Electron-paramagnetic-resonance scattering rates in metallic RbC_{60} and CsC_{60}

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We derive conduction-electron scattering rates in the metallic polymer phase of RbC_{60} and CsC_{60} from the investigation of the temperature-dependent conduction electron-spin-resonance linewidth at *X*- (9 GHz) and *W*-band (94 GHz) frequencies by applying the Elliott theory. We obtain scattering rates that favor an essentially isotropic electronic structure of the polymer phase.

INTRODUCTION

RbC_{60} and CsC_{60} have attracted considerable attention due to their large number of different phases. The most prominent example is the orthorhombic phase which emerges upon cooling the high-temperature fcc phase to temperatures below 350 K. Its outstanding characteristic is the formation of one-dimensional polymer chains by $[2+2]$ cycloaddition between the fullerene molecules.[1] This phase is metallic in the temperature range from 350 down to 50 K and undergoes a metal-to-insulator transition below 50 K.[2,3] The existence of one-dimensional chains of charged fullerenes together with the short spacing of the molecules along the chain direction led to the conjecture of a quasi-one-dimensional conductivity.[4]

This idea was reclaimed to be supported by two electron-spin-resonance (ESR) results: the narrowness of the conduction ESR (CESR) in comparison to metallic Rb_3C_{60} (Ref. 5) and the large asymmetric broadening of the resonance below the metal-to-insulator transition. The first was attributed to reduced spin relaxation as a consequence of the reduced electron scattering rate typical for low-dimensional electronic systems. The second was interpreted as antiferromagnetic resonance resulting from a spin-density wave,[6] a phenomenon typically occurring in quasi-one-dimensional systems like the Bechgaard salt $(TMTSF)_2PF_6$.[7] The notion of an antiferromagnetically ordered one-dimensional ground state was supported by ^{13}C NMR results showing strong magnetic fluctuations persisting up to room temperature.[8]

This interpretation has been challenged by theoretical calculations that favor a three-dimensional (3D) electronic structure[9,10] and by considering that the atoms participating in the polymer bonds are sp^3 hybridized and thus do not enhance conductivity along the chains.[11] From the discussion of alternative ground-state scenarios that would lead to a broad ESR signal,[12,13] a magnetic ground state seems plausible, but its nature—1D spin-density wave or 3D antiferromagnetic ordering—is still a matter of debate.

To resolve this question, further information on the dimensionality of the electronic structure has to be acquired. A first step into this direction was taken by de Swiet *et al.*, who determined the electron spin-density distribution on the fullerene molecule by ^{13}C NMR in CsC_{60}.[14] They found a concentration of the spin density near the equator of the fullerene, away from the polymer bonds, which thus gives rise to strong interchain coupling. Moreover, in a recent pub-

lication Sakamoto *et al.* constructed a temperature-pressure phase diagram of RbC_{60} using ESR and resistivity measurements.[15] They identified a typical Mott-Hubbard behavior, with an antiferromagnetically ordered metallic phase at low temperatures and high pressures, which can only be understood in terms of a 3D system. Furthermore, our group lately showed that the nonaxially symmetric and rather isotropic *g* tensor found in a RbC_{60} single-crystal investigation favors a fairly isotropic conduction-electron state.[16] In the present publication we analyze in detail the temperature-dependent CESR linewidth of RbC_{60} and CsC_{60} powder samples at standard (*X* band) and high fields (*W* band) applying the Elliott theory. The standard explanation of the narrow ESR linewidth in RbC_{60} in comparison to cubic Rb_3C_{60} in terms of a reduced conduction-electron scattering rate implicitly assumes a comparable spin-orbit coupling for both systems. Instead it seems more reasonable that the presence of three rubidium ions per C_{60} in Rb_3C_{60} will lead to a larger spin-orbit coupling compared with RbC_{60}. The same scattering rate would then naturally translate into an increased spin relaxation and hence a broader CESR line for Rb_3C_{60}.

EXPERIMENT

RbC_{60} and CsC_{60} powder samples have been prepared using the standard method with subsequent slow cooling of the samples from 400 K to room temperature. The samples, sealed in quartz tubes, were investigated using ESR at *X*- and *W*-band frequencies, i.e., at 9 and 94 GHz. *X*-band measurements were performed on a standard Bruker spectrometer equipped with a TE_{102} rectangular cavity. For the 94 GHz measurements a Bruker Elexsys 680 *W*-band spectrometer with a cylindrical cavity was employed. In *W* band *g*-factor anisotropies are enlarged by a factor of 10 with respect to *X* band. Measured *g* values have been corrected by comparison to a Li:LiF standard sample.[17]

ELLIOTT THEORY

The Elliott theory,[18] which was extended by Yafet,[19] allows us to relate the observed CESR linewidth and *g* factor to the intrinsic conduction-electron scattering rate in a metallic system.

