Conduction-electron spin resonance in the superconductor K_3C_{60}

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The conduction-electron spin resonance of the superconducting fulleride compound, K_3C_{60} ($T_c=19$ K) has been observed between 2.5 and 800 K at several frequencies from 9 to 225 GHz. Between T_c and $0.7T_c$ the spin lifetime of normal excitations increases as predicted by the theory of Yafet for scattering from nonmagnetic structural defects. At lower temperatures the CESR arises from states bound to vortices; here the spectrum is inhomogeneously broadened and an anomalous g shift is found. The anomalous temperature dependence of the g factor and linewidth in the normal state reported by Petit *et al.* is most important between 50 and 250 K, suggesting that these are related to the rotation of C_{60} ions.

The possibility of observing conduction-electron spin resonance (CESR) in the superconducting state was discussed by Kaplan[1] and de Gennes[2] in the mid-sixties, but the field remains largely unexplored. In the normal state, the homogeneous CESR linewidth is proportional to the spin relaxation rate T_1^{-1}, the CESR intensity is proportional to the static spin susceptibility, and the resonance field depends on the average g factor of electronic states at the Fermi energy. All of these may have interesting temperature (T) and magnetic field (H) dependences below T_c. In particular, T_1 in metals with no magnetic impurities is determined by spin-orbit scattering from defects and phonons, and is proportional to the momentum relaxation time, τ. The momentum relaxation of normal excitations in the superconducting state is not easy to measure by other methods.

CESR is most promising in the mixed state of type II superconductors. At finite H, states bound to vortices contribute along with quasiparticle excitations over the gap, and the resonance should persist to $T=0$. Maki[3] discussed the spin relaxation in gapless superconductors at finite H, while Yafet[4] considered the $H=0$ limit of a pure system. Coherence effects influence the spin relaxation of conduction electrons. Magnetic impurities increase $T_1^{-1}(T)$ just below T_c, similar to the Hebel-Slichter peak in NMR. On the other hand, spin relaxation of normal excitations over the gap, due to spin-orbit scattering on non-magnetic impurities, decreases monotonically to zero between T_c and $T=0$. Intuitively, at finite H and low T, T_1^{-1} will not differ much from its normal state value. In materials with large coherence length ξ, and thus a vortex core with large diameter, the density of quasiparticle states within the core is close to that of a cylinder with radius ξ in the normal state[5]. In this picture, the CESR intensity at $T=0$ and finite H is proportional to H/H_{c2} (H_{c2} is the upper critical field), and the relaxation rate is about equal to its normal state value.

There are only a few and rather contradictory CESR results below T_c. The difficulty is not related to the inhomogeneity of H. In contrast to NMR or ESR of localized moments embedded in a superconductor, field inhomogeneity caused by the vortex lattice does not broaden the line significantly if the vortex density is uniform. Rapid diffusion of electrons motionally narrows the field inhomogeneity in the mixed state since the spin diffusion length $\delta_{\mathrm{eff}}=1/3v_F\sqrt{T_1\tau}$ is usually much larger than the vortex separation (v_F is the Fermi velocity). In most superconductors spin relaxation is very fast and the CESR is broadened beyond observability. Below we summarize the few exceptions known to us.

Vier and Schultz[6] observed CESR of Nb foils below T_c using the transmission technique and analyzed their results in terms of BCS theory. An increase of the spin lifetime was found below T_c as predicted by Yafet,[4] and earlier by Maki[3] for spin-orbit scattering by normal impurities in gapless superconductors. An order of magnitude decrease of the intensity was observed below T_c, which was tentatively attributed to a decrease in the spin susceptibility. However, some puzzling questions remain. The resonance field 0.33 T was rather close to $H_{c2}=0.38$ T of the sample measured. Thus the comparison with Yafet's theory is questionable since it applies to spin relaxation of normal excitations in zero field, and states bound to vortices are not taken into account. The large decrease in resonance intensity below T_c is also difficult to understand; in a field close to H_{c2} the susceptibility associated with vortices is expected to approach that in the normal state.[7] In a second example, Graham and Silsbee[8] measured transmission ESR of Nb-coated Cu foils in a 0.3 T field. Above T_c Nb and Cu both contribute to spin relaxation since electrons freely diffuse through the Nb/Cu interface. Below T_c the contribution of Nb decreased considerably, and relaxation at low temperatures was about equal to that of bare Cu foils. These authors argued that the opening of the Nb gap inhibits diffusion through the interface such that electrons from the Cu metal cannot enter the Nb layer. A residual low temperature spin relaxation in Nb with H perpendicular to the layer was attributed to relaxation within vortices. Unfortunately H_{c2} of the thin Nb layer was not measured. The possibility of an increase in spin lifetime of the Nb layer below T_c was not considered. Finally, Delrieu *et al.*[9] reported CESR from the organic superconductor $(TMTSF)_2ClO_4$ below T_c. The rather unexpected properties were suggested to be related to the large anisotropy of the electronic structure.

