^{89}Y NMR Observations of Knight Shift Anisotropy and Motional Line Narrowing in $YBa_2Cu_3O_{7-\delta}$

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^{89}Y NMR spectra in an oriented sample of $YBa_2Cu_3O_{6.92}$ for magnetic field parallel and perpendicular to the c axis are presented. An anisotropic behavior of the Knight shift (K_s) above T_c is observed for the first time. A new phenomenon of motional line narrowing around 40 K is detected and interpreted in terms of a partial flux melting with characteristic correlation times of tens of microseconds. Comparisons with muon-spin-rotation results are also given.

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In most respects, the ^{89}Y nucleus is an ideal tool to investigate several relevant issues of high-T_c superconductivity through NMR experiments. The lack of a nuclear quadrupole moment and therefore the insensitivity to the electric-field gradients yields an intrinsically narrow ^{89}Y NMR line which allows one to achieve a precise evaluation of crucial parameters such as the Knight shift (K_s), the magnetic-field distribution in the vortex state, and the vortex motion [1], which are of great interest in view of the strongly anisotropic and inhomogeneous character of high-T_c superconductors [2]. Thus ^{89}Y NMR is a unique tool for the study of the microscopic properties of the vortex lattice, and in particular of vortex motion, leading to a fruitful comparison with the observations from other techniques such as muon spin rotation (μ^+SR) [3].

In this Letter accurate ^{89}Y NMR spectra in magnetically oriented Y-Ba-Cu-O (YBCO) powders, revealing new important phenomena, are presented. In particular, (a) above T_c an anisotropic K_s is observed; (b) the temperature dependence of the linewidth $\Delta\nu$ below T_c is given and, for the first time, a narrowing from vortex motion is evidenced; and (c) a comparison of the anisotropy of the linewidth $\Delta\nu_{ab}/\Delta\nu_c$ with μ^+SR data points out that muons and ^{89}Y nuclei probe different field distributions.

The oxygen content of the sample, from thermogravimetric analysis, was found to be $O_{6.92}$. $YBa_2Cu_3O_{6.92}$ powder grains, of an average diameter of 5 μm, were mixed with epoxy resin and oriented in a 7-T magnetic field. From the width of the ^{63}Cu(2) NMR central line for $\mathbf{H}_0 \parallel \mathbf{c}$ an angular spread around the c axis of less than 3° was inferred. The superconducting transition temperature was estimated with dc resistivity measurements and from the detuning of the NMR probe ($T_c = 89 \pm 1$ K). In the magnetic field $H_0 = 5.9$ T, where all ^{89}Y NMR measurements were performed, the irreversibility transition temperature obtained was $T_i = 77 \pm 1$ K for $\mathbf{H}_0 \parallel \mathbf{c}$ and $T_i = 85 \pm 1$ K for $\mathbf{H}_0$ in the a-b plane, in good agreement with previous findings [4]. The critical temperature in the presence of the magnetic field was estimated to be $T_c = 87 \pm 1$ K for $\mathbf{H}_0 \parallel \mathbf{c}$, according to the $H_{c2}(T)$ slope [4], while for $\mathbf{H}_0$ in the a-b plane there was a negligible change.

^{89}Y NMR experiments were performed with a Bruker MSL200 spectrometer using a $(\pi/2)_x$-τ-$(\pi)_y$ echo pulse sequence. The radio-frequency field ($H_1 \simeq 85$ G) was strong enough to allow a complete irradiation of the ^{89}Y NMR line at all temperatures, and the Fourier transformation of the echo signal provided reliable line shapes. In contrast with other cases [5] where two lines were present, a single line was observed in our sample in the whole temperature range, evidencing a high homogeneity of the oxygen stoichiometry [6].

First we briefly comment on the new and important observation of an anisotropic Knight shift above T_c. The NMR shifts ΔK for $\mathbf{H}_0$ parallel and perpendicular to the c axis (Fig. 1) allow one to evidence a sizable temperature dependence of the anisotropy factor $\Delta K_{\rm an} = (\Delta K_c - \Delta K_{ab})$. The demagnetization correction above T_c is negligible [7] and it cannot account for this anisotropy. The data at $T = 293$ K are in good agreement with previous results [8], while the temperature behavior observed in nonoriented powder [6] is similar to the one for $\mathbf{H}_0 \perp \mathbf{c}$, as could be expected.

