# Linear Low Temperature Spin Susceptibility in the Underdoped High $T_c$ Superconductor, Gd:$YBa_2Cu_4O_8$

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(Received 5 November 1996; revised manuscript received 12 May 1997)

The uniform spin susceptibility, $\chi_s$, is determined from the $Gd^{3+}$ high frequency ESR Knight shift in the underdoped high temperature superconductor, Gd:$YBa_2Cu_4O_8$ ($T_c = 82$ K) between 8 to 260 K. Measurements at two fields (5.4 and 8.1 T) permit high precision at low temperatures. In the range of $0.1T_c$ to $0.4T_c$, a linear temperature dependence of $\chi_s$ is observed with a large slope. The corresponding maximum $d$-wave superconducting gap is $\Delta_0 = 190$ K, 1.1 times the weakly coupled $d$-wave limit. The results support suggestions that the normal state gap observed below 180 K and the superconducting gap below $T_c$ have nodes with the same symmetry. [S0031-9007(97)04224-5]

PACS numbers: 74.25.Nf, 74.25.Ha, 74.72.Bk

Recently there is growing evidence for $d$-wave symmetry pairing [1,2] in high temperature superconductors. The characteristic nodes in the superconducting gap lead to a linear energy dependence of the density of states of normal excitations near the Fermi energy at zero temperature. The first clear indications for $d$-wave pairing came from the linear temperature dependence at low $T$ of the London penetration depth [3] and NMR Knight shift [4] in high purity $YBa_2Cu_3O_7$. Recently the $d$-wave symmetry has been confirmed by tunnel-junction interferometry [5] and Raman scattering [6]. One of the most intriguing open questions is the link between the anomalous normal state and superconducting state properties. The "underdoped" high $T_c$ superconductor, $YBa_2Cu_4O_8$, studied in this paper has rather different normal state properties to "optimally doped" systems like $YBa_2Cu_3O_7$. Normal state transport [7], magnetic susceptibility [8], and specific heat [9] measurements show that the density of states near the Fermi energy of both spin and charge excitations is already strongly reduced in underdoped systems at temperatures well above $T_c$. In optimally doped systems above $T_c$ there is no such anomaly in the density of states. One of the favored ideas is that strong antiferromagnetic spin fluctuations in the underdoped systems [10] lead to a gap or a pseudogap in the density of states. Recent angle resolved photoemission studies [11] suggest that the symmetry of the normal state pseudogap in underdoped materials has the same "$d$-wave" character as the superconducting gap. A similar suggestion has been made earlier from the analysis of specific heat and magnetic susceptibility [12]. In this paper we provide experimental support for this idea by showing that in a well-ordered underdoped system the density of states has a linear energy dependence well below $T_c$ with a slope which is comparable to that measured for optimally doped systems with no normal state pseudogap. This can only happen if the normal state gap is anisotropic with nodes at similar positions to those of the superconducting gap.

We present high precision spin susceptibility data at the rare earth site of Gd doped $YBa_2Cu_4O_8$ deduced from the high frequency $Gd^{3+}$ ESR Knight shift [13]. $Gd^{3+}$ ESR Knight shift complements $^{65}$Cu [8] and $^{17}$O [14] NMR Knight shift measurements. (Hyperfine fields are too small to measure the $^{89}$Y NMR Knight shift reliably below $T_c$.) The simple $Gd^{3+}$ ESR spectrum permits a much higher precision at low temperatures than NMR, and by combining data at two magnetic fields we can correct for diamagnetic screening in the superconducting phase. We find a linear temperature dependence of the spin susceptibility from about $0.4T_c$ to $0.1T_c$, the lowest temperatures of the present study. The magnitude of the spin susceptibility and the slope of its temperature dependence are significantly larger than previous estimates [15] based on the $^{65}$Cu Knight shift [8].