Conduction-electron scattering on impurities or phonons leads to spin relaxation if the subbands for the two spin orientations are mixed by spin-orbit coupling. Elliott showed
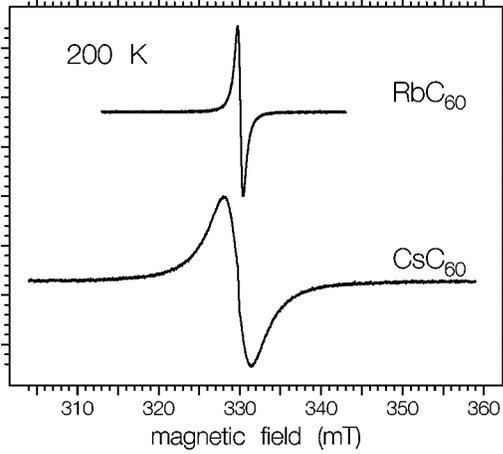
FIG. 1. X-band spectra of RbC_{60} and CsC_{60} powder samples at 200 K. The CsC_{60} resonance is considerably broader than that of RbC_{60}, which can be attributed to a larger spin-orbit coupling of the conduction electrons caused by the heavier cesium atom.

that the admixture of one subband to the other can be estimated by the ratio $\lambda/\Delta E$, where λ is the spin-orbit coupling constant and ΔE is the separation of the band in question and its neighbor bands having the same transformation properties. Thus, when switching on spin-orbit coupling, the wave function connected to the Zeeman state $|\uparrow\rangle$ becomes

$$(a_{\mathbf{k}}|\uparrow\rangle + b_{\mathbf{k}}|\downarrow\rangle)e^{i\mathbf{k}\cdot\mathbf{r}}.$$

The ratio b/a is determined by the strength of the mixing, i.e., by $\lambda/\Delta E$. Elliott demonstrated that the admixture leads to a g shift $\Delta g = g - 2.0023$, also proportional to the magnitude of the mixing. Hence the experimental determination of the deviation of g from the free electron value gives a measure of the influence of spin-orbit coupling on the band structure.

The probability that an electron scattering process leads to a spin flip is proportional to the square of the mixing strength which, following the above reasoning, can be expressed by the g shift Δg. Hereby Elliott established the relation between the scattering rate $1/\tau$ and the metallic spin-relaxation rate $1/T_1$:

$$\frac{1}{T_1} = \alpha \frac{\Delta g^2}{\tau}, \quad (1)$$

where α is a material-dependent parameter of order unity.[19] Because of the equivalence of transverse and longitudinal relaxation rates $1/T_2 = 1/T_1$ in metallic systems, the above expression can be related directly to the ESR linewidth:

$$\Delta B_{\mathrm{HWHM}} = \frac{1}{\gamma T_2} = \frac{\alpha}{\gamma}\frac{\Delta g^2}{\tau}, \quad (2)$$

where ΔB_{HWHM} is the half width of the resonance and $\gamma = g(\mu_{\mathrm{B}}/\hbar)$ is the gyromagnetic ratio.

Aside from the fact that optical measurements show the metallic character of RbC_{60} and CsC_{60},[3] there are two strong indications that the Elliott-Yafet theory can be applied to the metallic phase of RbC_{60} and CsC_{60}. One is the increase in
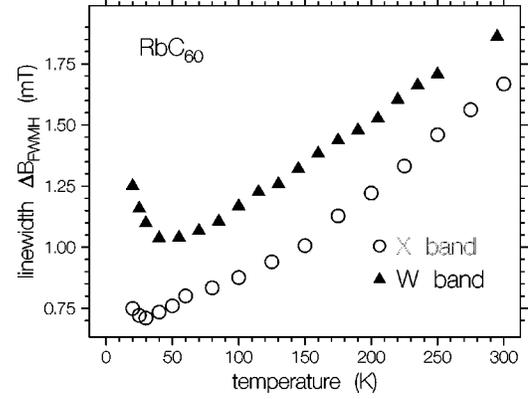

FIG. 2. Temperature dependence of the full ESR linewidth of RbC_{60} powder samples at X and W bands, as obtained from a Lorentzian fit to the resonance lines.

linewidth with temperature, which hints at a coupling of the spin relaxation to the electron-phonon scattering. The other one is the fact that the resonance observed for CsC_{60} is considerably broader than that for RbC_{60} (see Fig. 1). As one expects the heavier cesium atom to cause a larger spin-orbit coupling, this effect demonstrates the importance of spin-orbit coupling for spin relaxation in these materials.

