

ESR evidence for phonon-mediated resistivity in alkali-metal-doped fullerides

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The temperature dependence of ESR linewidths and g values for the fulleride superconductors K_3C_{60} , Rb_3C_{60} , and Na_2CsC_{60} are reported. Following the Elliott-Yafet theory of electronic relaxation in metals, we compare the temperature dependence of the linewidth divided by the square of the difference of g from the free-electron value with the temperature dependence of the resistivity. We show that the Elliott relation applies for all three compounds, implying a normal-state resistivity dominated by electron-phonon interactions. [S0163-1829(96)50830-1]

Since the discovery of superconducting fullerides, the mechanism giving rise to the normal-state resistivity has been controversial. The quadratic temperature dependence observed for thin films was attributed to electron-electron scattering by Palstra *et al.*,¹ while the same behavior observed on single crystals was analyzed by Wareka *et al.* in terms of lattice contraction and a linear $\rho(T)$ at constant volume, implying usual electron-phonon scattering.² In recent papers,^{3,4} Tanigaki *et al.* noted that the ESR linewidths of binary and ternary alkali- C_{60} compounds are correlated with the square of the spin-orbit coupling constant λ of the intercalated metal(s). They also pointed out that the linewidth decreases with decreasing T in compounds with small lattice constants and “low” T_c 's (e.g., Na_2CsC_{60}), while the opposite behavior, ΔH increasing with decreasing T , was observed in compounds with large lattice constants and “high” T_c 's (e.g., Rb_3C_{60}). This unusual behavior was attributed to an increasing influence of electronic correlations

with large lattice constants, presumably due to reduced bandwidth and the approach to Mott localization. In Ref. 4, the different ΔH vs T behaviors were interpreted as a deviation from the Elliott relation linking the electronic spin lifetime to the electron-phonon scattering time,⁵ this deviation being ascribed to a resistivity induced by electron-electron scattering. However, their analysis implicitly assumes that there is no temperature dependence of the ESR g value, e.g., $\Delta g = g_e - g$, where g_e is the free-electron g value, is temperature independent, as found for pure alkali metals.⁶ Here we show that in these materials g in fact is strongly temperature dependent and that, when this is taken into account and following Elliott⁵ and Yafet,⁷ all the prototypical binary and ternary fulleride superconductors behave as ordinary metals above T_c . Thus there is no need to invoke electron-electron scattering to explain the resistivity.

Important theoretical work was carried out in the mid-1950s on the electronic relaxation in inorganic metals, in particular regarding the effect of spin-orbit coupling on the ESR absorption line.^{5,7,8} The presence of spin-orbit interaction leads to Bloch states which are a mixture of the Zeeman states:

$$(a_{\mathbf{k}}| + > + b_{\mathbf{k}}| - >) e^{i\mathbf{k} \cdot \mathbf{r}},$$

the ratio $b_{\mathbf{k}}/a_{\mathbf{k}}$ providing an estimate of conduction electron relaxation times T_1 and the electron-phonon scattering time τ . Elliott estimated the ratio $b_{\mathbf{k}}/a_{\mathbf{k}}$ to be of order of λ/E ,

TABLE I. Room temperature values of g and $\Delta g = g_e - g$ for K_3C_{60} , Rb_3C_{60} , and Na_2CsC_{60} .

	K_3C_{60}	Rb_3C_{60}	Na_2CsC_{60}
g	2.0005	1.9886	1.9848
Δg	0.0018	0.0137	0.0175

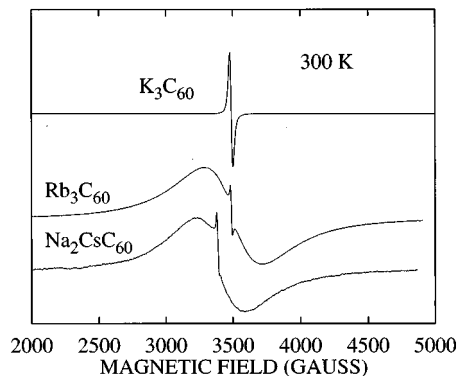


FIG. 1. Room temperature ESR spectra for K_3C_{60} ($\Delta H_{pp} = 16$ G), Rb_3C_{60} ($\Delta H_{pp} = 490$ G), and Na_2CsC_{60} ($\Delta H_{pp} = 365$ G). The narrow lines near the center of the latter two spectra are from trace paramagnetic impurities.