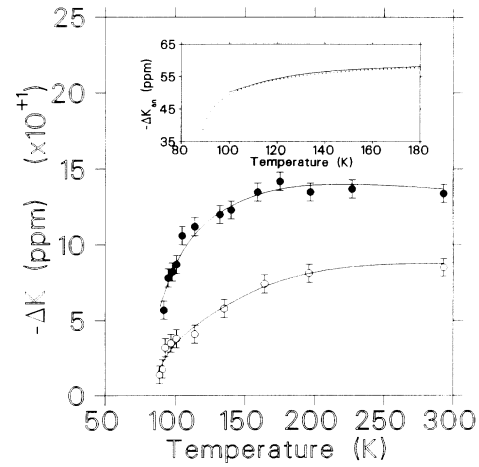

FIG. 1. Temperature dependence of ^{89}Y NMR shift ΔK above T_c for a magnetic field of 5.9 T parallel to the **c** axis (solid circles) or in the a-b plane (open circles). The ^{89}Y NMR line of an aqueous solution of YCl_3 was used as a reference. In the inset the temperature dependence of the shift anisotropy $\Delta K_{\rm an}$ (dotted line) is compared to the scaled susceptibility for a $YBa_2Cu_3O_{6.87}$ sample (solid line) [7].

ΔK in YBCO arises from two main contributions: a positive temperature-independent chemical shift and a negative temperature-dependent Knight shift (K_s) [6]. The K_s sign discriminates among the possible symmetries of the bondings between copper, oxygen, and yttrium ions and a negative value is a strong support for holes localized on O($2p\sigma$) orbitals [9]. The yttrium Knight shift in YBCO arises from a dominant coupling with oxygen O($2p$) orbitals and from a less relevant one with copper orbitals through a Cu($3d$)-Y($4d$) hybridization [10].

Our experimental data (Fig. 1) yield the new evidence that the total shift is highly anisotropic and that the anisotropy factor has a marked temperature dependence. As shown in Fig. 1 a comparison of ΔK_{an} with the susceptibility χ_m [7] evidences that $\Delta K_{\mathrm{an}}(T)$ originates mainly from $\chi_m(T)$. This observation points out that there is an anisotropic Knight shift, which may arise either from an anisotropic hyperfine coupling tensor or from an anisotropic susceptibility χ_s, or both. An anisotropic hyperfine coupling should originate from a hybridization of Y($4d$) orbitals either with Cu($3d$) orbitals or with O($2p$) orbitals. An anisotropic χ_s is also possible, and a value of $(\chi_s^c - \chi_s^{ab})/\chi_s^c \simeq 10\%$ is consistent with previous calculations based on the Mila and Rice model [11], as shown by Walstedt and Warren [12]. Although the ^{89}Y NMR shift alone does not allow us to discriminate the actual origin of the anisotropy, it singles out these two relevant sources.

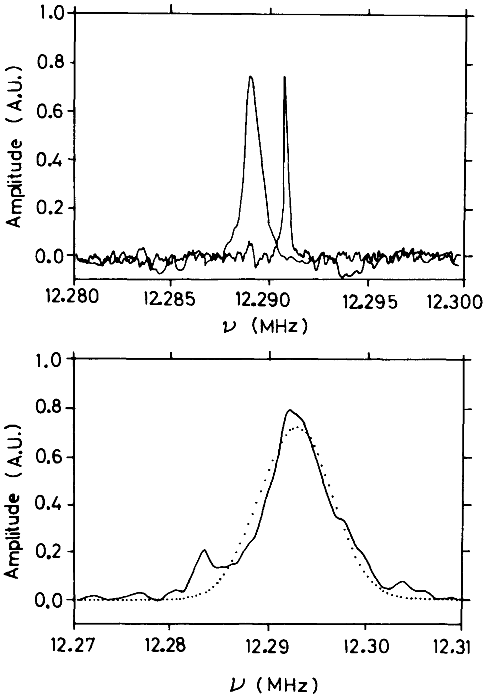

FIG. 2. ^{89}Y NMR line of the YBCO sample at $T=293$ K for $\mathbf{H}\parallel c$, compared to the one from the reference YCl$_3$ solution (upper panel). The broadened ^{89}Y NMR line at $T=44$ K, for the same orientation, is shown in the lower panel of the figure with a comparison to the best-fit function obtained from the Fourier transform of Eq. (1) for $\tau_c = 30\ \mu$s.