The $YBa_2Cu_4O_8$ powder sample with 1% Y substituted by Gd was magnetically aligned in epoxy resin along the $c$ axis. $Gd^{3+}$ ESR was measured at frequencies, $\omega/2\pi$ of 75.0, 150.0, and 225.0 GHz (fields centered around $H =$ 2.7, 5.4, and 8.1 T, respectively) with magnetic field along the $c$ axis. Results are consistent with previous 245 GHz data [16] on the same sample. The frequency of the Gunn diode mm wave source is stabilized to a quartz oscillator with a precision of $10^{-6}$. The absorption derivative with a small admixture of dispersion is observed for the mm-wave radiation transmitted through an 8 mm diameter sample fitted into an oversized waveguide. No resonant cavity is used, and there is no "vortex noise" which usually inhibits ESR studies below $T_c$ in conventional spectrometers.

In Gd doped $YBa_2Cu_3O_{6+x}$ and $YBa_2Cu_4O_8$ the ESR Knight shift arises from the weak exchange interaction of electrons in the $CuO_2$ layers with the localized $Gd^{3+}$ ion. The same interaction broadens the lines through spin lattice relaxation [17]. The $Gd^{3+}$ shift has the same temperature dependence as the $^{89}$Y NMR Knight shift in the temperature range where both can be measured [16].

 

The coupling constant is 10 times larger for $Gd^{3+}$ than for $^{89}Y$, and this allows the measurements to be extended to low temperatures. $Gd^{3+}$ is a nearly $S$ state $J = \frac{7}{2}$ ion. At the high frequencies used, the spectrum consists of seven fine structure lines: the central $-\frac{1}{2} \rightarrow +\frac{1}{2}$ transition and six satellite lines which are well resolved at low temperatures. Crystal fields are weak compared to the Zeeman energy and are negligible for the central line. Figure 1 shows the central line and the nearest fine structure transitions at 30 K. These lines were fitted to Lorentzian absorption derivatives with a small admixture of dispersion derivatives in order to determine the position of the central line. (The small admixture of dispersion arises from interference of rf fields transmitted through the sample along different paths and from eddy current shielding.) The line position is at the maximum of the absorption. At higher temperatures the Korringa spin lattice relaxation broadens the lines, the first satellites gradually merge with the central line, and a fit to a single line was performed above 70 K. The asymmetry due to the small distribution in crystalline alignment is negligible for the $\frac{3}{2}$-$\frac{1}{2}$ satellite ESR lines and zero for the central line. The correction for shifts due to demagnetization effects and magnetic field inhomogeneity in the superconducting state was taken into account by the analysis (see below). The uniform spin susceptibility, $\chi_s$, is obtained from the shift, ${}^{Gd}K = -(H_r - H_0)/H_0$ of the central $Gd^{3+}$ ESR resonance field $H_r$,

$$\chi_s = [{}^{Gd}K(T) - {}^{Gd}K(0)]/{}^{Gd}A\,.$$

As in previous work [10,15] the relative shift data ${}^{Gd}K(T)$ are presented with respect to $H_0 = \omega/\gamma_0$ with $g_0 = \gamma_0 h/(2\pi\mu_B) = 1.9901$. A free radical reference (BDPA with $g = 2.003\,59$) was used to calibrate fields. The effective "hyperfine constant" ${}^{Gd}A$ is proportional to the exchange interaction between itinerant electrons and localized $Gd^{3+}$ moments. A comparison [13,16] of $Gd^{3+}$ ESR with $^{89}Y$ NMR shows that ${}^{Gd}A$ is the same for Gd:$YBa_2Cu_3O_{6+x}$ for all values of $x$ and for Gd:$YBa_2Cu_4O_8$. We find ${}^{Gd}A = -15$ (emu/mole)$^{-1}$ from the static susceptibility [12] of $YBa_2Cu_3O_7$ ($2.7 \times 10^{-4}$ emu/mole) and the $Gd^{3+}$ Knight shift [13] of Gd:$YBa_2Cu_3O_7$ (4050 ppm) in the normal state. To obtain ${}^{Gd}A$, the core and Van Vleck contribution to the static susceptibility was estimated [12] to be $-0.4 \times 10^{-4}$ emu/mole, and we used ${}^{Gd}K(0) = 620$ ppm which is the value obtained in the present measurements after making corrections for demagnetizing effects.

