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Anisotropic Cu Knight shift and magnetic susceptibility in the normal state of $YBa_2Cu_3O_7$

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Precise measurements of the Knight shift at Cu(1) (chain) and Cu(2) (plane) sites have been made in the normal state of a $YBa_2Cu_3O_7$ powder sample, for which the c axis of each grain has been aligned in a magnetic field. By combining these data with the Knight shift data in the superconducting state and the anisotropic magnetic susceptibility, it is shown that (1) the anisotropy of the magnetic susceptibility is mainly due to the orbital moment of the $3d$ electrons, (2) the magnitude of the spin contribution to the Knight shift is similar at both sites, and (3) the isotropic part of the Cu hyperfine field is large and positive (112 kOe $/\mu_B$).

The measurement of the Knight shift K in superconductors provides useful microscopic information because it is essentially the only method by which one can measure the spin susceptibility in the superconducting state.[1] This holds for the case of the high-T_c copper oxide superconductors,[2] where several copper or oxygen sites having different local character may be relevant to the superconductivity. In spite of this, only a few measurements of the Cu Knight shift in $YBa_2Cu_3O_7$ have been reported so far.[3,4] This is mainly due to the strong quadrupole interaction at Cu sites, which broadens even the central $(I_z=-\frac{1}{2}\leftrightarrow\frac{1}{2})$ transition line in the high-field NMR spectrum of powder samples. We have found that NMR spectra similar to those of single crystals can be obtained by using uniaxially aligned powder. In this paper, we present anisotropic Cu Knight shift data in $YBa_2Cu_3O_7$ at both Cu(1) (chain) and Cu(2) (plane) sites in the normal state. Knight shift data taken in the superconducting state are presented in a separate paper,[5] although a part of those results are referred to in this paper in order to estimate separately the spin and orbital contributions to the Knight shift and the magnetic susceptibility.

The NMR experiments were carried out using a standard pulsed spectrometer. Cu NMR spectra were obtained by integrating the spin-echo intensity by a boxcar while sweeping the magnetic field. We followed the method of Farrel *et al.*[6] to produce aligned powder. A sintered pellet of $YBa_2Cu_3O_7$ prepared by standard ceramic techniques was ground into powder with grain size less than 20 μm. The magnetic susceptibility was found to be temperature independent (2.79×10^{-4} emu/mol f.u.) above the superconducting transition temperature $T_c=92$ K. The powder was then mixed with epoxy (Stycast 1266) and cured in a magnetic field of 4.2 T at room temperature. T_c of this mixture was confirmed to be the same as the original powder. X-ray diffraction measurements on another aligned sample made similarly showed good alignment (±3°) of the c axis of each grain along the direction of the magnetic field and a random distribution of the a axis in the plane perpendicular to the field.

Good alignment was also demonstrated in the NMR spectra as seen in Fig. 1. ^{63}Cu NMR spectra at 100 K and 85 MHz are shown for (a) a randomly oriented powder, (b) the aligned powder with magnetic field parallel to the c axis ($H\parallel c$), and (c) the aligned powder with magnetic field perpendicular to the c axis ($H\perp c$). Only the spectra corresponding to the central transition are shown, except in Fig. 1(b), where the two small peaks near 75 kOe originate from quadrupolar satellites of Cu(1) sites.

From the crystal structure, we know that the crystalline

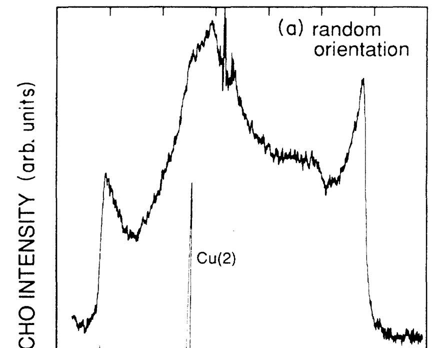

FIG. 1. ^{63}Cu NMR spectra at 100 K and 85 MHz of $YBa_2Cu_3O_7$ in (a) a randomly oriented powder, (b) the aligned powder with $H\parallel c$, and (c) the aligned powder with $H\perp c$. In (c), the assignment of the two lower field edges in the Cu(1) spectrum to either the a or b axis is rather tentative. The highest field edge in the Cu(1) spectrum corresponds to the direction 45° from a. The other small peaks not identified are due to materials in the NMR probe.

a, *b*, and *c* axes are the principal axes of both the electric field gradient and the Knight shift. The spectrum in Fig. 1(b) has exactly the same features as the frequency-swept ^{63}Cu spectrum obtained from single crystals with $H \parallel c$ reported by Pennington, Durand, and Zax.[4] From this and similar ^{65}Cu spectra they determined the principal values of the electric field gradient and the Knight shift along the *c* axis at both Cu sites, and assigned each line to a particular site and transition in an unambiguous way.[4] These assignments are shown in Fig. 1(b). It is known that the electric field gradient at Cu(2) sites is axially symmetric about the *c* axis, whereas that at Cu(1) sites is highly asymmetric.[4,7]

