Gd^{3+} ESR determination of the local spin susceptibility in $Gd:YBa_2Cu_3O_y$ high-temperature superconductors

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Gd^{3+} ESR at high fields in Gd-doped high-T_c superconductors is shown to be a precise probe of the conduction electron static spin susceptibility, χ. The Gd^{3+} ESR Knight shift at 245 GHz and the spin relaxation broadening at 245 and 9.2 GHz in $Gd_{0.01}Y_{0.99}Ba_2Cu_3O_y$ (with various values of y between 6.05 and 7.0) are in agreement with published ^{89}Y NMR data above 70 K and provide additional measurements at the rare earth site at much lower temperatures. In the superconducting compounds $\chi(T)$ differs strongly from the Yoshida function and at low T it follows a T or T^2 dependence. An anomalous ESR line shape is found at low T in the superconducting state; we provisionally attribute this to a small (10^{-2}–10^{-3} μ_B) static magnetic moment on planar Cu sites. [S0163-1829(96)05637-8]

I. INTRODUCTION

In high temperature perovskite superconductors the real part of the static homogeneous spin susceptibility χ, which in a metal is a direct measure of the density of states (DOS) at the Fermi surface, has an interesting behavior. The most important parameter determining χ is the density of holes in the CuO_2 planes.[1] The temperature dependence is qualitatively different for ''overdoped'' and ''underdoped'' systems. In underdoped systems a gap in the low energy spin[2,3] and charge[4] excitations already reduces χ at temperatures well above T_c. Optimally doped systems[3] have a temperature independent χ above T_c. $\chi(T)$ of overdoped systems is at present controversial.

In this paper we report measurements of χ using a microscopic probe, the Gd^{3+} electron spin resonance at high fields (8.8 T and 245 GHz) in $YBa_2Cu_3O_y$ with 1% Gd/Y substitution and with y ranging from the insulating antiferromagnet, $y=6.05$ through underdoped superconductors to the optimally doped $y=7.0$ compound. The present work utilizes the high resolution of high field ESR in measuring g shifts of localized moments arising from the interaction with conduction electrons. At the high fields of the experiment, crystal fields are only a small perturbation on the Zeeman levels of the nearly S state Gd^{3+} ions and the spectra are simple. In most cases the shifts of the resonance magnetic field with temperature or composition are proportional to changes in the static susceptibility without further corrections. The method is versatile; we measure χ with the oxygen content y ranging from 6.05 to 7.0 and this can be done both in the superconducting and the normal states of the metallic compounds. The anisotropy of the susceptibility is also determined.

The concept of measuring χ by ESR of a localized moment is similar to the more familiar case of NMR Knight shift. Conduction electrons overlap only slightly with the rare earth sites and the ESR of the localized Gd moment is a nonperturbative probe much like, e.g., ^{89}Y NMR. We find that the temperature dependence of the Gd ESR Knight shift ^{Gd}K (the relative g shift due to the conduction electrons) and spin lattice relaxation rate $^{Gd}T_1^{-1}$ follow the corresponding quantities for ^{89}Y NMR extremely well.

The functional form of the disappearance of χ at low temperatures in the superconducting state is qualitatively different for s wave and d wave pairing. Gd ESR is a more sensitive probe for this than ^{89}Y NMR because the coupling constant is an order of magnitude larger and so diamagnetic screening effects are less serious. However, in practice we run into difficulties in the interpretation of the ESR spectra of the superconducting compounds at low T. The most conspicuous anomaly is a splitting of the resonance line in oxygen depleted samples for magnetic field applied in the CuO_2 planes ($H\perp c$).

II. EXPERIMENT

A series of sintered $Gd_{0.01}Y_{0.99}Ba_2Cu_3O_y$ powders with $y=6.05$, 6.40 ($T_c=10$ K), 6.53 ($T_c=60$ K), 6.76 ($T_c=66$ K), and 7.0 ($T_c=92$ K) was prepared by standard solid state reaction methods. The 25 mg samples were magnetically aligned in araldite along the crystallographic c axis with a volume filling factor of 10%. ESR spectra were recorded in

Cambridge at a frequency of 9.2 GHz ($H=0.34$ T) and in Grenoble at 245 GHz ($H=8.8$ T) and in some cases at 158 GHz (5.6 T) and 296 GHz (10.6 T). In the Grenoble spectrometer the magnetic field dependent absorption of the far infrared light is measured. The sample is placed in an oversized waveguide and no cavity is employed. For both low and high frequencies the magnetic field is modulated at audio frequencies and the absorption derivative is detected.