The $Gd^{3+}$ shift (Fig. 2) shows the same temperature dependence at high temperatures as reported for $^{17}O(2,3)$ [14], $^{65}Cu(2)$ [8], and $^{89}Y$ [16]. Below $T_c$ the raw shift data depend on the resonance frequency (Fig. 2) and to obtain the Knight shift, the applied magnetic field, $H_a$, has to be corrected for the reversible macroscopic demagnetization ($M_{rev}$) and for a shift related to the vortex structure ($H_v$). Thus the magnetic field at the maximum of the resonance is $H_r = H_a - aM_{rev} - H_v$ with $a = 8\pi/3$ for a spherically shaped particle. It is evident from the differences between raw shift data at the three frequencies that such corrections are substantial.

Below the irreversibility line, superconducting vortices are pinned, and their distribution is inhomogeneous and magnetic field history dependent. At low temperatures the lines broaden and have a magnetic field history dependent shift. Only unimportant changes of the line shape are observed for temperatures above 8 K at 150 and

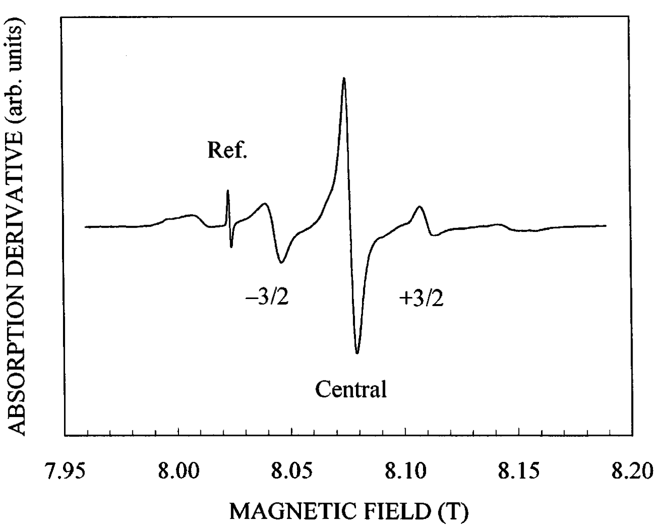


FIG. 1. Central line and first nearest satellites of $Gd^{3+}$ ESR spectrum of Gd:$YBa_2Cu_4O_8$ at $T = 30$ K. The spin susceptibility is derived from the shift of the central line with respect to the free radical reference. The unmarked outer lines are due to an unknown minority phase.