In this paper we report the observation of CESR in the superconducting state of the fulleride metal K_3C_{60}. We find the increase of normal excitation spin relaxation time below T_c expected for spin orbit scattering from nonmagnetic impurities. We also find an anomalous change of the g factor below T_c. K_3C_{60} is a good candidate for testing theories of CESR in superconductors. It is a type II superconductor with a high T_c of 19 K. The amplitude coherence length is short, $\xi=3$-4 nm, and correspondingly H_{c2} is large, 25 T at $T=0$. As K_3C_{60} consists of light elements only, spin-orbit interactions are weak and the spin relaxation time is long, so the resonance is easily observed. The sensitivity of the material to oxygen and the inadvertent growth of other paramagnetic impurity phases during synthesis are the main experimental difficulties. It should be noted however that phase-pure powders of fulleride superconductors are routinely (if tediously) obtained.[10]

K_3C_{60} samples were prepared using several doping methods. Powder samples termed as powder 1, 2, and 3 were prepared by vapor-phase doping C_{60} and were tested for purity by x-ray diffraction. Samples termed as crystal 1 and 2 were prepared by vapor-phase doping C_{60} single crystals at about 550 C using metallic K and KN_3, respectively as the alkali vapor source. X-ray diffraction showed that these samples consisted of a few large crystallites, each with $\sim 4°$ mosaicity. Crystal 2 was later ground to powder and is called powder 4. Doping homogeneity was characterized by their superconducting shielding fractions; only samples with close to 100% shielding were used. About 1% paramagnetic impurities hampered the quantitative analysis of K_3C_{60} CESR in powder samples at low T. The starting C_{60} crystals were sublimed from high-purity powders, so the doped crystals showed only very weak impurity ESR lines. Powder samples were mixed into vacuum grease to separate the grains and to provide good heat contact. Crystal samples were sealed in quartz EPR tubes under partial argon/helium pressure. Microwave absorption may heat the metallic sample at low T, so the power dependence of the resonance was carefully checked. Temperature was measured with a carbon-glass resistive thermometer placed outside the waveguide. dc magnetization was measured in a conventional SQUID magnetometer in a 5.5 T superconducting magnet. A Bruker ESP 300E spectrometer (with an ER 4114 HT cavity for high temperatures) was used for measurements at 9.5 GHz. CESR in the superconducting state was measured at Budapest using frequencies of 75, 105.1, 150, and 225 GHz corresponding to magnetic fields (at $g=2$) of 2.7, 3.8, 5.4, and 8.0 T, respectively. We used a high frequency spectrometer equipped with quartz-stabilized mm-wave sources, and a 9 T superconducting magnet.