Shifts of the high frequency ESR were measured with respect to a BDPA (a,g-bisdiphenyline-b-phenylallyl) marker with $g=2.00359$. For a simpler presentation, we quote relative shifts ${}^{\mathrm{Gd}}K=-\delta H/H$ where δH is the shift of the resonance field H from a value corresponding to $g=1.9901$ which we find to be the g factor for zero spin susceptibility. This definition agrees with the usual definition of the Knight shift as a frequency shift. At 9.2 GHz the chaotic generation of superconducting vortices by the modulating magnetic field[5] made measurements difficult or impossible below T_c. The 9.2 GHz spectrometer uses a resonant cavity and is sensitive to the phase change of the rf field induced by the generation of vortices. At 245 GHz there is no cavity and vortex noise was not observed.

The ESR Knight shift data presented here have not been corrected for the paramagnetism of Gd. At 10 K and 9 T the macroscopic magnetization of Gd magnetic moments in $Gd_{0.01}Y_{0.99}Ba_2Cu_3O_y$ is $4\pi M=4$ mT but at Gd sites this is reduced by local dipolar fields and demagnetization factors. For spherical particles, the resultant field at Gd sites equals the applied field and no correction is necessary. Although the shape of the crystallites is irregular, experimentally we found that this correction can be ignored. Such corrections would be easily observed as an extra shift and broadening at low temperatures in the insulating antiferromagnetic parent compound $y=6.05$. In fact this sample had a temperature independent resonance field and a linewidth of 4 mT between 10 and 80 K.

We measured the reversible and irreversible components of the magnetization, M_{rev} and M_{irrev}, from 0–12 T using a vibrating sample magnetometer in order to estimate corrections to the local field arising from diamagnetic screening in the superconducting state. For a spherical particle the reversible part alone gives a shift of $8\pi M_{\mathrm{rev}}/3$. The correction for M_{irrev} is less than expected from the magnetization measurements because below the irreversibility line the audio frequency modulation only penetrates to a limited depth (for example in the Bean model the field at the surface is equal to the applied field minus the reversible magnetization). This is clear from our data for $y=7.0$ and $H\perp c$ where $4\pi M_{\mathrm{irrev}}$ is 10 mT at 10 K but no hysteresis between up and down field sweeps was observed in the Gd spectra to within 0.5 mT. The remaining correction $8\pi M_{\mathrm{rev}}/3(10\ \mathrm{K})=3$ mT is small for $y=7.0$ and $H\perp c$ and it decreases slowly as T increases. For $y=6.76$ any corrections at 9 T are small because at 20 K, $4\pi M_{\mathrm{rev}}=1$ mT (2 mT) for $H\perp c$ ($H\|c$) and M_{irrev} is negligible. In the only case where the diamagnetic shift is large, $y=7.0$ and $H\|c$, data are only presented for $T>50$ K where $4\pi M_{\mathrm{irrev}}<5$ mT and $4\pi M_{\mathrm{rev}}<2$ mT.

III. LOCAL FIELDS SENSED BY Gd^{3+} ESR

Gd^{3+} ions ($S^{\mathrm{Gd}}=7/2$, $L\approx 0$) in dilute Gd:$YBa_2Cu_3O_y$ interact weakly with surrounding electrons with spin S^i. Over the full range of y the ESR spectrum is well described by a simplified Hamiltonian for magnetically dilute systems,[6,7]

$$H=g^{\mathrm{Gd}}\mu_B\mathbf{S}^{\mathrm{Gd}}\cdot\mathbf{H}+D\{(S_z^{\mathrm{Gd}})^2-\tfrac{1}{3}S^{\mathrm{Gd}}(S^{\mathrm{Gd}}+1)\}+\Sigma_\alpha J_\alpha S^{\mathrm{Gd}}{}_\alpha S^i{}_\alpha . \quad (1)$$

