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Conduction Electron Spin Resonance in Rb_3C_{60}

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The conduction electron spin resonance (CESR) of Rb_3C_{60} has been observed for the first time and the spin susceptibility found to be $\chi_s = (12.4 \pm 4) \times 10^{-4}$ emu/mol, in agreement with static measurements. The CESR linewidth is anomalously large, 1300 G at 30 K giving a spin lattice relaxation rate $T_1^{-1} = 9.0 \times 10^{-11}$ sec^{-1}, and we suggest that it is caused by large molecular disorder. The ESR line formerly assigned to Rb_3C_{60} arises from an unidentified nonsuperconducting phase Rb_xC_{60} which has a structural transition near 400 K and a thermal history dependent metal-insulator transition at lower temperatures.

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Determining the spin susceptibility χ_s and the spin lattice relaxation rate T_1^{-1} using conduction electron spin resonance (CESR) may help us to understand the origin of superconductivity in the alkali fullerenes [1]. In normal metals T_1 is closely related to the momentum relaxation time (τ) responsible for the electrical resistivity. In this Letter we report the first measurement of the intrinsic CESR of Rb_3C_{60} and show that χ_s is large in agreement with static measurements on the same sample and previous work [2,3]. The linewidth is anomalously large and does not behave as in pure metals, but is consistent with the large residual resistivity suggested by infrared measurements [4]. A narrow ESR line [5] arising from a nonsuperconducting Rb_xC_{60} phase (with x unknown) is also observed. This phase exhibits a complex behavior depending on thermal history. Preliminary CESR measurements on compounds of nominal composition K_3C_{60} also indicate the existence of two metallic phases, with the superconducting one again having an unusually large linewidth.

The CESR of Rb_3C_{60} and of Rb_xC_{60} has been observed in all five samples studied. Three of these [6] had *nominal* composition Rb_nC_{60} with $n=3$ and the others $n=2$ and 4. Most of the results presented here were obtained for an $n=3$ sample for which x-ray diffraction [7] and Meissner diamagnetism showed that the majority phase was Rb_3C_{60}. This 20 mg sample was prepared from pure C_{60} by reacting it at 225° C with Rb metal for 19 days in a specially shaped quartz tube which allowed ESR, superconducting quantum interference device (SQUID), and ac susceptibility measurements to be made on the same sample. The CESR lines at 9.4 GHz were integrated to obtain spin susceptibilities. According to the low temperature ESR the sample contained about 0.5% impurity spins per mole. The total static susceptibility χ_T was measured using a Quantum Design SQUID magnetometer at 5 T. A correction for ferromagnetic impurities was made and the sample holder background was measured by displacing the sample to the top of the quartz tube. A new software was written to correct the SQUID magnetometer response for the holder at each temperature.

Above 30 K the ESR absorption spectrum (Fig. 1, inset) has two distinct components: A narrow line which depends on temperature and thermal history is superimposed on a very broad and more intense line. The broad component does not depend on thermal history; its full absorption linewidth (ΔH) decreases from 1300 G at 30 K to 700 G at 400 K (Fig. 1), and we assign it to the CESR of Rb_3C_{60}. We could not assign the narrow component to any known Rb_nC_{60} compound. According to x-ray studies [8] Rb_nC_{60} with arbitrary n segregates into well defined phases having compositions of $n=0$, 3, 4, or 6. Since the $n=0$ and 6 phases are nonmagnetic insulators the only known candidate for the Rb_xC_{60} phase is $n=4$ for which the physical properties are not known. However, the dependence of the narrow ESR line on the nominal composition n does not support this assignment;

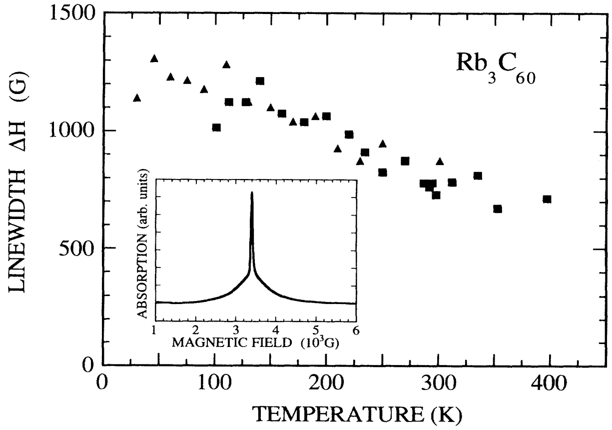

FIG. 1. CESR linewidth of Rb_3C_{60} versus temperature for two samples (squares and triangles). Inset: The broad Rb_3C_{60} and narrow Rb_xC_{60} ESR lines. The latter is instrumentally broadened.

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we observed Rb_xC_{60} with about the same intensity for $n=2$ and 3 and with a reduced intensity for $n=4$. Thus another possibility is that not all phases have yet been found by x-ray diffraction.