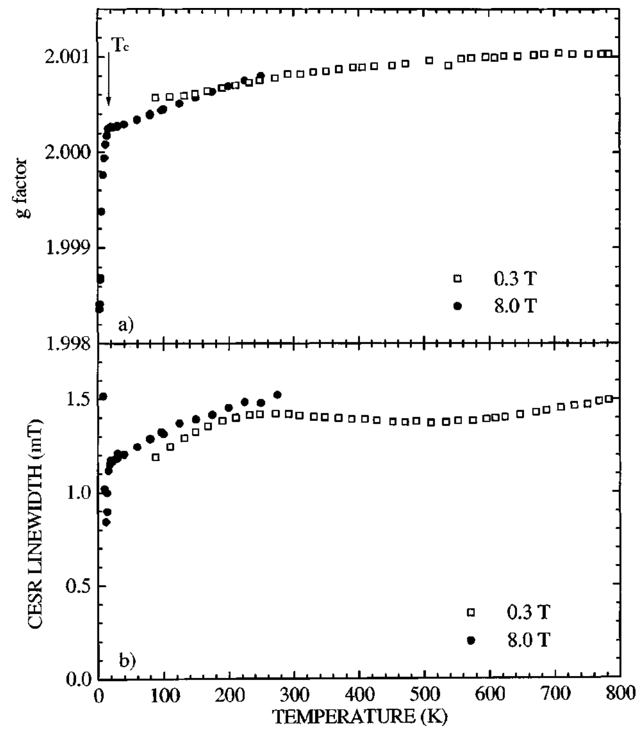

FIG. 1. Normal-state ESR properties of K_3C_{60}. (a) The g factor anomalously changes with temperature. (b) The linewidth measures the spin relaxation rate. Most of the changes are below 250 K (dots: 225 GHz; squares: 9 GHz).

In conventional 9 GHz spectrometers the so called ‘‘vortex noise’’ prevents observation of CESR in the superconducting state. Vortex noise is generated below the irreversibility line by the chaotic motion of vortices as H is swept. At high fields the irreversibility line shifts to lower T. In usual X-band spectrometers, vortex noise relative to the ESR signal is further enhanced by the use of resonant cavities. In our high frequency spectrometer no cavity was used.

Figure 1 shows the linewidth and g factor of K_3C_{60} sample powder 1 up to 800 K at 9 GHz and to 270 K at 225 GHz. At 9 GHz a small amount of paramagnetic impurity distorted the results below 100 K. At 225 GHz, impurity lines could be separately resolved at low T, and the g factor of K_3C_{60} was measured with high precision. Our g factors are measured with respect to a Mn/MgO standard with $g_{\mathrm{Mn}}=2.0009$. The Lorentzian linewidth (ΔH) was determined from fits to the measured spectrum which is a linear superposition of derivative absorption and dispersion. The linewidth in the normal state is independent of H, thus in the normal state there is no measurable g-factor anisotropy. This is a common feature in metals with cubic structures. The line shape is Lorentzian showing that it is lifetime broadened. The linewidth must be intrinsic since several samples showed the same T-dependent width. ΔH and the g factor are essentially T independent above 250 K. The g factor does not change between T_c and 50 K, then it increases up to about 250 K. This T dependence of the linewidth and g factor is anomalous, as first reported by Petit *et al.*[11] The usual phonon contributions to T_1^{-1} and $1/\tau$ in metals are proportional to each other, and increase monotonically with T while the g factor is constant. The observed T dependence of ΔH

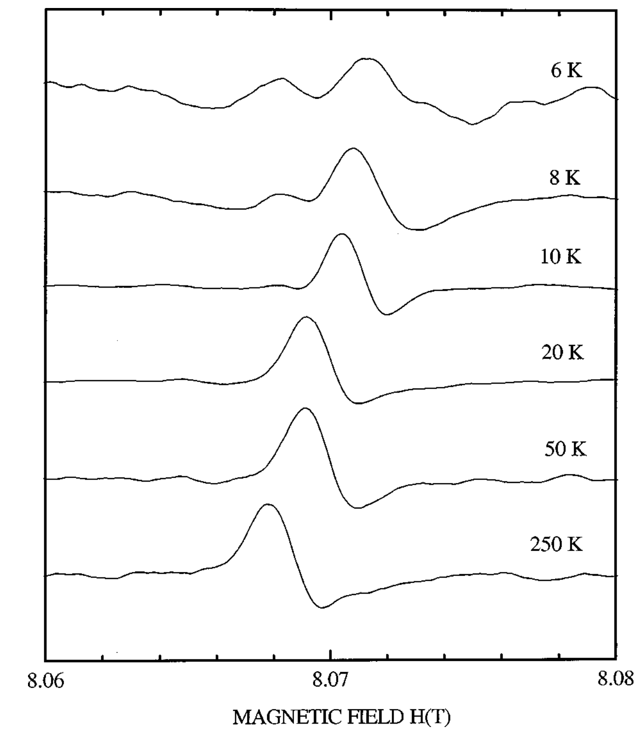

FIG. 2. Typical CESR spectra of a K_3C_{60} crystal at 225 GHz. In the normal state the resonance narrows and slowly shifts to higher fields with decreasing temperature. Below T_c the resonance progressively shifts to higher fields and has a minimum linewidth at 10 K. At 6 K chaotic motion of vortices increases noise.

