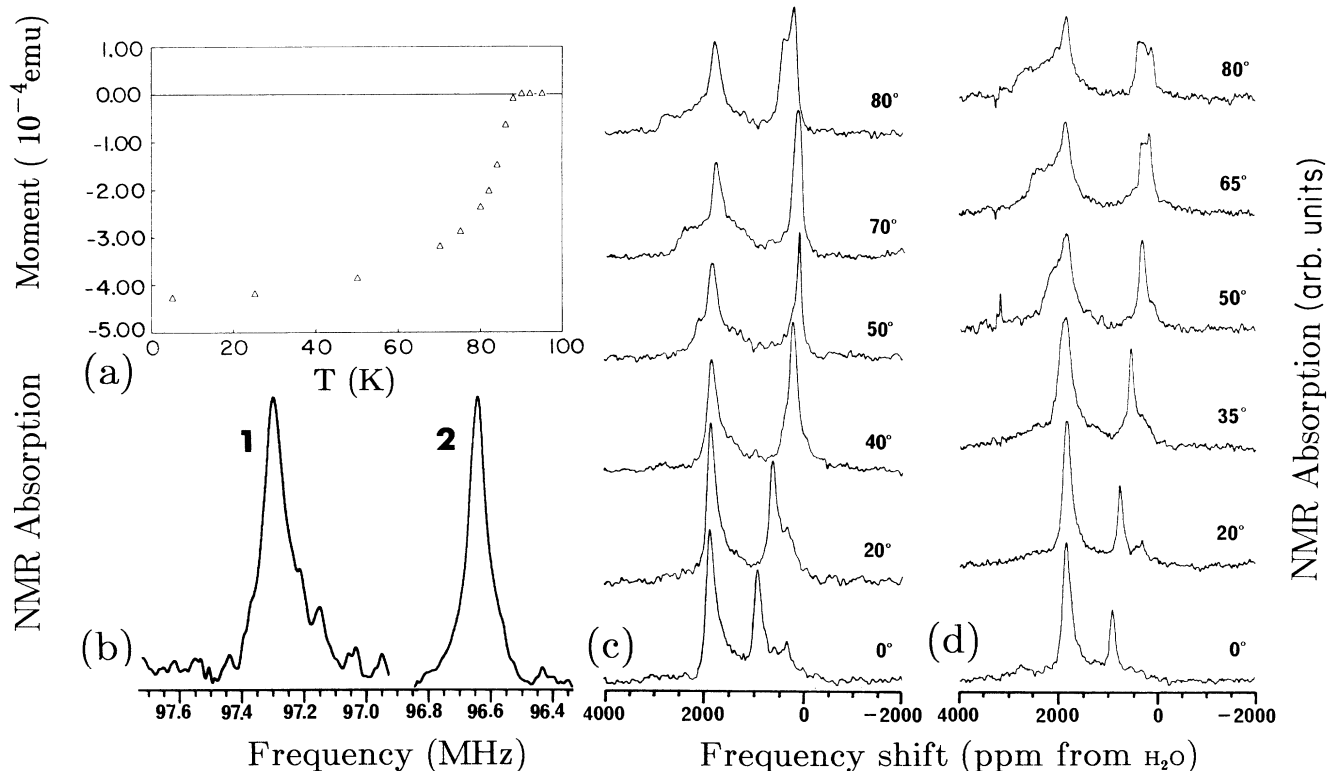$$\times (1 - \cos^2\theta)(9\cos^2\theta - 1) \times 10^6, \qquad (1)$$

FIG. 2. ^{63}Cu and ^{17}O NMR spectra of magnetically aligned YBa$_2$Cu$_3$^{17}O$_{7-x}$ in epoxy, together with SQUID results. (a) SQUID data on sample used for NMR (10 G field, a,b plane $\parallel$H$_0$). (b) ^{63}Cu NMR at 8.45 T, 300 K, θ=0°. (c) ^{17}O NMR at 8.45 T, 300 K, as a function of angle θ. (d) As (c) but at 11.7 T.

where δ_i is the isotropic shift, $\Delta\delta = \delta_\perp - \delta_\parallel$ is the chemical shift anisotropy, and e^2qQ/h is the quadrupole coupling constant.

We show in Fig. 3 the observed frequency shift of this peak as a function of θ, at both 8.45 and 11.7 T. Also shown are the theoretical curves for a site having $\delta_i = 458$ ppm, $\Delta\delta = 657$ ppm, $e^2qQ/h = 7.7$ MHz, and $\eta = 0$. The excellent fit of the angular dependence of the ^{17}O frequency shifts at both 8.45 and 11.7 T, together with intensity arguments (≈ 2 oxygens, assuming uniform labeling), strongly implies that this feature arises from the column oxygen, O(1). The near-to-axial symmetry of the O(1) site is presumably the result of a strong Cu(1)$-$O(1) bond, as evidenced by the short Cu(1)$-$O(1) bond length (1.846 Å), and long Cu(2)$-$O(1) bond (2.295 Å).[15] In effect, Cu(2) has little effect on O(1), consistent with the lack of any major shift of O(1) upon cooling into the superconducting state. The rather large e^2qQ/h value of 7.7 MHz is also consistent with a short Cu(1)$-$O(1) bond, and may imply a partial multiple-bond character between Cu(1) and O(1), as suggested from band-structure calculations.[16]