In the case when $H \perp c$, the field direction is random in the *ab* plane. We would then expect a two-dimensional powder pattern for Cu(1) sites due to the second-order quadrupolar effect. On the other hand, the Cu(2) line should be sharp if the Knight shift at Cu(2) sites is axial. These features are actually observed, as shown in Fig. 1(c). We conclude that the edges at 74.0, 74.6, and 77.0 kOe in the Cu(1) spectrum occur for those grains which have their *a* axis oriented at 0°, 90° ($H \parallel b$), and 45° relative to the magnetic field. This is discussed further below.

In order to determine the quadrupolar and magnetic (Knight) shifts separately, we took series of spectra at several different frequencies in the range 65–95 MHz. Corresponding to each peak and edge in the central transition spectra, we define $\Delta\nu$ as the difference between the resonance frequency ν_0 (85 MHz for the case shown in Fig. 1) and $\gamma_N H_{\text{res}}$, where H_{res} is the field at which the resonance is observed and γ_N is the nuclear gyromagnetic ratio (1.285 kHz/Oe for ^{63}Cu). We can express $\Delta\nu$ as[8]

$$\Delta\nu = K\gamma_N H_{\text{res}} + \frac{D}{(1+K)\gamma_N H_{\text{res}}} + \Delta'\nu . \tag{1}$$

The first term represents the magnetic (Knight) shift, the second term is the second-order effect of the quadrupolar interaction, and the last term is the small correction due to higher order effects of the quadrupolar interaction. $\Delta'\nu$ was calculated by numerical diagonalization of the nuclear-spin Hamiltonian including the magnetic Zeeman and electric quadrupole interaction using the principal values of electric field gradient given in Ref. 4. Strictly speaking, $\Delta'\nu$ is a function of the "internal" magnetic field $(1+K)H_{\text{res}}$. However, $\Delta'\nu$ is a very small quantity ($\Delta'\nu/\nu_0 \le 2\times 10^{-4}$) and $\Delta'\nu$ may be calculated at H_{res}, ignoring the difference between the applied and the "internal" field. From Eq. (1), we expect a linear relation between $\delta\nu/(\gamma_N H_{\text{res}})$ and $(\gamma_N H_{\text{res}})^{-2}$, where $\delta\nu = \Delta\nu - \Delta'\nu$:

$$\frac{\delta\nu}{\gamma_N H_{\text{res}}} = K + \frac{D}{(1+K)(\gamma_N H_{\text{res}})^2} . \tag{2}$$

This is actually satisfied to high accuracy as shown in Fig. 2. The intercepts of these lines give the principal values of the Knight shift.

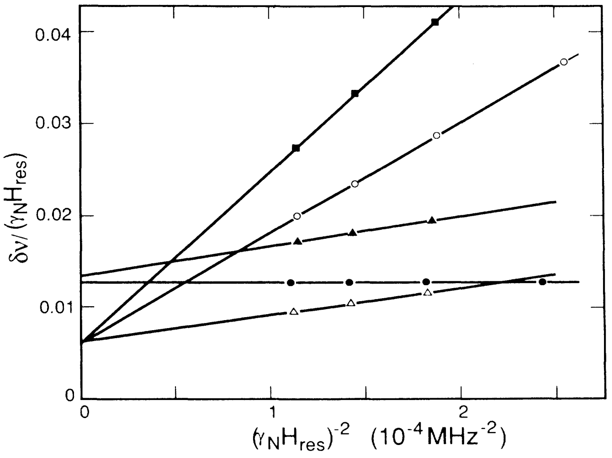

FIG. 2. $\delta\nu/(\gamma_N H_{\text{res}})$ is plotted against $(\gamma_N H_{\text{res}})^{-2}$ for different NMR frequencies. H_{res} is the field for resonance corresponding to Cu(2) with $H \parallel c$ (solid circles), Cu(2) with $H \perp c$ (solid squares), Cu(1) with $H \parallel c$ (open circles), Cu(1) with $H \parallel a$ (solid triangles), and Cu(1) with $H \parallel b$ (open triangles).