Our data are consistent with an isotropic g factor of $g^{\mathrm{Gd}}=1.9901$ which is independent of y and of temperature T. The energy difference between adjacent Zeeman levels for $H=9$ T is about 11 K and at low temperatures only the lower levels are populated. In this paper we discuss the central $m=-1/2\rightarrow+1/2$ transition, i.e., the transition between the fourth and fifth Zeeman levels. The drop in the population of these levels limits the high field experiments to temperatures above 10 K.

In Eq. (1) the crystal field and the exchange interaction with neighbouring Cu(2) and O atoms are characterized by the second order crystal field parameter D and the anisotropic exchange interaction parameter J_α, respectively, where α represents Cartesian coordinates. In Gd:$YBa_2Cu_3O_y$ these are small perturbations of the Zeeman energy at 9 T. A detailed account of crystal field effects taking into consideration higher order terms as a function of y is discussed in Refs. 8 and 9.

To first order the crystal field splits the Gd^{3+} resonance into seven allowed transitions. The central transition is independent of D for $H\|c$ and is shifted by about D^2/H for large values of $H\perp c$. Since in Gd:$YBa_2Cu_3O_y$ D lies[6–9] between 1.2 and 1.8 GHz (depending on y) and is nearly T independent, crystal field corrections are negligible (less than 1 mT) at 245 GHz for all magnetic field orientations. The fourth and sixth order crystal field terms [neglected in Eq. (1)] are even smaller. At 9 GHz crystal fields are comparable to the Zeeman term and for powders aligned along the c direction, but randomly oriented in the (a,b) plane, the ESR lines are inhomogeneously broadened for orientations of H other than $H\|c$.

In the single spin-fluid model for high-T_c oxides[10] the transferred hyperfine field from the Cu orbitals has the same T dependence as that from O orbitals. The Knight shift and the spin-lattice relaxation rates are[9,11]

$${}^{\mathrm{Gd}}K=J/(g^{\mathrm{Gd}}g^i\mu_B{}^2)\mathrm{Re}\{\chi(0,0)\}={}^{\mathrm{Gd}}A\chi, \quad (2)$$

$${}^{\mathrm{Gd}}T_1^{-1}=C_m k_B T/[2(g^i\mu_B)^2]\Sigma_q({}^{\mathrm{Gd}}A)^2 f(q)\mathrm{Im}\chi(q,\omega_L)/\omega_L , \quad (3)$$

where $\chi(q,\omega)$ is the generalized susceptibility, $f(q)$ a structure factor, and ω_L is the Gd^{3+} Larmor frequency. g^{Gd} and g^i are the gyromagnetic factors for the Gd^{3+} ions and electrons on the CuO_2 sheets, respectively. We refer to ${}^{\mathrm{Gd}}A$ as a ''hyperfine'' constant although here it arises from an exchange interaction between Gd $4f$ and CuO_2 electronic states. In Eqs. (2) and (3) we omitted the anisotropy for simplicity. We shall denote the shifts measured with H along c and in the (a,b) plane by ${}^{\mathrm{Gd}}K_c$ and ${}^{\mathrm{Gd}}K_\perp$, respectively. The factor C_m in Eq. (3) is the Barnes-Plefka[12] enhancement of the relaxation with respect to the Korringa relaxation of transitions $m\rightarrow m+1$. This enhancement occurs in exchange-coupled crystal field split systems where the g factors of localized and itinerant electrons are approximately equal but the relaxation of conduction electrons towards the ''lattice'' is strong enough to inhibit bottleneck effects. For a resolved fine