MEASUREMENTS AND DATA ANALYSIS

Figure 1 displays the spectra taken at 200 K at X band. For both materials a Lorentzian-type resonance is observed. The signals arise from the conduction electrons of the metallic polymer phase, which exists in the temperature range from about 50 to 350 K. Going from X- to W-band frequencies, g anisotropy leads to a broadening of the lines for both materials. If one fits all spectra with Lorentzian lines one obtains the temperature dependences shown in Figs. 2 and 3 for RbC_{60} and CsC_{60}, respectively. For RbC_{60}, however, W-band measurements reveal a slight asymmetry of the ESR line which is due to the partial resolution of g anisotropy. As we have already determined the g anisotropy of RbC_{60} single crystals,[16] we chose to simulate a powder pattern using this g
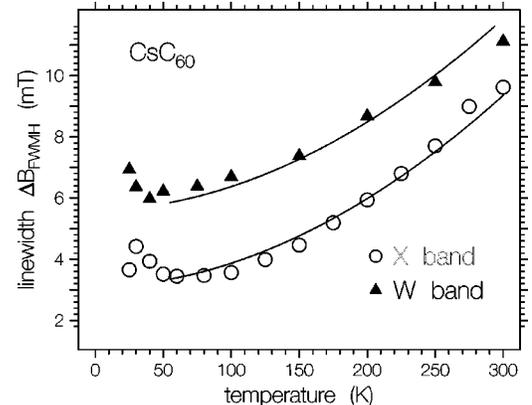

FIG. 3. Temperature dependence of the full ESR linewidth of CsC_{60} powder samples at X and W band. The solid lines correspond to the model function described in the text.
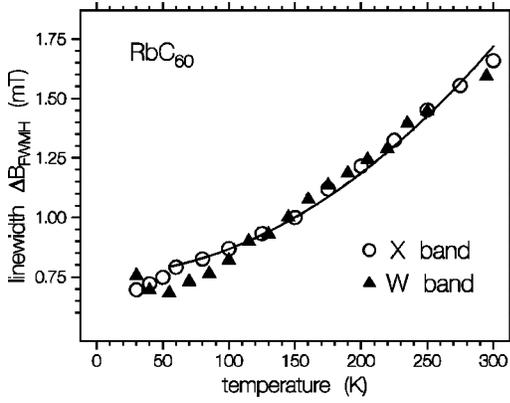
FIG. 4. Temperature dependence of the dynamic part of the ESR linewidth of RbC_{60} powder samples at X and W band. The solid line corresponds to the model function described in the text.

TABLE I. Parameters obtained from modeling the linewidth data for RbC_{60} and CsC_{60} with Δg referenced against the value of C_{60}^- ($g_{C_{60}} = 1.9999$). The parameters are further explained in the text.

	RbC_{60}	CsC_{60}
Δg	16×10^{-4}	27×10^{-4}
$\tau_p^{-1}(300)$ (s^{-1})	3.29×10^{13}	7.54×10^{13}
τ_{res}^{-1} (s^{-1})	2.61×10^{13}	3.42×10^{13}
Δg_{aniso}	3.0×10^{-4}	17.0×10^{-4}

anisotropy, which we convoluted with a Lorentzian fit function in order to match the spectra. The Lorentzian then contains the dynamic linewidth, whereas the influence of g anisotropy is taken account of by the powder simulation. Assuming the same spin dynamics at 9 and 94 GHz, X-band and W-band dynamic linewidths should be the same. However, the same dynamic width for both frequency bands could only be obtained by reducing the g anisotropy from Ref. 16 by roughly 20%, which, on the other hand, is within the errors assumed for the g tensor determination. The dynamic linewidths obtained by this method are displayed in Fig. 4.

In contrast to the linewidth, the g factor for both materials changes only very slightly in the temperature range of interest ($\delta g < 2 \times 10^{-4}$). RbC_{60} has a g factor of 2.0015 (± 0.0001), while the value for CsC_{60} is $g = 2.0026$ (± 0.0001).

We tried to model the temperature-dependent linewidth data using the following relation:

$$\Delta B_{FWHM} = \frac{\hbar}{\mu_B} \frac{\Delta g^2}{g} \frac{2}{\tau} + \frac{\Delta g_{aniso}}{g} B_0. \qquad (3)$$

The first term contains all contributions which are attributed to spin relaxation via spin-orbit coupling. This term corresponds to Eq. (2) with $\alpha = 1$. The second term is only applied for CsC_{60}, where no g-anisotropy information is available. It allows us to determine the g anisotropy Δg_{aniso} from the difference in linewidth between X and W bands. As described above, for RbC_{60} the g anisotropy is already taken account of by the convolution of an anisotropic powder pattern with a Lorentzian line.