The slopes of the lines in Fig. 2 for Cu(1) sites with $H \perp c$ can be compared with the calculated orientational dependence of the second-order quadrupolar shift at Cu(1) sites in the *ab* plane. From this comparison it can be shown that two lower field edges occur for those grains whose *a* or *b* axis is oriented in the field direction. In the same way we conclude that the higher-field edge occurs when the *a* axis is oriented at 45° relative to the field. We cannot determine which of the edges at lower field corresponds to $H \parallel a$, since the values of D in Eq. (2) for these edges are close to each other. However, the smaller Knight shift at about 74 kOe is close to that for $H \parallel c$ and is tentatively assigned to the *b* axis, because the nearest-neighbor oxygen coordination of Cu(1) sites is roughly symmetric about the *a* axis. Thus, the principal values of the Knight shift at 100 K are (in units of percent)

$$\begin{aligned}
\text{Cu(1)}:\ & K^{(a)} = 1.338 \pm 0.015\,, \quad K^{(b)} = 0.607 \pm 0.015\,, \\
& K^{(c)} = 0.600 \pm 0.01\,, \\
\text{Cu(2)}:\ & K^{(a,b)} = 0.607 \pm 0.01\,, \\
& K^{(c)} = 1.269 \pm 0.005\,.
\end{aligned} \tag{3}$$

These values of $K^{(c)}$ are consistent with the single-crystal result $[K^{(c)}(1) = 0.6 \pm 0.2,\ K^{(c)}(2) = 1.25 \pm 0.05\%]$.[4] When the magnetic field direction z coincides with one of the principal axes, the value of D in Eq. (2) is given by $(\nu_x - \nu_y)^2/12$, where $\nu_a = (eQ/2h)(\partial^2 V/\partial a^2)$, eQ is the nuclear quadrupole moment, and $(\partial^2 V/\partial a^2)$ is the a component of electric field gradient.[4] The values of D obtained from the slopes in Fig. 2 agree well with those derived from the values of ν_a given in Ref. 4, when a possible misalignment of the field by about 1.5° is taken into account. The temperature dependence of the Knight shift was measured up to 230 K. We assume that the relative change of D with temperature follows that of nuclear quadrupole resonance frequency reported by Mali *et al.*[9] We have confirmed this at Cu(1) sites with $H \parallel c$ at 230 K. All the principal values of the Knight shift were found to be temperature independent within 0.02%.

Generally, the Knight shift of a transition element in compounds consists of both orbital and spin parts, $K = K_{\text{orb}} + K_{\text{spin}}$. The magnetic susceptibility can be decomposed similarly: $\chi = \chi_{\text{orb}} + \chi_{\text{spin}} + \chi_{\text{dia}}$, the last term

TABLE I. Anisotropy of the Knight shift and the magnetic susceptibility.

		Cu(1)		Cu(2)		
		K_{orb} (%)	K_s (%)	K_{orb} (%)	K_s (%)	χ (emu/mol f.u.)
$H \parallel c$		0.31 ± 0.08	0.29 ± 0.08	1.35 ± 0.08	-0.08 ± 0.08	3.39×10^{-4}
$H \perp c$	$\parallel a$	1.18 ± 0.02	0.16 ± 0.02	0.24 ± 0.02	$0.37 + 0.02$	2.50×10^{-4}
	$\parallel b$	0.43 ± 0.02	0.18 ± 0.02			

being the core diamagnetic contribution which is estimated to be -1.75×10^{-4} emu/mol f.u.[10] In order to separately estimate K_{orb} and K_{spin} we use the Knight-shift data in the superconducting state, details of which are described in Ref. 5. There we argued that it is reasonable to assume that K_{spin} is reduced to zero at $T=0$ at both sites for all field directions, reflecting singlet pairing with no significant spin-orbit scattering. Then K_{orb} is given by extrapolating the Knight shift to $T=0$. The extracted values of K_{orb} and K_{spin} are listed in Table I. The relatively large error in these values results from a systematic error in the estimation of the diamagnetic field due to superconducting screening currents.[5] The values of the magnetic susceptibility for $H \parallel c$ and $H \perp c$ were obtained on aligned powder similar to that used in the NMR experiment after making corrections for the diamagnetic susceptibility of epoxy. These are also shown in Table I. The ratio $\chi_{\parallel}/\chi_{\perp}=1.36$ is slightly smaller than the value of 1.45 for a single crystal reported by Fukuda, Shamoto, Sato, and Oka.[11]

Since χ_{orb} is the sum of contributions from two Cu sites, $\chi_{\text{orb}}=\chi_{\text{orb}}(1)+2\chi_{\text{orb}}(2)$, χ_{orb} can be estimated by the relation $\chi_{\text{orb}}=[K_{\text{orb}}(1)+2K_{\text{orb}}(2)]N_A\mu_B/A_{\text{orb}}$ for each direction, where $A_{\text{orb}}=2\mu_B\langle r^{-3}\rangle$ is taken to be 6.3 a.u. from EPR data on compounds containing Cu^{2+}.[12] We obtain $\chi_{\text{orb}}^{(a)}=1.18 \times 10^{-4}$, $\chi_{\text{orb}}^{(b)}=0.64 \times 10^{-4}$, $\chi_{\text{orb}}^{(c)}=2.13 \times 10^{-4}$ (emu/mole f.u.). By subtracting χ_{orb} and χ_{dia} from the measured susceptibility, we get an almost isotropic spin susceptibility, $\chi_{\text{spin}}^{(c)}=3.01 \times 10^{-4}$, $(\chi_{\text{spin}}^{(a)}+\chi_{\text{spin}}^{(b)})/2=3.34 \times 10^{-4}$ emu/mol f.u., which are to be compared with the value 1.7×10^{-4} emu/mol f.u. estimated from band calculation.[13] The exchange enhancement of the spin susceptibility is not large.[14]

