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Implications on the Band Structure of the Isostructural Family Tetrathiafulvalene Tetracyanoquinodimethane (TTF-TCNQ), Tetraselenafulvalene Tetracyanoquinodimethane (TSeF-TCNQ), and Their Solid Solutions from Spin-Resonance Measurements

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We show that electron-phonon coupling plays a major role in the spin relaxation of the isostructural family of organic metals, (TSeF)$_x$(TTF)$_{1-x}$TCNQ (tetraselenafulvalene tetrathiafulvalene tetracyanoquinodimethane). The dependence of this relaxation on the fraction of TSeF in the donor chain suggests a picture of hybridized donor-acceptor bands for TSeF-TCNQ in contrast to the nonhybridized bands of TTF-TCNQ.

The origin of the EPR absorption linewidth in organic metals is presently unknown. An early attempt was made[1] to assign the linewidth of *N*-methyl-phenazinium–tetracyanoquinodimethane (NMP-TCNQ) in its metallic phase to spin-lattice relaxation (T_1), produced by the scattering of conduction electrons with the acoustic modes of the lattice vibrations. However, this contribution has been found[2] to be of relatively small importance for NMP-TCNQ, probably because of the small spin-orbit coupling of the atomic constituents.

Recently the synthesis of organic metals with larger spin-orbit couplings, as tetrathiafulvalene (TTF) TCNQ[3] and its isostructural selenium analog, tetraselenafulvalene (TSeF) TCNQ,[4] has opened new possibilities for observing spin-lattice relaxation involving spin-orbit interaction. The free cations of these salts have large, yet significantly different, spin-orbit couplings as indicated by g measurements in solution. We have measured the g value of TSeF and found it to be 2.027, while the g value of TTF was reported[5] to be 2.0084. Moreover, the isostructurality of the compounds makes feasible the preparation of the solid solutions (TSeF)$_x$(TTF)$_{1-x}$TCNQ where $0 \leqslant x \leqslant 1$. These solid solutions provide a system in which the effective spin-orbit coupling of the donor stack can be varied continuously while the structure is maintained.[6]

In the temperature range of metallic conductivity, the parent compounds and their solid solutions show a single EPR absorption line with a width that depends strongly on the relative fraction of TSeF in the donor chain, as is shown in Fig. 1. At room temperature the linewidth varies from 5 to 500 G over the range from $x = 0$ to $x = 1$. The origin of the linewidth appears to be similar for the different compositions, a conclusion that we infer from having observed marked insensitivity of linewidth anisotropy to composition.

The observed dependence of the linewidth on x indicates that the donor chain participates in the spin resonance. Moreover, the enormous rate of increase in the linewidth with increasing concentration of TSeF suggests that spin-orbit coupling plays a dominant role in the spin relaxation, because the most significant spin-related difference between TTF and TSeF is the much larger

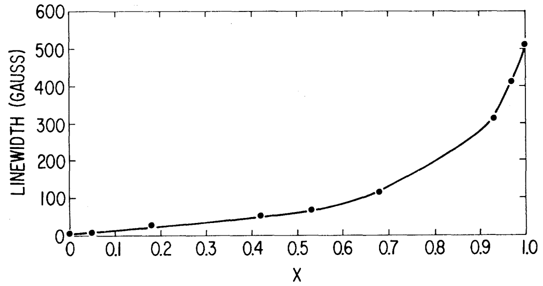

FIG. 1. Linewidth dependence for $H_{dc} \parallel c^*$ direction, on x — the fraction of TSeF in the donor chain. The measurements were taken at 300°K.

spin-orbit coupling of the Se compared with the S atoms.

One way in which the spin-orbit coupling can affect the measured linewidth is via incomplete averaging of the Larmor frequencies of the donor and acceptor chains. This mechanism will, however, introduce[7] a frequency dependence into the linewidth. No such dependence was observed[8] experimentally in going from X- to Q-band frequencies for TTF-TCNQ which served as a representative case.

A second plausible mechanism which was earlier suggested, by which spin-orbit interaction can affect the linewidth, is spin-lattice relaxation involving a combination of spin-orbit interaction and electron-phonon interaction. This relaxation mechanism, the dominant one in three-dimensional metals, was introduced by Overhauser[9] and further developed by Elliott[10] and Yafet.[11] According to this mechanism, the relaxation rate for systems consisting of a single kind of chain will be proportional[10] to the square of the deviation of the g value from the free-electron g value.

