Magnetic-Field-Induced Low-Energy Spin Excitations in $YBa_2Cu_4O_8$ Measured by High Field Gd^{3+} Electron Spin Resonance

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We have measured the spin susceptibility, χ_s, of the CuO_2 planes in the underdoped high T_c superconductor, $YBa_2Cu_4O_8$ by Gd^{3+} electron spin resonance (ESR) in single crystals and aligned powders in fields up to 15.4 T. At low temperatures and high fields, χ_s is enhanced slightly in the $B \parallel c$ orientation with respect to the $B \perp c$ orientation. The enhancement at 15.4 T ($\approx 0.15 H_{c2}$) at 16 K ($0.2\,T_c$) is small: approximately 10% of $\chi_s(T_c)$, suggesting that the second critical field of superconductivity, $H_{c2} \approx 100$ T, would *not* suppress the pseudogap. This work demonstrates the potential of high field ESR in single crystals for studying high T_c superconductors.

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The structure of vortex lines in high temperature superconductors (HTSCs) may shed light on the microscopic mechanism of superconductivity. The earliest d-wave pairing theories implied that the zero temperature spin susceptibility should scale with magnetic field as $(B/H_{c2})^{1/2}$ [1,2] in contrast to the linear dependence in an s-wave superconductor. A rigorous solution of the Bogoliubov–de Gennes equations in the mixed state [3] reveals that quasiparticles in d-wave superconductors are not bound to vortices, and predict a space averaged density of states (DOS) $N(0) \propto (B/H_{c2})^{\gamma}$, where $0.4 \leq \gamma \leq 1$ depending on the temperature and the model used [4,5]. A number of experiments were targeted at the field dependence of the DOS in $YBa_2Cu_3O_{7-\delta}$. Scanning tunneling microscopy [6] resolves the DOS at and around vortices, but is unsuitable to measure the total DOS [7]. Bulk experiments on nearly optimally doped $YBa_2Cu_3O_{7-\delta}$ include heat capacity [8], infrared transmission [9], thermal conductivity [10], and high field muon spin rotation [11]. Most of these experiments, together with early NMR on planar copper and oxygen [12], indicated some increase in the DOS with magnetic field but were inconclusive about its magnitude.

Underdoped HTSCs—which also possess a pseudogap in the normal state—are of special interest, as it is unclear how the pseudogap is related to the d-wave superconducting gap. An indication whether high magnetic fields suppress the pseudogap or not may contribute to understanding its nature. Also, most theoretical calculations of the quasiparticle spectra in HTSCs depend on the assumption that Landau's theory of the Fermi liquid is applicable below T_c, which is still to be justified by experiments. A recent ^{63}Cu NMR study on $YBa_2Cu_4O_8$ at high fields [13] reports a sizable field-induced DOS for B in the (a,b) plane, implying a large enhancement for $B \parallel c$. In contrast, we show that for $B \parallel c$ the DOS enhancement is small and incompatible with a suppression of the pseudogap at $B = H_{c2}$.

In this Letter, we report the spin susceptibility of $YBa_2Cu_4O_8$ obtained by high field electron spin resonance (ESR) spectroscopy of Gd^{3+} in Gd:$YBa_2Cu_4O_8$. Gd^{3+} is a nonperturbing probe of the CuO_2 spin polarization [14]. We search for low-energy spin excitations induced by high magnetic fields in the superconducting phase. Our goal is to determine the field dependence of the anisotropy of the susceptibility, $\chi_s^c - \chi_s^{ab}$, from the Gd^{3+} ESR shift. The anisotropy is a measure of the magnetic field induced DOS along c since H_{c2} in the (a,b) plane is several times larger than in the c direction. We measure both oriented powder (OP) and untwinned single crystal (SX) samples at several temperatures, frequencies, and magnetic field orientations. SX data are used to determine the zero field splitting (ZFS) parameters in the spin Hamiltonian of Gd^{3+} in Gd:$YBa_2Cu_4O_8$ with precision. This allows us to model powder spectra and measure shifts in the OP sample in both $B \parallel c$ and $B \perp c$ orientations with high accuracy. Diamagnetic effects inhibit SX measurements at low temperatures.