The above assignment differs from previous work [5] which did not observe the broad line and attributed the narrow line of Fig. 1 to Rb_3C_{60}. With our assignment the spin susceptibility derived from ESR agrees with the static measurement. The integrated ESR intensity of Rb_xC_{60} varies from sample to sample and is only a small fraction of that of Rb_3C_{60}. The magnetic properties of Rb_xC_{60} depend on thermal history while the superconducting properties of the sample do not, confirming that Rb_xC_{60} is not the superconducting phase; it is a metal at high temperatures and an insulator at low temperatures.

The superconducting transition of Rb_3C_{60} is observed by ESR and SQUID at 29 K and is the same for annealed and quenched materials to within 0.2 K. ac susceptibility showed a fractional diamagnetism of 28% at 4.2 K, the difference between the quenched and annealed states being less than the measurement error of $\pm0.3\%$. The fraction f of Rb_3C_{60} is more than 28% because typical crystallite dimensions (3-5 μm) are comparable with the penetration depth of 0.44 μm measured by muon spin rotation [9] and assuming spherical particles we estimate a superconducting volume fraction $f=0.62\pm0.15$. The value of f is in apparent contradiction with the x-ray diffraction spectrum [7] on the same sample which showed no trace of any phase other than Rb_3C_{60}. The Rb_xC_{60} must be amorphous or have small (≈10 nm) crystallites. Another constraint on sample morphology is that only electrically isolated phases give distinct ESR lines; for a metal all inhomogeneities are averaged within the distance, $\delta_{\text{eff}}=(1/3v_F^2\tau T_1)^{1/2}$, over which electrons diffuse within a spin lifetime. In Rb_3C_{60} this is of order 1 μm (v_F is the Fermi velocity).

Figure 2 shows that the spin susceptibilities of Rb_3C_{60}, χ_s^{ESR} and χ_s^{SQUID}, measured by the two methods are in good agreement. $\chi_s^{\text{ESR}}=[(7.7\pm2)\times10^{-4}/f]$ emu/mole between 30 and 300 K. After correcting the raw data χ_T for the core diamagnetism, $\chi_d=-3.28\times10^{-4}$ emu/mole from all the Rb ions and C_{60} molecules [2], the static susceptibility is $\chi_s^{\text{SQUID}}=(\chi_T-\chi_d)/f=[(9.1\pm0.5)\times10^{-4}/f]$ emu/mole in the quenched state at 200 K where χ_s of Rb_xC_{60} is negligible (see below). Correcting for the fraction $f=0.62\pm0.15$ of the sample which is Rb_3C_{60} we find $\chi_s^{\text{ESR}}=(12.4\pm4)\times10^{-4}$ emu/mole at 300 K and $\chi_s^{\text{SQUID}}=(14.7\pm4)\times10^{-4}$ emu/mole (at 200 K) in good agreement with Ref. [2]. The value of χ_s^{ESR} is more reliable because, unlike χ_T, it is not affected by Landau diamagnetism and possible Van Vleck paramagnetism. From χ_s^{ESR} we estimate the density of states at the Fermi level, $N_s=\chi_s/\mu_B^2$. We find $N_s=38$ states/eV per Rb_3C_{60} which is 3 times larger than $N=13$ states/eV per Rb_3C_{60} obtained from band calculations [10,11]. Thus, as noted by Ramirez *et al.* [2], electron-electron correlations may be essential in determining χ_s although it can also be enhanced by polaron effects.

The linewidth of Rb_3C_{60} is anomalously large (Fig. 1) and we suggest that it is caused by molecular disorder. In almost all pure metals the CESR linewidth arises from a homogeneous broadening of the Zeeman levels by spin lattice relaxation (with a rate T_1^{-1}) induced by static or dynamic disorder via the spin orbit coupling of conduction electrons to the lattice [12,13], i.e, $\Delta H=(2/\gamma)T_1^{-1}$ where γ is the gyromagnetic ratio. T_1 is several orders of magnitude longer than τ and any anisotropy in γ is motionally narrowed. The spin scattering of conduction electrons by phonons has been shown to be proportional to the momentum scattering rate and hence to the electrical resistivity [13]; i.e., $T_1^{-1}=K\tau^{-1}$. This holds for the alkali and noble metals [14] over a large range of temperatures. K is specific to the metal, and increases roughly as λ^2, the square of the spin orbit coupling. The shift of the g factor from the free electron value 2.0023 is a measure of λ, $\Delta g=\lambda/E_0$ where E_0 is of the order of the Fermi energy. The empirical Elliott-Yafet relation [12,13]

$$T_1^{-1}=\alpha(\Delta g)^2\tau^{-1} \tag{1}$$

is fulfilled in normal metals with α varying by less than an order of magnitude. Atomic disorder gives rise to spin flip and momentum scattering which are related in the same way. Equation (1) is valid with about the same value of α for dislocation induced scattering [15].