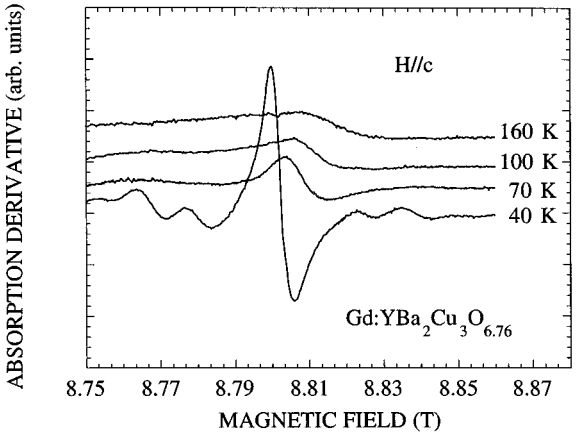

FIG. 1. Typical Gd^{3+} ESR spectra at 245 GHz for $y=6.76$. Note shift and broadening with T. The gain is set arbitrarily for each spectrum. At 40 K ''wiggles'' around the central transition are $-3/2\rightarrow-1/2$ and $1/2\rightarrow3/2$ transitions.

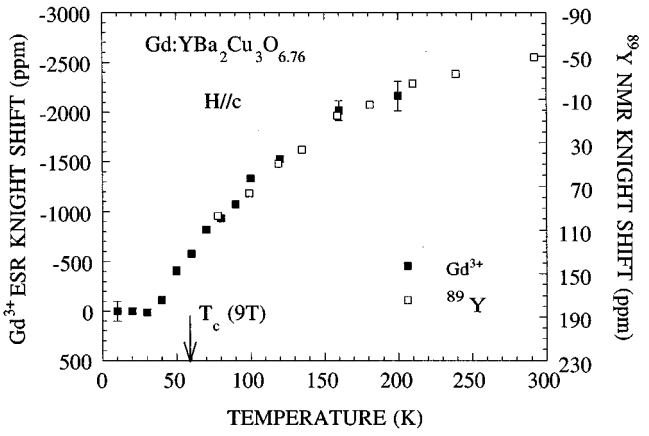

FIG. 2. Comparison of Gd^{3+} ESR and ^{89}Y NMR Knight shifts (Ref. 3) ESR: $H\|c$, $y=6.76$. NMR: unoriented powder, $y=6.75$. The best fit yields a ''hyperfine'' coupling constant ratio $^{Gd}A/^{89}A=10.5$.

structure and $g\mu_B H>k_B T$, $C_m=S(S+1)-m(m+1)$ and for the central transition $C_{-1/2}=16$. In undoped $YBa_2Cu_3O_y$ the conduction electron spin relaxation to the ''lattice,'' i.e., to impurities and phonons, is evidently strong since the conduction ESR is too broad to be observed and therefore bottleneck effects cannot play any role.

IV. EXCHANGE AND CRYSTAL FIELD EFFECTS ON THE Gd^{3+} ESR OF $Gd:YBa_2Cu_3O_y$

Figure 1 shows some typical spectra at 245 GHz for an oxygen depleted system with $y=6.76$ and $H\|c$. The central $-1/2\rightarrow+1/2$ transition at 8.80 T and 40 K is shifted towards higher fields and broadens with increasing temperature. The temperature dependent shift and broadening are characteristic of a Gd^{3+} ion weakly coupled to surrounding electrons via a negative exchange interaction.

In oxygen depleted samples the crystal field at the Gd sites depends on the first neighbor oxygen chain configuration.[8,9] At high fields the shift of the central transition due to the crystal field is negligible. The low temperature central transition is narrow because the resonance fields for Gd sites with various oxygen configurations are the same. On the other hand, the satellite lines for oxygen depleted samples have a structure reflecting variations of the crystal field with the oxygen occupancy of first neighbor sites around the Gd^{3+} ions. For example for $y=6.76$ the $-3/2\rightarrow-1/2$ and $+3/2\rightarrow+1/2$ transitions appear as three pairs of lines on each side of the central transition (Fig. 1). The outermost pair at 8.755 and 8.855 T corresponds to Gd sites with all four first neighbor oxygen chains occupied while the inner pairs correspond to sites surrounded by three or two oxygen chains only. Intensities are in agreement with expectations for a homogeneous $y=6.76$ oxygen content and there are no significant spatial fluctuations of y.