TABLE II. Room temperature values of g and $\Delta g = g_e - g$ for alkali metals estimated from Ref. 6.

	Li	Na	K	Rb	Cs
g	2.0022	2.0015	1.9997	1.9984	1.9923
Δg	0.0001	0.0008	0.0026	0.0039	0.0100

where E is the energy difference between the considered band and the nearest one which has the same symmetry transformation properties. The parameter λ/E depends on details of the band structure. However, Elliott showed that λ/E may be well approximated by the deviation of the g value from that of the free electron, leading to the Elliott relation between T_1 and τ :

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

where α is a temperature-independent but material-dependent parameter of order unity,⁷ $\Delta H_{1/2}$ is the halfwidth of the ESR absorption spectrum, and γ is the electron gyromagnetic ratio. If the resistivity is dominated by electron-phonon scattering, this becomes

$$\Delta H_{1/2} = \frac{1}{\gamma T_1} = \frac{\alpha'}{\gamma} \Delta g^2 \rho, \quad (2)$$

shown by Elliott to be valid at temperatures above the Debye temperature θ_D . Subsequently, Yafet⁷ showed that T_1 is proportional to the τ measured by resistivity at any T , establishing the validity of the Elliott relation even at low temperature. Beuneu and Monod verified the linearity between $\Delta H/\rho$ and Δg^2 for pure inorganic metals⁶ for temperatures down to $0.14\theta_D$.

Here we follow the same approach by measuring carefully the g values for K_3C_{60} , Rb_3C_{60} , and Na_2CsC_{60} , whereby we can discuss the resistivity via Eqs. (1) and (2) without having to estimate λ/E . Samples were prepared as described previously⁹ and were verified to be essentially single phase by x-ray diffraction. ESR experiments were performed using a standard Bruker ESP310 spectrometer equipped with a frequency meter and a NMR gaussmeter. The ESR spectra of K_3C_{60} , Rb_3C_{60} , and Na_2CsC_{60} at room temperature are shown in Fig. 1. The dramatic increase in linewidth with increasing (average) alkali-metal mass is a qualitative indication of the importance of spin-orbit coupling, similar to observations on alkali-intercalated graphite.^{10,11} The spectra for Rb_3C_{60} and Na_2CsC_{60} also exhibit an additional, extremely narrow line near the center of the main spectra. These prevent a straightforward determination of the g value from the resonant field, either from the intercept of the derivative spectrum with the baseline or from the maximum of the absorption line (first integral of the recorded spectrum).

TABLE III. Room temperature g values of $Na_2Cs_xC_{60}$ for $x=0.25, 0.5, 0.75$, and 1.0 .

$Na_2Cs_{0.25}C_{60}$	$Na_2Cs_{0.5}C_{60}$	$Na_2Cs_{0.75}C_{60}$	Na_2CsC_{60}
1.998	1.997	1.994	1.985

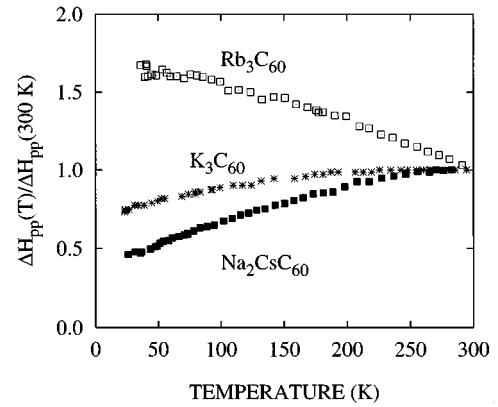


FIG. 2. Temperature dependence of the ESR linewidth for K_3C_{60} , Na_2CsC_{60} , and Rb_3C_{60} normalized at 300 K.