Now we are going to present and discuss the most important findings of the present work, namely, the low-temperature rigid-lattice structure of the vortices and the evidence of their motion above 40 K. As shown in the spectrum reported in Fig. 2, for $T < T_c$ the singularities expected from a regular triangular vortex lattice [13] are smeared out by the distribution of demagnetization factors N_i and possibly by pinning effects. In order to characterize the field distribution $f(B)$ by means of ^{89}Y NMR we carried out a Gaussian fit of the spectra and derived from it the full width at half intensity $\Delta\nu$ (see Fig. 3). Since at low temperatures ($T \simeq 7$ K) one can assume that the vortex lattice is rigid, then, by neglecting any extra broadening due to N_i distribution, the penetration depth $\lambda_{ab}(0)$ can be derived from the second moment of the best-fit Gaussian line. Since $\langle \Delta B_{ab}^2 \rangle^{1/2} = 0.0609\Phi_0/\lambda_{ab}^2$ [14], one obtains $\lambda_{ab}(0) \simeq 150$ nm. This value is in good agreement with previous findings with different techniques, like μ^+SR and dc magnetization measurements [3].

The ratio between the linewidths for the two orientations of the magnetic field, at low temperatures, $\Delta\nu_{ab}(0)/\Delta\nu_c(0) \simeq 1.5$ (see Fig. 3), agrees with the results of ^{89}Y NMR reported in Refs. [5,8]. However, this ratio is significantly smaller than the findings by μ^+SR, namely, 3-5 [3], or by dc magnetization, $\simeq 5$. This difference is too big to be attributed to misalignment effects. A simple estimate [13,15], in fact, shows that for a ratio of the effective masses of around 25 a misalignment of more than 15° around the c axis is required to obtain a ratio of 1.5 between the linewidths for the two orientations. Thus, we suggest that muons and yttrium nuclei probe different field distributions $f(B)$. Do they probe different $f(B)$ in both directions or in only one direction? Recent

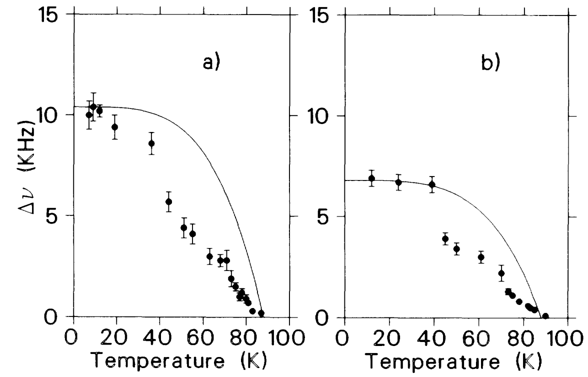

FIG. 3. ^{89}Y NMR full width at half intensity $\Delta\nu$ vs T below T_c, for orientation of the magnetic field parallel (a) or perpendicular (b) to the c axis. The solid lines represent the expected behavior due to the temperature dependence of the penetration depth. The constant value 1.1 kHz ($\Delta\nu$ for $T > T_c$) has been subtracted.

μ^+SR experiments [16] performed on the same $YBa_2Cu_3O_{6.92}$ sample show that the value of $\langle \Delta B^2 \rangle$ measured by μ^+SR and ^{89}Y NMR is the same, within 5%, when the field is in the a-b plane. Therefore we conclude that the two probes detect the same field distribution for $\mathbf{H}_0 \perp \mathbf{c}$ but different ones for $\mathbf{H}_0 \parallel \mathbf{c}$.

The temperature dependence of the linewidth (see Fig. 3), compared to the trivial one expected for the temperature dependence of the penetration depth in the usual two-fluid model, reveals a novel and interesting process of line narrowing (see Fig. 3). This narrowing, observed around 40 K (well below T_i) and undetected by muons [3], indicates the onset of fast vortex motion with characteristic correlation times smaller than the inverse of the rigid-lattice linewidth. Fast vortex motion starts when thermal fluctuations overcome the coupling energy between vortex rings in different CuO_2 layers [1] and brake the rigidity of the vortex lattice. In this regime vortex motion can be either thermally activated or diffusive (melted phase) depending on the intensity of the external field [17,18]. At higher fields it is more likely for each vortex to be scattered by the repulsive interaction from another vortex rather than to move across a pinning center, leading to a diffusive motion. At lower fields the higher probability of moving across pinning centers leads to a crossover to a thermally activated motion.

One can tentatively describe the motion in terms of a single characteristic correlation time τ_c and analyze the temperature dependence of the linewidth in the light of a melting process (τ_c constant in the melted phase) or of a thermally activated regime with $\tau_c = \tau_0 e^{U/T}$. In this analysis we assume a two-fluid-model temperature dependence of the rigid-lattice second moment $\langle \Delta B^2 \rangle (T)$, as μ^+SR experiments have evidenced [3].