V. SPIN SUSCEPTIBILITY OF $YBa_2Cu_3O_y$ DETERMINED FROM Gd^{3+} SHIFTS

A. Comparison of Gd^{3+} ESR and ^{89}Y NMR Knight shifts

Figure 2 demonstrates the similarity of local fields measured by Gd ESR and ^{89}Y NMR. The T dependence of the Gd shift is in excellent agreement with ^{89}Y Knight shift data of Alloul *et al.*[3] at temperatures above 80 K where data for both set of experiments are available. In Fig. 2 the Gd shift for $y=6.76$ and $H\|c$ is compared to the average ^{89}Y shift $^{89}K_{av}$ of Alloul *et al.*[3] on an unoriented sample with a similar y. Two parameters, the ratio of the hyperfine constants, $R=^{Gd}A/^{89}A$ and the zero for the ^{89}Y shift, $^{89}K_{av}(0)$ are fitted to the data using the relation $^{Gd}K_c(T)-^{Gd}K_c(0)=R[^{89}K_{av}(T)-^{89}K_{av}(0)]$. We find $R=10.5\pm1$ and $^{89}K_{av}(0)=192\pm20$ ppm with respect to YCl_3. $^{89}K_{av}(0)$ is in reasonable agreement with a reported value of 150 ppm (Ref. 13) obtained from an extrapolation of high T ^{89}Y NMR data.

We find the same value of R for all oxygen concentrations y, i.e., the ''hyperfine'' constant, ^{Gd}A is independent of y. This strongly supports our interpretation of the Gd ESR shift as a measure of the spin susceptibility. The large value of R means that Gd ESR is a sensitive probe of the spin susceptibility. This is especially advantageous at low temperatures where the linewidth is narrow. At low temperatures the long NMR spin relaxation rates and small shifts make precise ^{89}Y shift measurements difficult or impossible.

The anisotropy of the Gd Knight shift is small above 50 K and we find $^{Gd}K_c/^{Gd}K_\perp=1.12\pm0.05$ for both $y=6.76$ and 7.0. The Gd ESR shift anisotropy is consistent with the expected anisotropy of the Cu transferred hyperfine field due to the anisotropy of the g factor of the Cu ions. The ^{89}Y Knight shift has a larger anisotropy; $^{89}K_c/^{89}K_\perp=1.29\pm0.03$ has been reported by Alloul *et al.*[13] and 1.45 ± 0.02 by Takigawa *et al.*[14]

B. Spin susceptibilities of $Gd:YBa_2Cu_3O_y$ with $H\|c$

Figure 3 shows the Gd^{3+} shifts versus T for various values of y. The data shown are for $H\|c$ except for $y=6.58$ which was an unoriented sample. Diamagnetic corrections are unimportant for the data shown. For the optimally doped system the susceptibility is large and T independent above T_c. The superconducting transition appears as a sharp decrease in χ. In the insulating antiferromagnetic $y=6.05$ compound the polarization at the antiferromagnetic wave vector

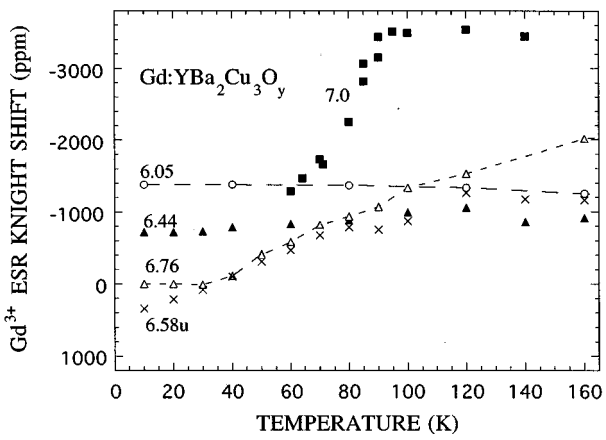

FIG. 3. Gd^{3+} ESR Knight shifts at 245 GHz for $YBa_2Cu_3O_y$ with $y=7.0$, 6.76, 6.44, and 6.05 all aligned with $H\|c$ and for an unaligned sample with $y=6.58$.