Concerning the first term, the determination of the g shift Δg raises some questions: In the Elliott theory as described above, Δg is the deviation of the g factor from the free-electron value. Now it is a well-known fact that the g factor of discrete C_{60}^- ions is found in the range from 1.994 to 2.001,[20] resulting from an intrinsic spin-orbit coupling of the C_{60} anion. In the fulleride salt there is additional spin-orbit coupling due to the electronic band-structure formation and admixture of the counter ion wave functions. One might con-

ceive the case that the two contributions shift the g factor in opposite directions; then the total g shift with respect to the free-electron value is not a good measure of the strength of the spin-orbit coupling of the conduction band.

Applying the reasonable assumption that in CsC_{60} the electrons are subject to a larger spin-orbit coupling than in RbC_{60} (heavy atom effect), one would expect that the spin-orbit contribution to Δg is larger in CsC_{60} than in RbC_{60}. However, the experimental values are $\Delta g = 2.0015 - 2.0023 = -0.0008$ for RbC_{60} and $\Delta g = 2.0026 - 2.0023 = 0.0003$ for CsC_{60}. We therefore conclude that the proper reference for the spin-orbit contribution to the relaxation rate is not the free-electron value $g_e = 2.0023$, but rather the C_{60}^- ion value, for which we use $g_{C_{60}} = 1.9999$ in the following.[20]

The scattering rate can be expressed by the sum $\tau^{-1} = \tau_{ph}^{-1} + \tau_{res}^{-1}$ with a temperature-dependent phonon part $\tau_{ph}(T)^{-1}$ and a temperature-independent residual part τ_{res}^{-1}. The phonon part is modeled by a power law as $\tau_{ph}(T)^{-1} = \tau_{ph}^{-1}(300)(T/T_{300})^\beta$, with the scattering rate $\tau_{ph}^{-1}(300)$ at room temperature $T_{300} = 300$ K. The temperature-independent rate τ_{res}^{-1} represents scattering of conduction electrons from lattice defects and impurities.

To exclude the influence of line broadening caused by the low-temperature phase below 50 K, we applied our model function only in the temperature range from 60 to 300 K. We assumed the exponent β to be the same for both materials and took it to be $\beta = 2$, which is close to the values obtained from an unrestricted fit of this parameter. The resulting model functions, without the g anisotropy term for RbC_{60} and with the g term for CsC_{60}, are plotted as solid lines in Figs. 4 and 3, respectively. We note that X- and W-band data are fitted with a single parameter set; the resulting parameters are summarized in Table I.

DISCUSSION

The scattering rates found are with $\tau^{-1} \approx 10^{13}$ s^{-1} at room temperature within an order of magnitude the same as those found for classical 3D metals like copper or silver. On the other hand for quasi-one-dimensional systems like (fluoranthenyl)$_2$PF$_6$ or related compounds the linewidth corresponds to interchain scattering rates which are in the range $10^{10} - 10^{11}$ s^{-1}.[21] The Elliott relation (2) implies that this also holds for 1D systems which exhibit a large ESR linewidth, like (TMTSF)$_2$PF$_6$ with about 200 G at ambient temperatures.[22] The reason is the strong spin-orbit coupling,

in the case of $(TMTSF)_2PF_6$ induced by the substantial electron density at the heavy selenium atoms, which leads to a large g shift and therefore to large ESR linewidths, even for small scattering rates. Hence our results lead to the conclusion that the electronic conduction in RbC_{60} and CsC_{60} is rather isotropic. The narrower linewidths in comparison with Rb_3C_{60} are the consequence of a reduced spin-orbit coupling, which might result from the smaller number of alkali ions in RbC_{60}. No indication of a reduced scattering rate due to dimensionality effects has been found. Therefore the low-temperature phase transition is not likely to be viewed as an instability of a quasi-1D system against the formation of a spin-density wave. On the contrary, the 3D nature of the electronic state favors a 3D antiferromagnetic ground state.

We note that the impurity scattering is rather large and reflects the fact that this type of material suffers from finite polymer chain lengths. Also the expected orientational disorder of the orthorhombic domains will introduce severe grain-boundary scattering so that the large residual broadening can be rationalized. In fact this also explains why it is difficult to observe long-range magnetic order in the low-temperature phase.[13]

Comparing CsC_{60} with RbC_{60} we find a much larger g anisotropy for CsC_{60}, which indicates an appreciable admixture of cesium orbitals to the conduction-band wave function.

In summary, we have analyzed the ESR scattering rates of the conduction-electron spins in RbC_{60} and CsC_{60} in the temperature range 60–300 K by applying the Elliott theory to the temperature-dependent ESR linewidth at X- and W-band frequencies. The observed scattering rates are consistent with a 3D metallic character of the conduction electrons and therefore challenge the conjecture of quasi-1D-electronic state in these materials. As a note of caution we remark, however, that finite polymer chain lengths can obscure any possible 1D behavior.

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