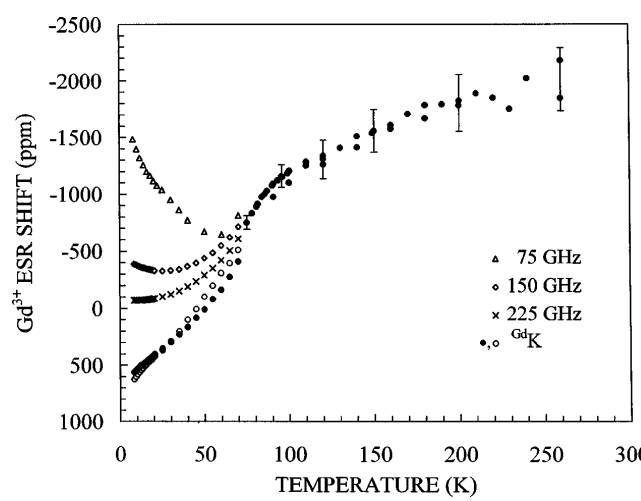


FIG. 2. Solid circles: Corrected $Gd^{3+}$ ESR Knight shift data which are proportional to the uniform susceptibility at the rare earth site in Gd:$YBa_2Cu_4O_8$. Diamagnetic shielding corrections below $T_c$ are derived from the raw data at 150 GHz (diamonds) and 225 GHz (crosses) at fields of 5.4 and 8.1 T, respectively. The temperature dependence of the shift at 75 GHz (triangles) and 2.7 T is dominated by shielding current effects, but combination with 225 GHz data yields roughly the same susceptibility (open circles). Error bars (below 50 K, size of the symbols) show $\pm 10\%$ of the linewidth.

225 GHz. The broadening is small (0.3 and 0.1 mT at 150 and 225 GHz, respectively) compared to the linewidth (3.5 mT), and the inhomogeneity of the field does not affect the results appreciably. We eliminated the shifts due to the irreversible magnetization by averaging data recorded with increasing and decreasing applied magnetic fields. The sweep direction dependent shift is small; at 225 GHz it is noticeable below 20 K only, and its largest value is $\pm 0.4$ mT ($\pm 50$ ppm) at 8 K. We tested that results do not depend on magnetic field sweep rate.

The remaining corrections increase with decreasing temperature but are only weakly dependent on the applied field in the range of our measurements. If corrections for the reversible part are independent of field, as discussed below, the corrected shift is ${}^{\mathrm{Gd}}K = \gamma_0[H_a(\omega_1) - H_a(\omega_2)]/(\omega_2 - \omega_1) + 1$ where $H_a(\omega_1)$ and $H_a(\omega_2)$ are the applied fields at resonance for frequencies $\omega_1$ and $\omega_2$. Figure 2 shows data from a combination of results at $\omega_1/2\pi =$ 225 GHz and $\omega_2/2\pi = 150$ GHz where we assume that the corrections to $H_a$ are independent of field between 5.4 and 8.1 T. Similar results are found from a combination of the 225 GHz data with the less precise 75 GHz data.

We believe that the field dependence of the corrections to ${}^{\mathrm{Gd}}K$ is indeed small for the following reasons. The main contribution to $H_v$ is independent of field and proportional to $1/\lambda^2$ where $\lambda$ is the London penetration depth. Only a small field dependence is expected due to vortex fluctuations [18]. For fields well above the lower critical field $H_{c1}$, $M_{\mathrm{rev}}$ is proportional [19] to $\ln(H_{c2}/H)$ and is expected to decrease only about 12% between 5.4 and 8.1 T if we estimate $H_{c2} = 100$ T for the upper critical field. Our own macroscopic magnetization measurements on the same samples confirm that $M_{\mathrm{rev}}$ is nearly field independent in the range of interest. We measured the magnetization parallel and perpendicular to the $c$ axis, $M_{\mathrm{rev}\parallel}$ and $M_{\mathrm{rev}\perp}$, respectively, with a vibrating sample magnetometer under the same conditions as used for the ESR study. Contributions to the magnetization from $Gd^{3+}$ ions and the small amount of impurity phase make the corrections to ${}^{\mathrm{Gd}}K$ derived directly from these data unreliable. However, the difference $\Delta M = M_{\mathrm{rev}\parallel} - M_{\mathrm{rev}\perp}$ which does not contain these unknown isotropic terms changes by less than 10% between 5.4 and 8.1 T, and this again supports the assumption of a field independent correction.

This analysis neglects the possibility of a magnetic field dependent density of states at the Fermi level. The corresponding shift for a $d$-wave superconductor [20] at zero temperature is of the order of ${}^{\mathrm{Gd}}A\chi_n(H/H_{c2})^{1/2}$ where $\chi_n$ is the normal state susceptibility. Depending on the values of $\chi_n$ and $H_{c2}$ this may or may not be significant at 8.1 T and low temperatures. The normal state gap or pseudogap is probably not affected by the magnetic field and $\chi_n$ may be small. Data at a third, larger field are needed to measure the field dependence of the density of states.