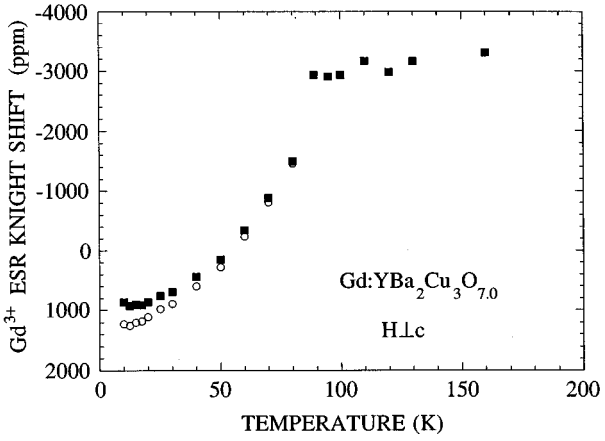

FIG. 4. Gd^{3+} ESR Knight shift [proportional to the conduction electron spin susceptibility, $\chi(T)$] of $YBa_2Cu_3O_{7.0}$ (squares). The open circles show $^{Gd}K_c$ corrected for diamagnetic shifts.

is cancelled at the Gd site by symmetry. There is however a relatively large χ at all temperatures arising from the $q=0$ polarization of the static localized Cu moments.

The susceptibilities of the $y=6.76$ and 6.58 samples have similar values at low T with apparently no anomaly at T_c. The physical properties of these underdoped systems have been successfully described by a phenomenological model supposing a temperature independent gap[15] in the low energy excitation spectrum. The change in χ at the superconducting transition is very small because the electronic entropy is reduced by this gap.[15] For $y=6.44$ there is no magnetic order; the conductivity is metallic and the superconducting transition at 10 K (for $H=0$) is suppressed to much lower values in the field of the experiment. However, the density of states at the Fermi level of the $y=6.44$ compound is not zero as expected for a true gap; it is reduced to 20% of the normal state value of the optimally doped compound. This agrees with a recent analysis[15] of specific heat data for the same series of compounds.

C. Spin susceptibility of Gd:$YBa_2Cu_3O_{7.0}$ with $H\perp c$

Figure 4 shows the T dependence of $^{Gd}K_\perp$ ($H\perp c$) for $y=7.0$. According to Eq. (2) this is proportional to the CuO_2 plane spin susceptibility. $^{Gd}K_\perp$ follows well the Knight shift of ^{63}Cu for $H\perp c$ reported by Barrett *et al.*[16] Above T_c the shift is temperature independent.

Below T_c, $\chi(T)$ depends on the symmetry of the gap function. In a simple weak coupling isotropic s-wave superconductor, $\chi(T)$ is given by the Yoshida function. At temperatures much below T_c it decreases exponentially, in contrast to the d-wave singlet case where it is proportional to the temperature. We find that below T_c, $^{Gd}K_\perp$ initially falls faster than the Yoshida function and is not as flat below $T_c/2$. Between 10 and 20 K no variation is observed in the raw data to within ± 50 ppm but when the corrections for M_{rev} are included the data are consistent with a linear T dependence of $\chi(T)$ corresponding to a $13\pm 3\%$ increase in $\chi(T)/\chi(T_c)$ between 0 and 30 K. However, a fit to a T^2 law is equally good below 40 K.

For $H\perp c$ the resonance has an anomalous shape at low temperatures: it consists of a narrow peak and a tail towards higher fields. Figure 4 displays the shift of the narrow component. As discussed below, the spectra for $H\perp c$ and $y<7.0$ are split into two lines which cannot be explained in terms of a field independent susceptibility. Until this problem is solved the interpretation of $^{Gd}K_\perp(T)$ remains somewhat ambiguous.