We estimate τ_r, the low temperature residual momentum scattering time of Rb_3C_{60}, from Eq. (1) by using $\Delta H=1300$ G (Fig. 1) and making the plausible assumption that $\Delta g=2\times10^{-3}$, the value measured for Rb_xC_{60}. We use $\alpha=4.8$, the value appropriate for Na which is a simple metal and has a g shift [16] (and thus a spin orbit coupling) not very different from that of Rb_3C_{60}. We find $\tau_r=1.8\times10^{-15}$ sec and using the free electron value for e/m with $n=4.0\times10^{21}$ electron/cm^3 obtain an estimate for the residual resistivity $\rho=m/e^2n\tau_r$ of 0.45 mΩcm. The residual resistivity of Rb_3C_{60} has not yet

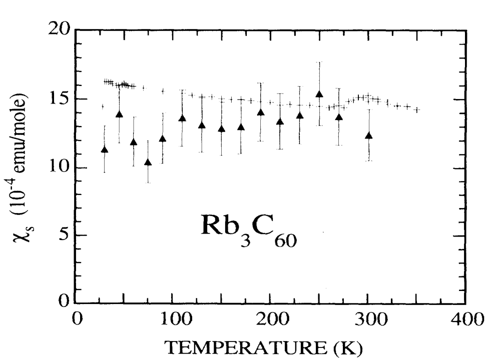

FIG. 2. Spin susceptibility of Rb_3C_{60} measured by CESR (triangles) and SQUID (crosses) in the quenched state. Corrections made to the raw data are explained in the text. The increase in χ_s^{SQUID} above 270 K arises from Rb_xC_{60}.

been measured directly but 0.4 mΩ cm was estimated from infrared reflectivity [4]. This crude estimate supports the idea that the anomalously large spin relaxation in Rb_3C_{60} arises from spin orbit scattering by an unusually large molecular disorder. Estimates from the calculated band structure lead to even higher values for ρ; using the relation $1/\rho = \Omega_p^2 \tau_r / 4\pi$ and the calculated value of the plasma frequency [11] $\Omega_p = 1.2$ eV we find $\rho = 1.9$ mΩ cm.

The decrease in T_1^{-1} with increasing temperature is also anomalous. In Rb_3C_{60} the phonon contribution is expected to be of the order of that in light metals, e.g., in Na $T_1^{-1} = 1 \times 10^8$ sec^{-1} at 300 K [16] which is 2 orders of magnitude less than the residual rate in Rb_3C_{60}. The increase in T_1^{-1} by fluctuating fields from molecular reorientation is unimportant since the frequency of such reorientations [17] below ambient temperature is many orders of magnitude less than the electronic Larmor frequency. Thus, while one may understand why the linewidth does not increase significantly with increasing temperature, the observed *decrease* is not explained in a simple way. One possibility is a gradual increase of the molecular disorder as the temperature is lowered. The most likely source of this disorder is the low symmetry of the C_{60} molecule which is not compatible with the ideal fcc structure [18]. Linked to this orientational disorder there may be a disorder in the position of the center of mass or a deformation of the molecule, which increases as the temperature is reduced. From relation (2) we expect a slight increase in resistivity at lower temperatures. Direct measurements of $\rho(T)$ are controversial [19,20] and may be affected by other metallic phases.

In contrast to Rb_3C_{60}, Rb_xC_{60} in its metallic phase has a spin relaxation which follows the pattern of normal metals [Fig. 3(a)]. Above 440 K Rb_xC_{60} is in thermal equilibrium and the peak-to-peak derivative linewidth [21] $\Delta H_{pp} = 31 \pm 1$ G is independent of temperature or thermal history. Below 440 K physical properties depend on thermal history in a complicated way. For slow cooling and heating from 500 to 300 K a hysteretic transition in the ESR linewidth with no change in the spin susceptibility is observed at about 400 K. After slow cooling the linewidth at 295 K is much less than its high temperature value, and depends on the cooling rate. It also depends on the thermal history below 295 K, although this was not studied in detail. The hysteretic transition at 400 K may be due to phase separation or a structural transition. Quenching freezes the high temperature phase into a metastable state at low temperatures.

We shall discuss two types of thermal cycle A and Q which differ in their cooling rates between 500 and 295 K (Fig. 3): A, cooled in several minutes or slower from 500 K to ambient temperature; Q, quenched from 500 K to liquid nitrogen temperatures in a few seconds. Data were taken with increasing temperature between 4.2 and 295 K in cycle Q and an additional full temperature cycle between 295 and 500 K was made in cycle A.