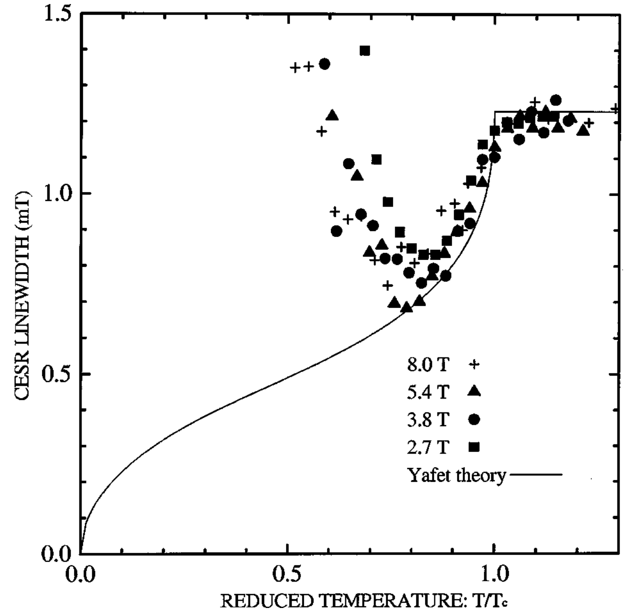

FIG. 3. CESR linewidth vs reduced temperature of K_3C_{60} at various magnetic fields in the superconducting state. The sharp decrease of the relaxation rate below T_c is field independent. Below 0.7 T_c the broadening is inhomogeneous. The solid line is the theoretical prediction of Yafet for scattering of normal excitations on nonmagnetic impurities.

and g factor may reflect changes in the electronic structure coupled to structural disorder which accompanies the gradual onset of molecular rotations.[12–14] The residual linewidth is most probably due to some well-defined structural disorder. Besides orientational disorder, K vacancies[10] are probably an efficient source of spin-orbit scattering.

T-dependent spectra of a high purity crystal (crystal 1) at 225 GHz are shown in Fig. 2. Below T_c the line shifts to higher H, and the width has a minimum at about 10 K. We could not measure the intensity quantitatively; however we did observe a sudden intensity decrease just below T_c without much further decrease below $T_c/2$. Above 10 K the line shapes are Lorentzian while at lower T they are inhomogeneously broadened. Linewidth versus reduced temperature T/T_c at various magnetic fields are summarized for this crystal in Fig. 3. The same features were observed in powder samples. $T_c(H)$ was determined to better than ± 0.5 K by the sudden decrease of linewidth and intensity at T_c. Our $T_c(H)$ data agree well with the linear relation $dH/dT_c = -2.1$ T/K found by Buntar *et al.*[15] In the crystal, vortex noise increases below 0.7–0.8 T_c and the data are somewhat dependent on field history. Spectra shown in Fig. 2 are taken after cooling in the applied field.

Figure 4 shows the shift data converted to g factor for several samples at 8 T. Screening currents reduce the local field, leading to an apparent shift of the resonance. The diamagnetic correction was estimated from dc magnetization. At fixed T the correction decreases, while the g-factor shift increases with increasing H. As discussed in Ref. 16, at 8 T the diamagnetic shift is a small correction to the g-factor shift. In powdered samples vortex noise did not appear and the shifted and broadened CESR was well observed at 2.5 K and 225 GHz. At this low T the resonance is clearly due to electrons bound to vortex cores. This g-factor shift is unexpected in the simple model where vortex cores are approximated as normal state metallic cylinders.