We note that the data presented in Fig. 4 are the most precise determination of $\chi(T)$ in $YBa_2Cu_3O_{7.0}$ below T_c to date. The weak coupling to conduction electrons limits ^{89}Y NMR Knight shift measurements to temperatures above T_c. Barrett *et al.*[16] have measured the ^{63}Cu NMR Knight shift in $YBa_2Cu_3O_{7.0}$ and have shown that below T_c $\chi(T)$ does not follow the expectations for a BCS s-wave singlet weak coupling superconductor. The precision of ^{63}Cu NMR is however not sufficient to determine the temperature dependence of $\chi(T)$ at low temperatures. For $H\|c$ the ^{63}Cu NMR spectrum is simple and narrow. Unfortunately in this geometry there is nearly no coupling between the conduction electrons and the Cu nuclei. For $H\perp c$ the coupling is strong enough to give rise to reasonable shifts but the analysis of the NMR

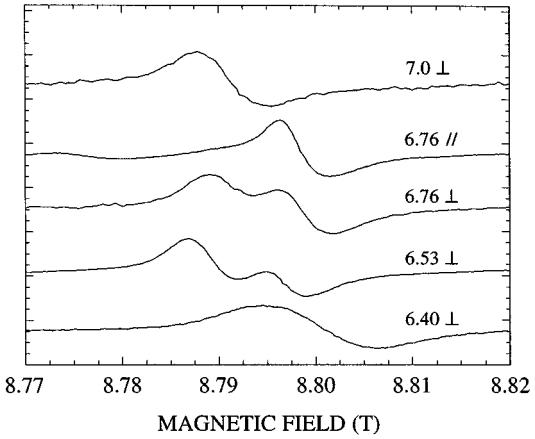

FIG. 5. Gd^{3+} ESR spectra at 245 GHz and 20 K for various values of y. $\|$ and $\perp$ denote directions of the applied field H with respect to the c axis. Note the line splitting for $H\perp c$ and $y=6.76$ and 6.53.

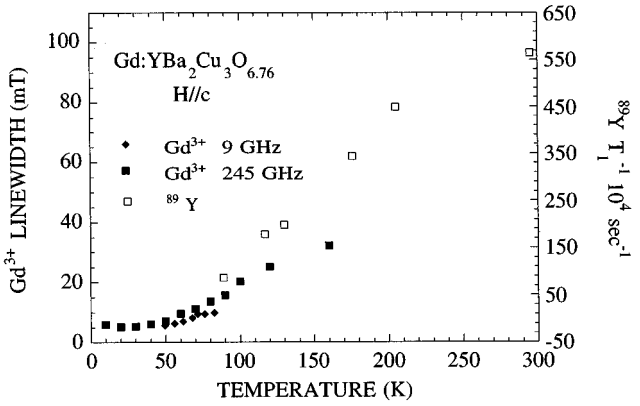

FIG. 6. Comparison of Gd^{3+} ESR linewidth ΔH and ^{89}Y NMR spin lattice relaxation rate T_1^{-1}. The scales are chosen to match the two sets of data at low T with $^{Gd}A/^{89}A=10.5$ and assuming Eq. (3) is valid.

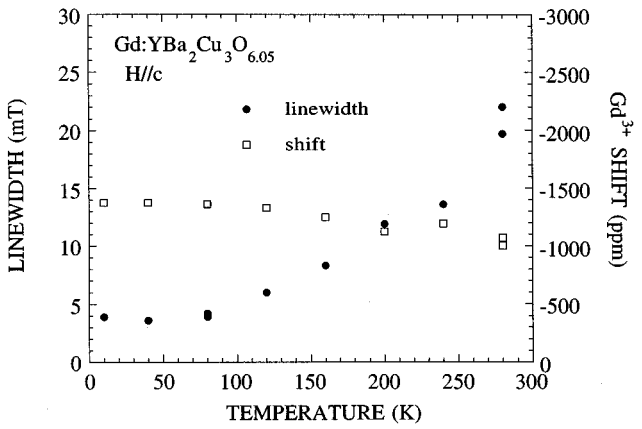

FIG. 7. Shift (relative to $g=1.9901$) and linewidth versus temperature of the central $m=-1/2\rightarrow+1/2$ Gd^{3+} ESR transition of the antiferromagnetic insulator parent compound $y=6.05$ at 245 GHz ($H=8.8$ T).

spectrum is uncertain. In addition to the broadening by quadrupolar effects and by the inhomogeneous penetration of the applied magnetic field, Barrett *et al.*[16] found an unexplained broadening of the ^{63}Cu NMR linewidth at low temperatures.