We show in Fig. 4 the results of a search for satellite transitions of the oxygen atoms whose central ($\frac{1}{2}, -\frac{1}{2}$) transitions are depicted in Figs. 1-3. From second-order perturbation theory,[13] the frequencies for the ($\pm\frac{1}{2}$, $\pm\frac{3}{2}$) and ($\frac{1}{2}, -\frac{1}{2}$) transitions, with $\theta = 0°$, are

$$\nu_{(\pm 1/2, \pm 3/2)} = \nu_0 \pm \frac{3}{20}\chi_{zz} , \tag{2}$$

$$\nu_{(1/2, -1/2)} = \nu_0 + \frac{1}{200\nu_0}(\chi_{xx} - \chi_{yy})^2 , \tag{3}$$

where $\chi_{aa} = eQV_a/h$ are the Cartesian components of the electric-field-gradient tensor and ν_0 is the center of the resonance. The z axis is defined along the crystal c axis. We observe satellite ($\pm\frac{1}{2}, \pm\frac{3}{2}$) transitions at ≈ 350 kHz from the central ($\frac{1}{2}, -\frac{1}{2}$) transitions for a $\theta = 0°$ sample. Using this value, together with the observation that the difference in frequency shift between $\theta = 0°$ ^{17}O spectra at 8.45 and 11.7 T is ≈ 90 ppm, we can calculate from Eqs. (2) and (3) the principal components of the
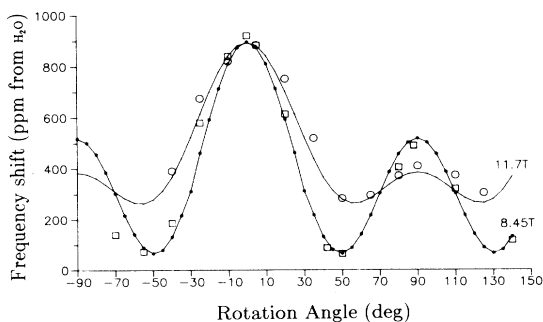
FIG. 3. ^{17}O NMR frequency shifts of peak proposed to arise from O(1), as a function of rotation angle θ at 8.45 and 11.7 T. Solid lines, theoretical curves based on $\delta_i = 458$ ppm, $e^2qQ/h = 7.7$ MHz, $\eta = 0$, $\Delta\delta = 657$ ppm. Open squares, 8.45 T data. Open circles, 11.7 T data. All spectra recorded at 300 ± 2 K.
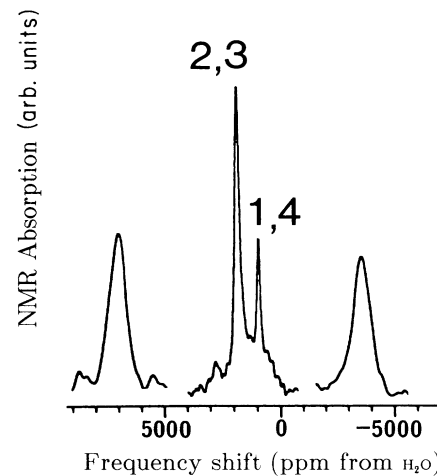
FIG. 4. 11.7 T ^{17}O NMR spectra of magnetically ordered YBa$_2$Cu$_3$^{17}O$_{7-x}$ showing ($\pm\frac{1}{2}, \pm\frac{3}{2}$) satellite and ($\frac{1}{2}, -\frac{1}{2}$) central transitions.

electric-field-gradient tensor for the O(2,3) site, as follows:

$$(\chi_{xx}, \chi_{yy}, \chi_{zz}) = \pm(-3.5, +5.8, -2.3) \text{ MHz} .$$

We cannot tell the difference between x and y in the molecular frame. Given our expected experimental errors, this result implies an $|e^2qQ/h|$ value of $\approx 5-6$ MHz, with near axial symmetry ($\eta \approx 0-0.2$) about an axis perpendicular to the c axis, a result in good agreement with the wholly empirical estimate of e^2qQ/h based on electronegativity considerations, of ≈ 5 MHz, for the ^{17}O e^2qQ/h for the oxygen in a Cu$-$O$-$Cu bond.[17]

Finally, we have recently become aware of the ^{17}O NMR work of Wzietek et al.[18] on a sample of YBa$_2$Cu$_3$O$_{7-x}$ exchanged at 300 °C, which they believe enriches primarily at the chain O(4) site. By conducting a similar exchange we enriched primarily one site centered at ≈ 200 ppm. We have already assigned the peaks at ≈ 1800 and ≈ 450 ppm to O(2,3) and to O(1), respectively, consistent with their assignment of the chain site, O(4).

In summary, ^{17}O NMR spectroscopy has been shown to provide an insight at the atomic level into the magnetic properties of the YBa$_2$Cu$_3$O$_{7-x}$ high-T_c oxide superconductor. Three types of oxygen sites have been assigned, only those associated with the planes being strongly affected upon attainment of the superconducting state. Additionally, e^2qQ/h, η, and $\Delta\delta$ values for specific sites have been determined. The method of magnetic ordering seems particularly attractive, since it can provide not only improved resolution (and spectral assignments), but also offers greatly improved sensitivity over powder samples.

Note added in proof. Using improved orientation conditions, we have recently observed splittings of the $\pm\frac{3}{2}$ and $\pm\frac{5}{2}$ satellite transitions of the ~ 1810-ppm peak, at 11.7 T. The electric-field-gradient parameters are approximately 10% higher than reported above. Each satellite is split into two peaks having approximately equal intensity, indicating slightly different electric field gradients, strongly supporting our assignment to O(2,3).

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