The experiments were carried out on the high field ESR spectrometers in Budapest and Grenoble. In Budapest, a quartz oscillator stabilized Gunn diode was used as a mm-wave source at $f = 75$, 150, and 225 GHz. In Grenoble, we used the same setup with a Gunn oscillator at 95, 190, and 285 GHz, an optically pumped far infrared laser at 349 and 429 GHz, and a sweepable 17 T NMR magnet. The frequency of 429 GHz corresponds to 15.4 T central Gd^{3+} resonance field. The radiation is transmitted through the sample in an oversized waveguide and no cavity is used. We detect the derivative of the absorption with respect to magnetic field. The magnetic field is calibrated by a reference sample, BDPA (a,g-bisdiphenyline-b-phenylallyl), at each sweep. The powder sample Gd:$YBa_2Cu_4O_2$ was sintered by a standard solid state reaction, with 1% of Y substituted by Gd. The powder with a characteristic grain size of 5 μm was mixed with epoxy resin, and aligned in a magnetic field. SX samples of typical dimensions $1 \times 1 \times 0.2$ mm^3 were grown by the self-flux method at 1100 °C in 600 atm of O_2. $T_c = 80$ K in both the SX and the OP samples.

The exchange induced shift of the Gd^{3+} ESR lines is similar to the ^{89}Y NMR Knight shift and yields the spin susceptibility of the CuO_2 planes. We define the Gd^{3+} ESR shift, in analogy with the NMR notation as

$$^{\mathrm{Gd}}K^{\alpha}(B_0, T) = -[B_m^{\alpha}(B_0, T) - B_0]/B_0 \qquad (1)$$

with $B_0 = hf/g_0\mu_B$, where f is the microwave frequency and the arbitrary zero of $^{\mathrm{Gd}}K$ is defined by $g_0 = 1.9901$. B_m^{α} is the measured resonance field as deduced from the measured positions of the Gd^{3+} lines (after correcting for the ZFS, i.e., B_m^{α} would be the resonance field of a similar probe with no ZFS). Then

$$^{\mathrm{Gd}}K^{\alpha}(B_0, T) = K_0^{\alpha} + {}^{\mathrm{Gd}}A\chi_s^{\alpha}(B_0, T) - B_{\mathrm{dia}}^{\alpha}(B_0, T)/B_0\,, \qquad (2)$$

where $K_0^{\alpha} = (g_{\mathrm{Gd}}^{\alpha} - g_0)/g_0$ plays the role of the NMR chemical shift. We denote by g_{Gd}^{α} the "pure" g factor of Gd^{3+} in Gd:$YBa_2Cu_4O_8$ from which the exchange with the CuO_2 spins is eliminated. g_{Gd}^{α} (thus K_0^{α}) is independent of magnetic field and temperature [15], and its anisotropy is small. The spin susceptibility of the CuO_2 planes is defined by $\chi_s^{\alpha}(B, T) = M_s^{\alpha}(B, T)/B$ where M_s^{α} is the CuO_2 spin magnetization. The Gd^{3+} shift due to the electronic exchange interaction between Gd^{3+} and CuO_2 is linked to the susceptibility through the constant $^{\mathrm{Gd}}A \approx -15$ mole/emu [16] (in analogy with the NMR hyperfine constant). We neglect the anisotropy of $^{\mathrm{Gd}}A$, since a comparison of the anisotropy of the shifts in the normal state $YBa_2Cu_3O_7$ [14] and antiferromagnetic $YBa_2Cu_3O_6$ [15] shows that the anisotropy of the product $^{\mathrm{Gd}}A\chi_s^{\alpha}$ is approximately 5%. $B_{\mathrm{dia}}^{\alpha}$ is the bulk demagnetizing field of the supercurrents in the crystallites. In this Letter we shall estimate the vortex contribution to χ_s^c at high magnetic fields from ΔB defined by $-\Delta B/B_0 = (^{\mathrm{Gd}}K^c - {}^{\mathrm{Gd}}K^{ab}) - (K_0^c - K_0^{ab}) = {}^{\mathrm{Gd}}A(\chi_s^c - \chi_s^{ab}) - (B_{\mathrm{dia}}^c - B_{\mathrm{dia}}^{ab})/B_0$ [see Eq. (2)]. Here $^{\mathrm{Gd}}K^{\alpha}$ is measured directly [Eq. (1)], and $K_0^c - K_0^{ab}$ is determined from the high field data at high temperatures. Unlike the ^{89}Y case, $B_{\mathrm{dia}}^{\alpha}$ is not prohibitively large since $^{\mathrm{Gd}}A$ is 10 times greater than the ^{89}Y hyperfine constant, ^{89}A.