A linear low temperature dependence of the spin susceptibility extending to $0.1T_c$ is the main result of the present study. $\chi_s$ measures the density of states within a few kT from the Fermi surface. Thus $n(E)$ is energy dependent on the scale of 1 meV, and this is a strong support for $d$-wave pairing for which the gap function has nodes. While our results make a simple $s$-wave pairing with an anisotropic gap rather unlikely, they do not exclude a mixed $s$-wave and $d$-wave state.

For a $d$-wave superconductor the low $T$ slope of the spin susceptibility is $a_{\mathrm{spin}} = [\chi_s(T)/\chi_s(T_c)]/(T/T_c) = (\ln 4)kT_c/\Delta_0$. We find from Fig. 3 a linear dependence below $0.4T_c$ with $a_{\mathrm{spin}} = 0.59$, and this gives $\Delta_0 = 2.3kT_c$ which is only a factor $\alpha = 1.1$ larger than $2.1kT_c$ expected from the weak $d$-wave limit. We have no susceptibility data of comparable quality for optimally doped systems. However, in a first approximation, the slope of the quasiparticle fraction in the low temperature limit measured by the magnetic penetration depth, $a_\lambda = 2\Delta\lambda(T)/\lambda_0/(T/T_c)$ has the same value as $a_{\mathrm{spin}}$. From the $(a, b)$ plane penetration depth data of Hardy *et al.* [3] on optimally doped $YBa_2Cu_3O_7$ single crystals, $a_\lambda = 0.54$ if the value of $\lambda_0 = 150$ nm is assumed [3,21]. The similarity of $a_{\mathrm{spin}}$ in the underdoped $YBa_2Cu_4O_8$ system to $a_\lambda$ in optimally doped $YBa_2Cu_3O_7$ implies that the low energy quasiparticle excitations in the superconducting state of $YBa_2Cu_4O_8$ are not much influenced by the presence of the pseudogap at high temperatures.

Penetration depth measurements on underdoped thin films usually show power law dependences typical of a finite density of states at the Fermi surface [22] which in a $d$-wave superconductor may arise from relatively small structural disorder. Our data end at $0.1T_c$, and we cannot exclude a power law dependence with an exponent greater than 1 at lower temperatures. $YBa_2Cu_4O_8$ is an underdoped system but unlike oxygen deficient $YBa_2Cu_3O_{6+x}$, it has no disorder in the structure. The large value of the slope indicates that the linear dependence is intrinsic

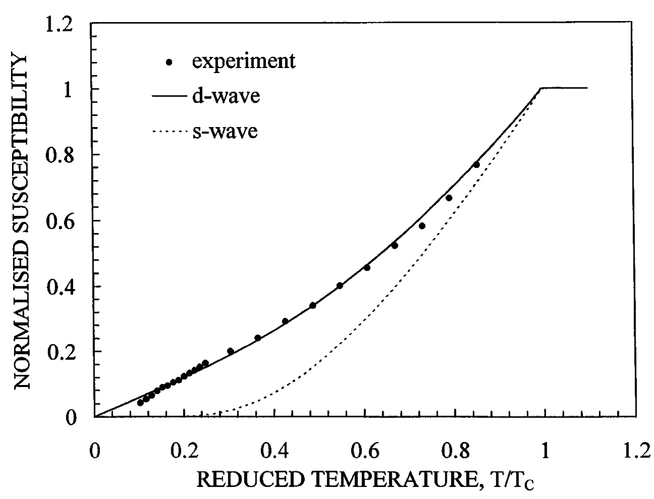


FIG. 3. Normalized spin susceptibility versus reduced temperature. Note the linear temperature dependence at low temperatures. Solid line: Fit to a $d$-wave coupling model with maximum gap $\Delta_0 = 2.3kT_c$. Light dashed line: $s$-wave weak coupling Yoshida function.

and that there is a node in the gap function of underdoped systems.