In Fig. 3 we compare linewidth data with the variation of T_1^{-1} calculated by Yafet (for relaxation on nonmagnetic impurities)[4] for a weak coupling s-wave superconductor in the zero magnetic field limit:

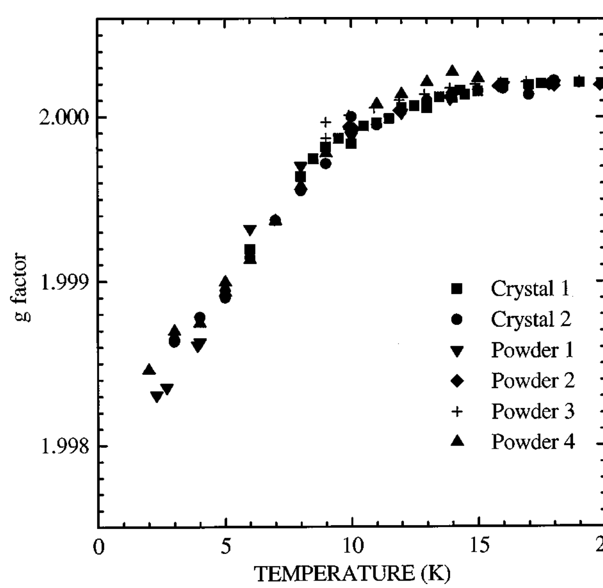

FIG. 4. Variation of the g factor below T_c of several powder and crystal K_3C_{60} samples measured at 225 GHz.

$$\frac{(1/T_1)_S}{(1/T_1)_N}=\frac{\int_{\Delta(T)}^{\infty}\left(\frac{\partial f(E_{\mathbf{k}})}{\partial E_{\mathbf{k}}}\right)dE_{\mathbf{k}}}{\int_{\Delta(T)}^{\infty}\frac{E_{\mathbf{k}}}{\sqrt{E_{\mathbf{k}}^2-\Delta(T)^2}}\left(\frac{\partial f(E_{\mathbf{k}})}{\partial E_{\mathbf{k}}}\right)dE_{\mathbf{k}}}. \quad (1)$$

$E_{\mathbf{k}}=\sqrt{\epsilon_{\mathbf{k}}^2+\Delta_{\mathbf{k}}^2}$, $f(\epsilon_{\mathbf{k}})=[\exp(\epsilon_{\mathbf{k}}/k_BT)+1]^{-1}$, where $\epsilon_{\mathbf{k}}$ is the spectrum of normal state excitations. The relaxation below T_c is proportional to the normal state relaxation rate, and the temperature variation depends only on the energy spectrum of quasiparticle excitations. For $\Delta(T)$ we used *s*-wave weak coupling BCS results in Eq. (1). The decrease of linewidth down to 0.7 T_c shows that this simple model is qualitatively correct. The inhomogeneous penetration of the static magnetic field into arbitrarily shaped crystallites is a plausible explanation for the inhomogeneous linewidth increase at lower *T*. The increase of ΔH below 0.7 T_c is stronger at lower applied fields where diamagnetic corrections are larger.

Magnetic impurities would increase relaxation below T_c, thus the observed decrease confirms that the relaxation is due to spin-orbit scattering from some structural disorder. Phonons are unlikely to be important at low *T*. The decrease of T_1^{-1} as a function of $t=T/T_c(H)$ is independent of *H*. This universal behavior is not expected to extend to fields comparable to $H_{c2}(T=0)$. The resonance is dominated by states in the vortex cores at all *T* when *H* is comparable to H_{c2} and Eq. (1) is not valid. Intuitively, at such high fields, no lifetime narrowing is expected if vortex cores behave as normal metal cylinders with a radius of ξ. The fields of the experiment correspond to $H/H_{c2}=0.1$-0.3 and $T_1^{-1}(t)$ is expected to display a minimum at the temperature where states bound to vortices become as important as normal excitations over the gap. A minimum is observed in the linewidth, but at present we cannot separate the homogeneous and inhomogeneous contributions below 0.7 T_c and thus we are unable to confirm the minimum in $T_1^{-1}(t)$.

In conclusion we have observed the conduction-electron spin resonance in the superconducting state of K_3C_{60} in a broad temperature and magnetic field range. The initial increase of spin lifetime below T_c predicted by Maki and Yafet is observed. At temperatures much below T_c where states bound to vortices are dominant the *g* factor has an anomalous shift, the origin of which has yet to be established.

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