The temperature independent ZFS parameters of the nearly pure S state $S = 7/2$ Gd^{3+} ion were obtained from the SX data. The ZFS of Gd^{3+} is smaller than the Zeeman splitting in the fields employed, and the spectrum consists of the seven allowed fine structure transitions, whose relative positions depend little on the ESR frequency but are sensitive to the orientation of the sample with respect to magnetic field. Spectra of single crystals were recorded in the temperature range 30–70 K. Figure 1(a) shows the 225 GHz spectra of an untwinned SX with magnetic field along the three crystalline axes at 40 K. The principal axes of the spin Hamiltonian of the Gd^{3+} in its orthorhombic environment coincide with the crystalline axes. At 40 K Gd^{3+} ESR lines are narrow and about the same width for all transitions showing that there are no strains or inhomogeneities in the high quality crystals. Although the small microwave penetration depth necessitates a few hours of averaging for each spectrum, the potential to use Gd^{3+} ESR in small single crystals is clear, e.g., to measure internal fields around impurity atoms. The use of resonant cavities renders conventional X-band ESR spectrometers unsuitable to study the superconducting state. Although there are several reports on Gd^{3+} ESR in perovskites, we do not know of any other report on the ESR of HTSC single crystals below T_c. Measuring the positions of the lines with magnetic fields in several orientations and at three frequencies allows us to fit the ZFS parameters of