Motional effects on the NMR line can be evaluated in closed form only for limiting situations of slow $[\tau_c^2 \gg (\langle \Delta B^2 \rangle \gamma^2)^{-1}]$ and fast $[\tau_c^2 \ll (\langle \Delta B^2 \rangle \gamma^2)^{-1}]$ motions. An approximate expression for the free-induction decay in the presence of a random Brownian motion is [19]

$$s(t) = \exp\{-\gamma^2 \langle \Delta B^2 \rangle \tau_c^2 [\exp(-t/\tau_c) - 1 + t/\tau_c]\} . \quad (1)$$

By fitting ^{89}Y NMR lines with the Fourier transform of the above equation (see Fig. 2) and by assuming a two-fluid-model temperature dependence for $\langle \Delta B^2 \rangle$ an evaluation of the behavior and of the values of τ_c is possible. Thus, it is possible, from the above analysis, to compare the experimental behavior of $\Delta\nu(T)$ with the one expected for the two model situations for τ_c, namely, a sudden melting with τ_c constant or an activated temperature dependence of τ_c.

In Fig. 4, line a gives the behavior for the assumption of a thermally activated motion with $U = 500$ K [20] and $\tau_0 = 10^{-9}$ s [21]. It is evident that although an activated temperature dependence of τ_c could explain the jump in $\Delta\nu$ around 40 K, it would imply a narrowing faster than the one experimentally observed at higher temperatures. Instead, line b, showing the $\Delta\nu(T)$ behavior expected in the case of a jump for τ_c to a constant value above 40 K (vortex melting), is in good agreement with the experimental results, for a correlation time $\tau_c^{\parallel} = 30$ μs for $\mathbf{H}_0 \parallel \mathbf{c}$. For $\mathbf{H}_0$ in the a-b plane the fitting of the experimental data in the light of Eq. (1) also gives a satisfactory fitting, yielding for the effective correlation time $\tau_c^{\perp} = 55$ μs. As regards the temperature dependence of the line shape, it appears to agree qualitatively with the predictions from Eq. (1): At low temperatures the line shape is Gaussian-like, while close to T_c it is more Lorentzian-like. The values obtained for τ_c explain why the muons cannot detect the flux melting. In fact, muons could observe a narrowing only for correlation times τ_c shorter than the inverse of the corresponding muon rigid-lattice linewidth (> 100 kHz). Although the numerical values for the effective correlation time should be considered only as qualitative estimates, we remark that the longer τ_c for the field in the a-b plane can be associated with a restriction of the diffusional motions across CuO_2 planes.

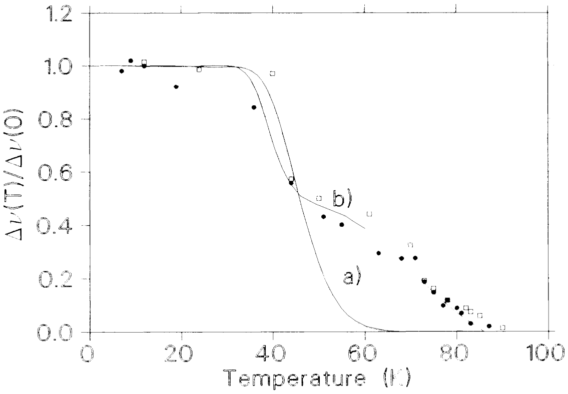

FIG. 4. Normalized temperature dependences of the linewidths for the field along the c axis (solid circles) or in the a-b plane (open squares) compared to the theoretically expected behavior for, line a, thermally activated flux motion; and line b, flux melting.

The conclusion in favor of a temperature-independent τ_c and of a partially melted phase above 40 K in $H_0 = 5.9$ T is also supported by magnetization relaxation experiments [18]. Finally we mention that our data are partially different from those obtained by Brom and Alloul [5]. A possible origin of this difference is related to the oxygen deficiency ($O_{6.92}$) of our sample [22]. In fact, a larger oxygen deficiency implies a weaker Josephson coupling between CuO_2 planes which leads to a lower correlation between the motion of vortex rings in different planes and to a higher anisotropy [1,15].

In conclusion, a careful study of the ^{89}Y NMR spectra in an oriented $YBa_2Cu_3O_{7-\delta}$ sample has allowed us to detect a clear anisotropy of the Knight shift above T_c. The analysis of the spectra below T_c has evidenced for the first time motional narrowing phenomena that can be accounted for by a flux melting occurring at 40 K, well below the irreversibility temperature T_i, with a characteristic correlation time of the order of tens of microseconds, too large to be detected by muons.

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