Instead we first verified that the derivative spectra were symmetric at all temperatures, then determined the resonant field from ΔH_{pp} , the midpoint between the extrema. The temperature independent line shapes imply a constant ratio $\Delta H_{pp}/\Delta H_{1/2}$, thus allowing a reliable measure of $T_1(T)$.¹²

The room temperature g values for the three compounds are given in Table I. Comparison with the g values for alkali metals, Table II,¹³ shows the same variation from compound to compound, confirming the effect of alkali-metal spin-orbit coupling on the ESR line.³ The variation of the 300 K g value with increasing x for $Na_2Cs_xC_{60}$ also supports the alkali-metal effect on the ESR linewidth (see Table III).

Comparison of the Δg 's in Tables I and III shows that the deviation from the free-electron value is much stronger for Rb_3C_{60} and Na_2CsC_{60} than for the corresponding metals, metallic particles or clusters¹⁴ or theoretical values.¹⁵ This implies that the single ESR line observed in the alkali-metal-doped fullerenes cannot be attributed to a spin species in exchange configuration or resonance, as for example jumping from a C_{60} molecule to an alkali-metal ion at some high frequency. If this were the case, the observed g value would lie between that of an isolated spin on the molecule [~ 2.0 (Ref. 16)] and that of the metal. This observation provides a further proof that the conduction electron spin wave function probes the spin-orbit splitting induced by alkali-metal ions.

The temperature variation of the linewidth (normalized to 300 K) is shown for the three compounds in Fig. 2. The

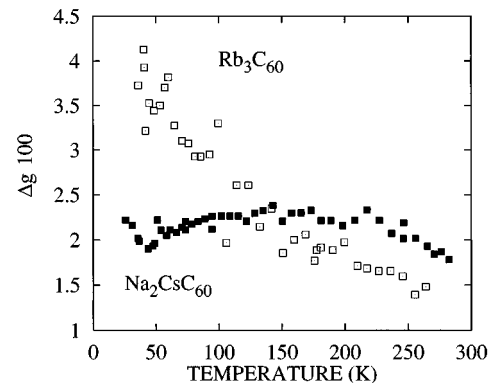


FIG. 3. Temperature dependence of $\Delta g = g_e - g$ for Rb_3C_{60} and Na_2CsC_{60} . The value for K_3C_{60} is much smaller (not shown), increasing monotonically by 25% as T decreases from 300 K to 50 K.

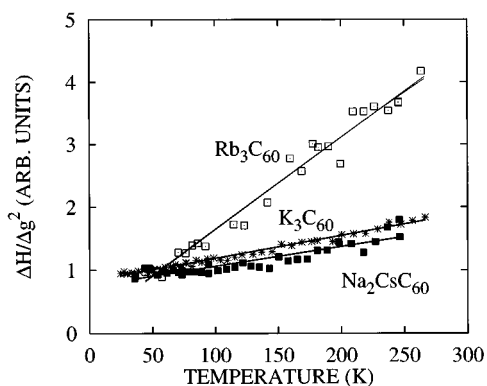


FIG. 4. Temperature dependence of $\Delta H_{pp}/\Delta g^2$ (normalized at low temperature) for K_3C_{60} , Na_2CsC_{60} , and Rb_3C_{60} . Solid lines are linear fits (Ref. 16).

observed thermal behaviors are comparable to those reported previously. However, we also observe a significant temperature dependence of Δg as shown in Fig. 3, very strong for Rb_3C_{60} , weaker for Na_2CsC_{60} and K_3C_{60} . This latter effect must obviously be taken into account in a proper assessment of the applicability of Elliott theory to the resistivity of fullerides *via* Eq. (2).

In Fig. 4 we plot $\Delta H_{pp}/\Delta g^2$ vs T for Rb_3C_{60} , K_3C_{60} , and Na_2CsC_{60} , normalized to their low temperature values to eliminate the contribution of the material-dependent α' constant in Eq. (2). All three exhibit a linear variation implying from Eq. (1) that the scattering rate $1/\tau$ increases linearly with increasing T .¹⁷ Since the measured ESR parameters ΔH and g are independent of volume, this result is consistent with linear $\rho(T)$ at constant volume.²

The agreement with Elliott-Yafet theory is also good when material variations in α' are taken into account. For example, the quantity $\Delta H_{pp}/\Delta g^2$ at 250 K is about twice as large for Rb_3C_{60} compared to K_3C_{60} , consistent with direct measurements of the resistivity.^{1,18} Thus far there have been no reports of electrical resistivity for Na_2CsC_{60} ; from Fig. 4 we expect it to be comparable to that of K_3C_{60} .