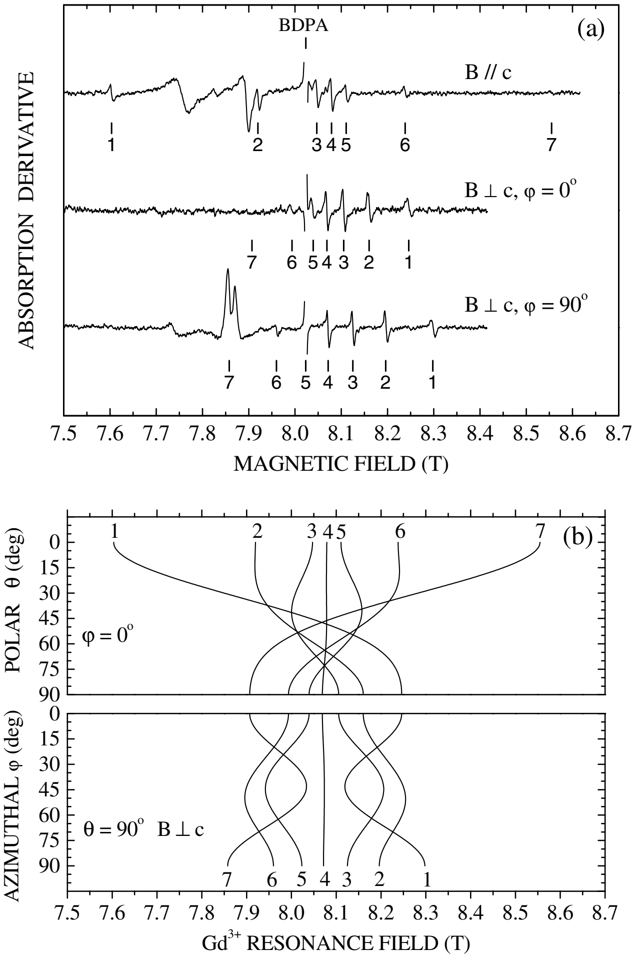

FIG. 1. (a) Gd^{3+} ESR spectra of a single crystal Gd:$YBa_2Cu_4O_8$ taken with magnetic field along the three crystalline axes at $T = 40$ K and $f = 225$ GHz. Neither twinning nor mosaicity is observed. The field reference BDPA is cut out for clarity. Numbers $1, \ldots, 7$ denote transitions $|-7/2\rangle \rightarrow |-5/2\rangle, \ldots, |+5/2\rangle \rightarrow |+7/2\rangle$, respectively. Bars (|) show simulated line positions. We do not know whether $\varphi = 0°$ belongs to $B \parallel a$ or b. (b) Positions of the lines calculated from the spin Hamiltonian of Gd^{3+} as a function of magnetic field orientation at 225 GHz.

Gd^{3+} [17]. Details of the spin Hamiltonian in a similar compound, $YBa_2Cu_3O_{6+x}$, were published elsewhere [15]. The spin Hamiltonian describes the SX spectra well; the difference between the calculated and measured line positions is always less than the linewidth. The simulated line positions as a function of orientation used for evaluating the OP spectra are indicated in Fig. 1(b).

Once the ZFS parameters are obtained from the SX, the Gd^{3+} shifts, ${}^{\mathrm{Gd}}K^{\alpha}(B,T)$, may be deduced with high accuracy from the OP spectra. To obtain the increase of χ_s^c with magnetic field we use ${}^{\mathrm{Gd}}K^{\alpha}$ measured at several T and B in both $\alpha = c$ and ab directions as shown in Fig. 2. These data are uncorrected for reversible diamagnetic fields, while a small irreversibility in $B_{\mathrm{dia}}^{\alpha}$ at low T and low B is eliminated by averaging ${}^{\mathrm{Gd}}K^{\alpha}$ of spectra taken with field swept up and down at the same temperature [16]. At low T and high B the central lines fade away, and we could therefore measure the shift in 15.4 T reliably only above 15 K. The dependence of the normalized shift on the resonance frequency (Fig. 2) is in a large part caused by diamagnetic shielding. However, as shown below, in the c direction at high fields there is also some contribution from the vortex spin susceptibility.

We assume that only χ_s^c has a measurable field dependence at the fields employed, and that of χ_s^{ab} may be neglected. This is consistent with our main result below that

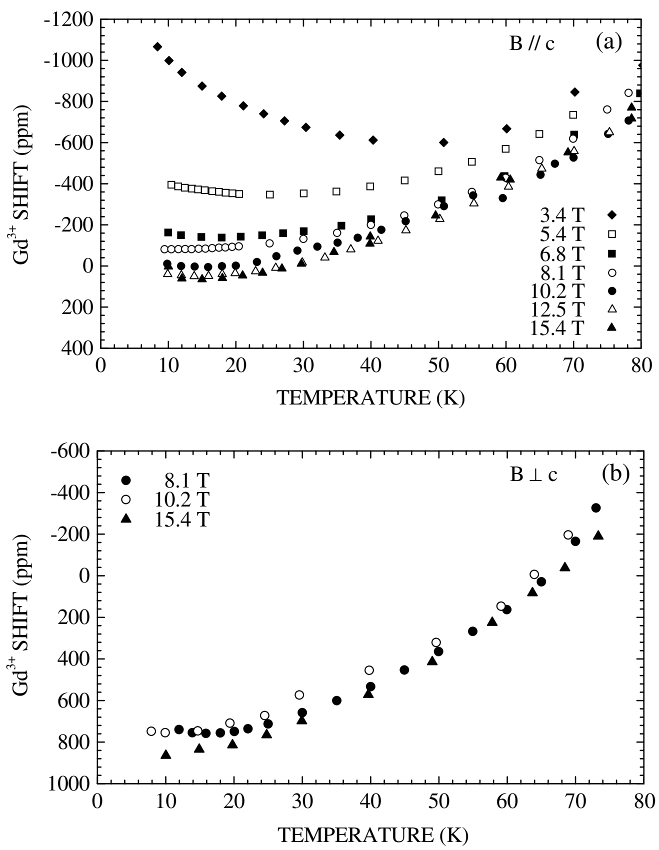

FIG. 2. Normalized Gd^{3+} ESR shifts, ${}^{\mathrm{Gd}}K^{\alpha}(B,T)$, in the OP sample as a function of temperature at several magnetic fields. (a) $\alpha = c$, (b) $\alpha = ab$.