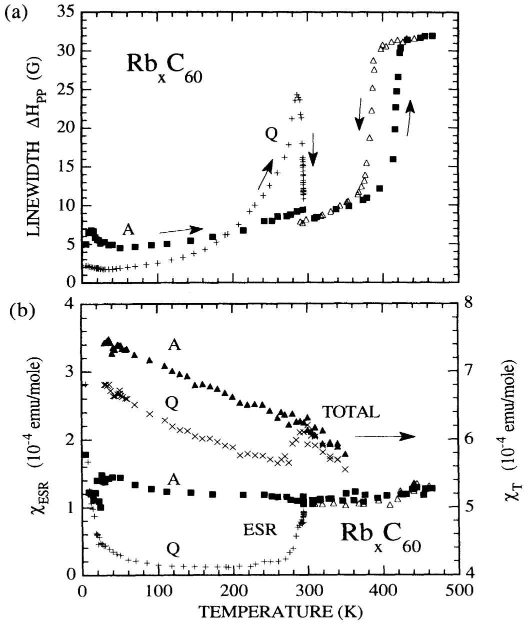

FIG. 3. (a) ESR linewidth and (b) raw data for ESR and SQUID susceptibility (χ_T; see text) in the annealed (A) state (squares, triangles) and after quenching (Q) from 500 to 77 K (multis, plusses). In (a) note hysteretic transition at about 400 K and the relaxation of Q into A at 300 K. In (b) note the decrease in χ_s below 295 K indicating a metal-insulator transition in state Q. In state A a metal-insulator transition seen in the raw ESR data below 40 K is below 50 K if the Curie contribution from impurities is subtracted.

Our results for ΔH_{pp} on cycle A below 300 K shown in Fig. 3(a) are in fair agreement with reported data [5]. The spin susceptibility for cycle A, shown in Fig. 3(b), is temperature independent from 50 K up to 500 K to within 10%. Thus Rb_3C_{60} is a metal with a reasonably large density of states. However, in contrast to Rb_3C_{60} there is no anomalous spin scattering in Rb_xC_{60}. At 50 K the linewidth ΔH_{pp} is between 2 and 5 G for cycle A, depending on the cooling rate, and it increases smoothly by 4 G up to 300 K [Fig. 3(a)]. The corresponding spin relaxation rate due to phonons, $T_1^{-1} = 6 \times 10^7$ sec^{-1}, is similar to that of Na. Equation (1) suggests that Rb_xC_{60} has 2 orders of magnitude higher conductivity than Rb_3C_{60}.

According to the ESR spin susceptibility data for Rb_xC_{60} [Fig. 3(b)] the metallic phase is not stable at low temperatures either for the quenched or the annealed states. In the quenched state a metal-insulator transition occurs between 250 and 290 K and is observed both by ESR and SQUID magnetometry. Magnetic impurities dominate the ESR spectrum of the quenched state below 160 K. In the annealed state a decrease of the ESR intensity (with the Curie term subtracted) shows that a transition occurs below 50 K but in this case magnetic defects and the superconducting transition of Rb_3C_{60} mask the decrease in the static susceptibility.

Quenching from 500 K drastically alters the temperature dependence of ΔH_{pp} of R_xC_{60} [Fig. 3(a)]. The linewidth increases continuously from 1.8 G at 30 K to 25 G at 290 K. The quenched state relaxes to the annealed one at 295 K where ΔH_{pp} decreases in time without any change in intensity. The time dependence of ΔH_{pp} is nonexponential; it fell to 11.5 G in 16 h.

Comparing the properties of Rb_3C_{60} and Rb_xC_{60} may lead to an insight into the origin of superconductivity in alkali fullerenes. Both Rb_3C_{60} and, at high temperatures, Rb_xC_{60} are metals with comparable spin susceptibilities, yet there is a sharp contrast between their spin relaxation rates T_1^{-1}, which for normal metals is simply related to the momentum relaxation rate τ^{-1}. In its metallic phase Rb_xC_{60} behaves like a normal metal while Rb_3C_{60} has an anomalously large spin-flip relaxation rate which increases at lower temperatures. Orientational disorder is present in all known fullerenes so it cannot be the only cause of the anomalous linewidth. It seems possible that the electron-lattice interaction could be stronger in Rb_3C_{60} than in Rb_xC_{60} and this is the cause of the enhancement of the spin lattice relaxation rate by 2 orders of magnitude. In other words, there may be a direct link between the anomalously large spin-lattice relaxation rate and the occurrence of superconductivity. The other possibility is that the superconducting compound has a stoichiometry slightly deviating from the ideal Rb_3C_{60} composition.

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Note added.— After submission of this work a new phase with the composition of Rb_1C_{60} has been reported by Zhou *et al.* [22] which has different high and low temperature structures. It is likely that $x=1$ in the component Rb_xC_{60} discussed in this paper.

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