In Fig. 3 we compare our low temperature data with the curves expected for (a) an isotropic weakly coupled *s*-wave superconductor (Yoshida function), (b) best fit to a *d*-wave superconductor with $\alpha = 1.1$, i.e., with a gap slightly larger than expected for the weak coupling limit. For the *d*-wave case we use a gap function of $\Delta = \Delta_0 \cos 2\phi$ appropriate for a system with a two-dimensional band structure. For the temperature dependence of $\Delta_0$ in the *d*-wave weak coupling limit we numerically solved the gap equation following Won and Maki [23]. For the strong coupling case we use the usual approximation of "scaling" the ratio of $\Delta_0/kT_c$ and the weak coupling solution of $\Delta(T)$ for the temperature dependence of the density of states. Clearly, only the *d*-wave superconductor gives a reasonable fit.

Pines and Wrobel [15] analyzed the uncorrected $YBa_2Cu_4O_8$ $^{65}$Cu Knight shift data of Bankay *et al.* [8] in terms of a nearly antiferromagnetic Fermi liquid and suggested that below $T_c$ the data can be fitted to the theoretical expression for a strongly coupled *d*-wave superconductor. After correction our data differ significantly from the uncorrected values of Bankay *et al.*, but their analysis remains qualitatively correct since we find larger values for both $\chi(T)$ and $\chi(T_c)$ and so the normalized susceptibility is not changed much. We find $\chi(T_c)/\chi_0 = 0.33$ for the decrease of the susceptibility between temperatures much larger than the normal state gap and $T_c$. Here we assumed that $\chi_0$, the high temperature limit for the susceptibility of $YBa_2Cu_4O_8$, is equal to the normal state susceptibility of optimally doped $YBa_2Cu_3O_7$. The larger value of $\chi(T_c)$ derived in the present work may mean that $YBa_2Cu_4O_8$ is closer to optimum doping than previously supposed.

The calculated curves of Fig. 3 assume an energy independent normal state density of states. The large change in slope of $\chi_s(T)$ at $T_c$ (Fig. 2) implies that at the superconducting transition the density of states abruptly decreases in an energy range of the order of $kT_c$ about the Fermi level. However, an energy independent density of states above $T_c$ cannot account for the anomalous temperature dependence of transport properties and spin susceptibility in $YBa_2Cu_4O_8$. A gap in the normal excitation spectrum with a value of $E_g = 180$ K has been used to describe the Knight shift [8,16] of $YBa_2Cu_4O_8$, and similar values were deduced [7] from transport measurements. In these earlier works a normal state gap with a finite energy width or a pseudogap with a finite density of states in all directions (i.e., without nodes) was assumed. Such assumptions are, however, contrary to our findings. If the gap had no density of states in a finite energy range, then the susceptibility would be temperature independent for temperatures much less than the gap. Instead, we find a temperature dependence which extends to at least $T = 8$ K. Our observation of a linear low temperature dependence of the spin susceptibility in a system with both a normal state and a superconducting gap implies that these have the same *d*-wave symmetry. This result is in agreement with a recent ARPES study [11] of underdoped $Bi_2Sr_2CaCu_2O_{8+d}$.

This work was supported by the Hungarian state Grant No. OTKA T 015984 and the CEE Human Capital and Mobility Associated Contract No. ERBCIPDCT940014. We are indebted to J. W. Loram, J. R. Cooper, and J. L. Tallon for illuminating discussions and J. R. Cooper for magnetization measurements. One of us (A. J.) acknowledges the IRCS University of Cambridge, U.K., for hospitality during several short visits. We are indebted to R. Combescot for information on the calculation of $\Delta(T)$.

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