the field dependence of χ_s^c is weak, since even if there is some field dependence of χ_s^{ab}, it is significantly smaller than that of χ_s^c, because of the much higher $H_{c2}^{(ab)}$. Diamagnetic corrections to B_m^{ab} are also smaller than to B_m^c as $\lambda_c \gg \lambda_{ab}$ holds for the penetration depths. The measured field dependence of ${}^{\mathrm{Gd}}K^{ab}$ is weak [Fig. 2(b)], and at 15.4 T we neglect the diamagnetic correction. At 15.4 T the raw ab data are already a good approximation of the spin susceptibility. Indeed, the shift at 15.4 T decreases with temperature at low T and the slope is close to that expected for a pure d-wave superconductor. In the weak coupling limit the low temperature slope of the susceptibility of a d-wave superconductor with $T_c = 80$ K corresponds to a ${}^{\mathrm{Gd}}K$ shift of 10 ppm/K [16].

Diamagnetic corrections are not negligible for lower fields and in the c direction, and we estimate the field dependence of B_{dia}^c from classical expressions and recent numerical results [18–22]. Above the vortex lattice melting temperature the magnetic field inhomogeneity due to vortices is motionally averaged and B_{dia}^c equals the bulk demagnetization, which is roughly proportional to $\ln(H_{c2}/B)$ [18–20]. Therefore one expects a 15%–30% reduction in B_{dia}^c from 8 to 15 T. Our bulk susceptibility measurements on the OP sample agree with such a reduction. A shift, $\Delta B_{\mathrm{saddle}}$, in addition to demagnetization appears when the vortex lattice freezes, because the magnetic field distribution is asymmetric and peaked at the saddle point, which is different from the average field. If the superconducting coherence length, ξ_{ab} is negligibly small, $\Delta B_{\mathrm{saddle}}^{(0)} \approx 0.037\Phi_0/\lambda_{ab}^2 \approx 3$ mT in a triangular vortex lattice with $\lambda_{ab} = 160$ nm [21]. However, numerical studies show [20,22] that already in fields where the distance between vortices is much larger than ξ_{ab}, $\Delta B_{\mathrm{saddle}}$ is reduced significantly. Corti *et al.* [23] found a 3 mT field distribution due to vortices in a $YBa_2Cu_4O_8$ aligned powder for $B \parallel c$ at 9.4 T below 10 K, and the corresponding shift is expected to be a fraction of this value.

Now we estimate the increase of χ_s^c at $B = 15.4$ T and $T = 16$ K, the lowest temperature where experimental uncertainties are small at all fields. Figure 3 shows $\Delta B = -({}^{\mathrm{Gd}}K^c - {}^{\mathrm{Gd}}K^{ab})B_0 + (K_0^c - K_0^{ab})B_0$, the anisotropy of the shifts as a function of field. In ΔB the anisotropy of K_0^{α} is taken into account but ΔB is uncorrected for reversible diamagnetic effects. The anisotropy of the "chemical shift" $K_0^c - K_0^{ab} = -500 \pm 70$ ppm was measured from the $B_0 = 15.4$ T data at $0.9T_c$. Above this temperature a Korringa-like relaxational broadening of the Gd^{3+} lines reduces precision. This value of $K_0^c - K_0^{ab}$ is consistent with what is found in the $YBa_2Cu_3O_{6+x}$ family [14,15]. Figure 3 shows that there is a small field dependent contribution to $\chi_s^c(B_0,T) - \chi_s^{ab}(B_0,T) = -[\Delta B - B_{\mathrm{dia}}^c(B_0,T)]/{}^{\mathrm{Gd}}AB_0$. ΔB varies little with field, at higher fields it is constant or increases slightly. In Fig. 3 we illustrate the variation of the reversible diamagnetic shift using $M_{\mathrm{dia}}(B) = M_{\mathrm{dia},0}\ln(H_{c2}/B)$, assuming $H_{c2} = 100$ T and that the field dependence of χ_s^c is