D. Anomalous splitting of Gd^{3+} ESR at low temperatures

The Gd^{3+} ESR spectra show a puzzling complexity for $H\perp c$ at low temperatures in the superconducting state (Fig. 5). For $H\|c$ there is no anomaly for any oxygen concentration. Also, for a $y=6.40$ sample which is not superconducting at 9 T, there is no anomaly. The anomaly is evident at the intermediate concentrations, $y=6.53$ and 6.76 below 40 K, where for $H\perp c$ the line is split into two components. One line appears near the resonance field of the $y=6.76$ compound with $H\|c$ while the resonance field for the other is lower by $\Delta H_s=7.5$ mT. A most important observation is that ΔH_s was unchanged to within ± 0.2 mT when the frequency was increased from 245 GHz (8.8 T) to 296 GHz (10.6 T) for the $y=6.76$ sample at 22 K. The same splitting was also observed at 158 GHz. The anomaly may be caused by a small magnetic moment on the Cu planes which orders magnetically below 40 K. Further experiments are needed to verify this hypothesis. Although it is an unconventional explanation we note that in heavy fermion superconductors, small static moments are not at all uncommon.[18]

Explanations involving a distribution of Knight shifts due to, e.g., an inhomogeneity of oxygen content cannot account for the field independent splitting. The splitting is too large to be explained by the inhomogeneous penetration of magnetic field due to the superconducting vortex structure. At low temperatures and similar magnetic fields the broadening of the ^{89}Y NMR line caused by the vortex lattice[17] is much less than the splitting of the Gd^{3+} ESR observed by us.

VI. COMPARISON OF Gd^{3+} AND ^{89}Y SPIN LATTICE RELAXATION RATES

The T dependence of the Gd linewidth in the $y=6.76$ compound is compared to the ^{89}Y spin lattice relaxation rate of Alloul *et al.*[3] in Fig. 6. The increase of the linewidth ΔH with temperature is the same at 9 and 245 GHz (Fig. 6). The somewhat larger residual linewidth for 245 GHz reflects a small inhomogeneity of the Knight shift. Most of the observed T dependence of the Gd linewidth arises from overlap with electrons on the CuO_2 layers because measurements on the insulating compound show that other contributions are small. Between 10 and 77 K the linewidth for $y=6.05$ is constant to within 0.3 mT and a small T dependence of 0.08 mT/K was observed above 100 K (Fig. 7). This relaxation broadening is induced by the phonon modulation of the crystalline field and does not change much with y.[8] Therefore we neglect the phonon contribution, and the Gd spin lattice relaxation is approximately given by $^{Gd}T_1^{-1}=^{Gd}\gamma[\Delta H(T)-\Delta H(T=0)]\sqrt{3}/2$ with $^{Gd}\gamma=2\pi g^{Gd}\mu_B/h$.

Comparison of relaxation rates and shifts of Gd^{3+} and ^{89}Y show that in the perovskite superconductors Eq. (3) is relatively well obeyed. The ratio of Gd^{3+} and ^{89}Y shifts and the ratio of relaxation rates are both independent of T and oxygen content y. The ratios of hyperfine constants, $^{Gd}A/^{89}A$ derived from $^{Gd}K/^{89}K$ and $^{89}T_1/^{Gd}T_1$ using Eqs. (2) and (3) are 10.5 ± 1 and about 8, respectively. In comparing the relaxation rates we used in Eq. (3) the low T limit, $C_m=16$ for the $m=-1/2$ Gd^{3+} resonance. This is clearly an overestimate of C_m at high temperatures where the satellite and central lines overlap. Recently Shaltiel *et al.*[19] have shown that this problem can be avoided by measuring the Gd^{3+} relaxation rate for the $7/2\rightarrow 5/2$ transition.

VII. SUMMARY AND CONCLUSION

We have shown that high field Gd^{3+} ESR is a powerful technique for exploring the microscopic local properties of high-T_c oxides. It is complementary to ^{89}Y NMR in that it is more suitable for the superconducting state. An anomalous splitting of the line for $H\perp c$ has been discovered—it seems to indicate that new ideas are required to understand the local field at the Y site at low temperatures.

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