The large anisotropy of K_{orb} at the Cu(2) sites can be understood in a simple picture of Cu^{2+} ions placed in a tetragonal crystal field, i.e., with one d hole in the highest $d(x^2-y^2)$ state. The orbital susceptibility is given by

$$\chi_{\text{orb}}^{(a)}(2)=2\mu_B^2\sum_m |\langle m | L_a | d(x^2-y^2)\rangle|^2/\Delta E_m . \quad (4)$$

Here the summation is over the d_ϵ states and ΔE_m is the energy interval between $\langle m|$ and $\langle d(x^2-y^2)|$. If ΔE_m is the same for all $\langle m|$ the anisotropy of χ_{orb} results from the anisotropy of the matrix elements, and we get $\chi_{\text{orb}}^{(c)}(2)=4\chi_{\text{orb}}^{(a,b)}(2)=8\mu_B^2/\Delta E$. This anisotropy is close to that of K_{orb} at the Cu(2) site: $K_{\text{orb}}^{(c)}(2)/K_{\text{orb}}^{(a,b)}(2)=5.6$. If we use the results of band calculations,[13] $\Delta E=2.4$ eV, we get $\chi_{\text{orb}}^{(c)}(2)=1.08 \times 10^{-4}$ emu/mol Cu, which is in agreement with that estimated from K_{orb}: $K_{\text{orb}}^{(c)}(2)N_A\mu_B/A_{\text{orb}}=9.6 \times 10^{-5}$ emu/mol Cu. The anisotropy of K_{orb} at Cu(1) sites is somewhat smaller which may be because both d_ϵ and d_γ states are involved in the Fermi surface, as suggested by the band calculations.[13]

K_{spin} is related to χ_{spin} by the relation $K_{\text{spin}}=(A_{\text{dip}}+A_{\text{CP}})\chi_s/(N_A\mu_B)$, where A_{dip} and A_{CP} represent the dipolar and the core polarization hyperfine field per Bohr magneton of spin moment, respectively. Because χ_{spin} is nearly isotropic, the dipolar field does not contribute to the powder average, $\langle K_{\text{spin}}\rangle=(K_{\text{spin}}^{(a)}+K_{\text{spin}}^{(b)}+k_{\text{spin}}^{(c)})/3$. Assuming that A_{CP} is roughly the same for the two sites, A_{CP} can be estimated from the relation, $2\langle K_{\text{spin}}(2)\rangle+\langle K_{\text{spin}}(1)\rangle=A_{\text{CP}}\langle\chi_{\text{spin}}\rangle/(N_A\mu_B)$, which gives $A_{\text{CP}}=112$ kOe/μ_B. This value is rather hard to explain, because A_{CP} is usually negative and of the order of -100 kOe/μ_B, for most of transition-metal compounds.[15] A_{CP} can be positive when there is appreciable s character at the Fermi level. This may be associated with the spin of holes on neighboring oxygens whose $2p$ orbitals overlap the Cu nuclei. It is also remarkable that $\langle K_s(1)\rangle=0.21\%$ is close to $\langle K_s(2)\rangle=0.24\%$, indicating similar spin density at both sites.

The anisotropy of K_{spin} at Cu(2) sites is slightly smaller than the expected dipolar field for the $d(x^2-y^2)$ state. For the $d(x^2-y^2)$ state, $A_{\text{dip}}^{(a,b)}=-A_{\text{dip}}^{(c)}/2=2\mu_B\langle r^{-3}\rangle/7$ is calculated to be 105 kOe/μ_B. Assuming equal spin susceptibility at both sites, the anisotropic part of K_{spin} at Cu(2) site gives a value 69 kOe/μ_B.

In conclusion, the principal values of the anisotropic Knight shift in the normal state of $\text{YBa}_2\text{Cu}_3\text{O}_7$ were determined at both Cu(1) and Cu(2) sites. By combining measurements of the anisotropy of the magnetic susceptibility and the Knight-shift results in the superconducting state, we conclude that (1) the spin contribution to the Knight shift is roughly the same for Cu(1) and Cu(2) sites, (2) the anisotropy of the magnetic susceptibility is primarily of orbital origin and the spin susceptibility is nearly isotropic, and (3) the isotropic part of the hyperfine field is positive in contrast to most other transition-metal compounds.

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