In Fig. 5 we compare $\Delta H_{1/2}/\rho$ vs Δg^2 data for inorganic metallic elements at 300 K (Ref. 6) with the present results for alkali-metal-doped fullerides at several temperatures. The two solid lines on this log-log plot are of slope 1, corresponding to $\tau/T_1 = \alpha' \Delta g^2$ with two different values of α' . Most of the elemental metals lie within an order of magnitude of the upper line ($\alpha' = 10$) while K_3C_{60} and Rb_3C_{60}

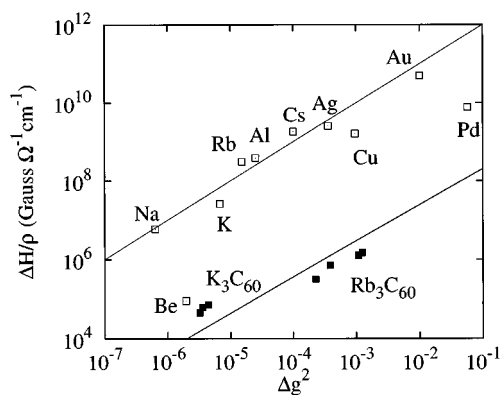


FIG. 5. Log-log plot of $\Delta H_{pp}/\rho$ vs Δg^2 for inorganic metals at 300 K [open squares (Ref. 6)] and binary alkali-metal-doped fullerides at several temperatures (filled squares, this work). Solid lines are Eq. (2) with $\alpha' = 10$ (upper line) and 0.005 (lower line).

are reasonably well represented at all T by the lower one ($\alpha' = 0.005$). Recalling that $\alpha' = \alpha n e^2 / m^*$, where n is the charge carrier concentration and m^* the effective mass, the ratios $n/m^* \sim 10^{23} - 10^{24}$ for inorganic metals and $\sim 10^{21}$ for alkali-metal-doped fullerides¹⁹ suggest an offset of 2–3 orders of magnitude between the two families (neglecting any differences in α), in good agreement with what is observed. The value of $\alpha' = 0.005$ estimated for alkali-metal-doped fullerides leads to an electron-phonon scattering time of the order of 10^{-15} s. Estimating the Fermi velocity as 10^8 cm/s,¹⁹ a mean free path in the range 1–10 Å is obtained. Despite the crudeness of these estimates based on free-electron theory, the values obtained are fully consistent with the reported physical properties of the cubic fulleride conductors.

Our experiments show that the Elliott relation correlating the spin lifetime and the electron-phonon scattering time holds for cubic metallic alkali-metal-doped fullerides, and that the unusual temperature dependence of the ESR linewidth is not due to electron correlations. We conclude that the normal-state resistivity arises from electron-phonon interactions, in agreement with Ref. 2, and that the observed difference between the two kind of metals lies in their inner nature, inorganic vs organic.

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¹¹The sensitivity of the ESR linewidth to alkali-metal mass results from nonvanishing overlap between conduction electrons and dopant core orbitals. The conclusion for graphite compounds is that, absent other strong spin relaxation mechanisms, even a

- small overlap suffices for ΔH to be dominated by the spin-orbit interaction.
- ¹²Determining ΔH from ΔH_{pp} also avoids introducing an artificial T dependence which can occur when the linewidth is comparable to the maximum field sweep, 6000 G in our case. While an accurate absolute value of $\Delta H_{1/2}$ for Rb_3C_{60} may be obtained at 300 K (linewidth $\sim 1/20$ the sweep range), $\Delta H_{1/2}$ at low T is strongly perturbed as ΔH_{pp} increases to values close to the sweep range.
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