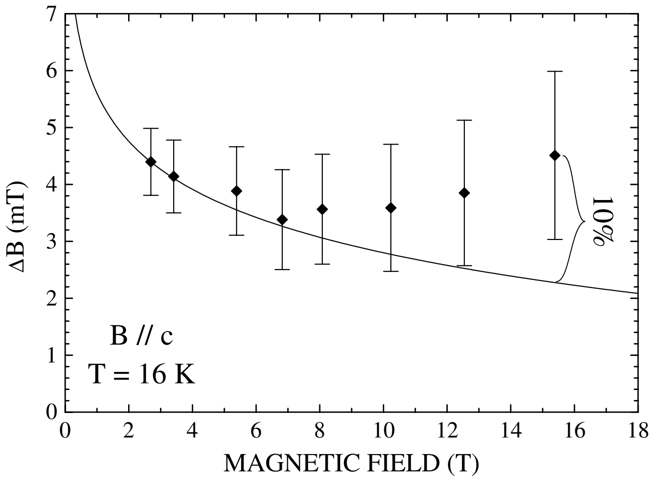

FIG. 3. Field dependence of the spin susceptibility and the diamagnetic correction at 16 K in absolute field scale. The solid line is a rough estimate of $B_{\mathrm{dia}}(B, 16\ \mathrm{K})$ (see text). The error bars represent the *maximum* error in the measurement. Most of the error is caused by the uncertainty in $K_0^c - K_0^{ab}$; therefore it will be strongly correlated between experimental points. The brace shows 10% of the Gd^{3+} shift measured in 15.4 T at T_c.

negligible below 3 T; i.e., we slightly overestimate B_{dia}. At 15.4 T the shift anisotropy is $\Delta B = 4.5 \pm 1.5$ mT, while $M_{\mathrm{dia}} \approx 2.3$ mT. As seen in Fig. 3, the vortex contribution to $\chi_s^c(B_0 = 15.4\ \mathrm{T}, T = 16\ \mathrm{K})$ is of the order of 10% of the normal state spin susceptibility at T_c.

According to the semiclassical scaling relations for the spin susceptibility derived by Kopnin and Volovik [4], and the more sophisticated study of Ichioka *et al.* [5], in a d-wave superconductor $\chi_s \propto (B/H_{c2})^\gamma$ with $\gamma = 0.4$ in the low temperature regime, and $\gamma \approx 1$ in the low field regime. We are close to the crossover [24], $15.4\ \mathrm{T}/H_{c2} \approx 16\ \mathrm{K}/T_c$, but whatever γ is in our case, the 10% enhancement implies that the spin susceptibility of the underdoped $YBa_2Cu_4O_8$ below T_c is restored to $\chi_s(T_c)$ at maximum in a magnetic field of H_{c2}. Thus the pseudogap is little affected by magnetic fields that suppress superconductivity. Nowadays the most popular approach to explain the microscopic origin of the pseudogap is that it is associated with superconducting fluctuations above T_c [25]. In a naive picture, in which the normal state spin gap were due to incoherent Cooper pairs, breaking of the pairs by a magnetic field would restore the spin susceptibility to the value measured at $T \gg T_c$, which is approximately 3 times as much as $\chi_s(T_c)$. Our result differs from that of Zheng *et al.* [13] since they find an enhancement of the spin susceptibility with B *in the* (a, b) plane of similar magnitude as we do for $B \parallel c$.

In conclusion, we found that at $T \ll T_c$ an applied field of $\approx 0.15 H_{c2}$ enhanced the spin susceptibility of the underdoped $YBa_2Cu_4O_8$ by only $\approx$3% ($\approx$10%) of its normal state susceptibility measured at room temperature (at T_c). This suggests that even an applied field of H_{c2} would not destroy the pseudogap.

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