For the present case of donor and acceptor chains, each with its own partially filled band, having small or negligible interchain hybridization, but large enough interchain coupling of spins such that the spin-hopping rate exceeds the differences in the Larmor frequencies, the linewidth is given[8] by

$$T_2^{-1} = \alpha_D/T_{2D} + \alpha_A/T_{2A}, \tag{1}$$

where α_D and α_A are the respective fractions of the total susceptibility on the donor and acceptor chains, and $1/T_{2D}$ and $1/T_{2A}$ are the respective linewidths of the donor and acceptor chains. Since Δg_A (the deviation of the g value from the free-electron value for the acceptor chain) is only[12] 2×10^{-4}, the dominant term in (1) will be the donor-chain contribution. Therefore the measured linewidth is expected to be proportional to $(\Delta g_D)^2$:

$$T_2^{-1} = \gamma_D (\Delta g_D)^2. \tag{2}$$

Figure 2 shows γ_D as a function of x. The Δg_D values necessary for this plot were taken from low temperature ($T \leq 20°\text{K}$) g values of the corresponding compounds.[13] As previously shown[8] for TTF-TCNQ and as will be presently shown[14] for the other compositions studied in this paper, the measured g values in this low-temperature regime correspond to the donor-chain g values. Figure 2 brings out two very interesting features:

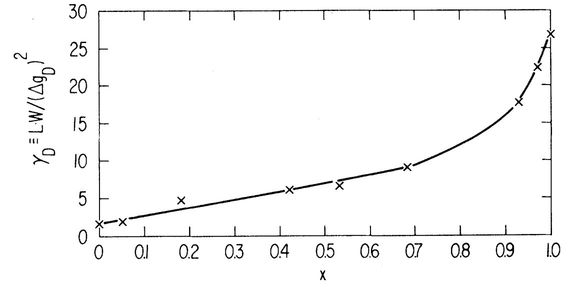

FIG. 2. $\gamma_D = LW/(\Delta g_D)^2$ [where LW is the room temperature linewidth, $(\Delta g_D)^2 = (g_D - g_e)^2$, g_D is the donor-chain g value, and g_e is the free-electron g value] as a function of x — the fraction of TSeF in the donor chain. g_D values were taken from low-temperature ($T \leq 20°\text{K}$) measurements.

(1) The values of γ_D (or linewidths) are very small in comparison to the expected values from Elliott's relationship[10] evaluated for three-dimensional (3D) metals—two orders of magnitude smaller for TTF-TCNQ, for example.

(2) The variation of γ_D with x also indicates an anomalous dependence of the spin-flip matrix element on x, because if the spin-orbit coupling alone were varied by changing the concentration of TSeF on the donor chain, one would expect the whole change in the matrix element to be reflected in the change of Δg_D, and the quantity γ_D would be independent of x. Furthermore, since measurement of the g values of the isostructural series at room temperature indicates that γ_D has a tendency to decrease with increasing x, the spin-flip matrix element is expected to have an even stronger anomalous dependence on x than that shown for γ_D.

To understand the small values of γ_D and their x dependence, we consider how Elliott's analysis of linewidth and resistivity for an isotropic three-dimensional (3D) metal must be modified for a quasi-one-dimensional metal. We neglect electron-electron interactions, mode softening,[15] fluctuating Peierls gap, etc., recognizing that these should be considered especially at low temperatures; but we believe the marked drop in the linewidth-to-resistivity ratio in going to one dimension (1D) will survive in some modified way when these effects are included.

In 3D metals, the dominant electron-phonon scattering processes contributing to both linewidth and resistivity scatter electrons within a shell of width 2 kT straddling the Fermi surface, with or without spin-flip scattering. The relative magnitudes of these processes depend only on the spin-orbit interaction strength through $(\Delta g)^2$, which can be determined independently.

In electronically 1D systems (with flat energy surfaces) the scatterings from $\vec{k}$ to $\vec{k}'$ are of two kinds, both of which are sharply reduced from 3D, much more in their contribution to the linewidth than to the resistivity: (1) $k_\parallel' \simeq k_\parallel$. When an acoustic phonon is involved, these matrix elements vanish approximately (this occurs in 3D only when $\vec{k}' \simeq \vec{k}$). The reduction in resistivity is less than in linewidth since forward scattering contributes little in 3D, too. (2) $k_\parallel' \simeq -k_\parallel$. The spin-flip-scattering matrix element is approximately zero by time-reversal invariance, further reducing the linewidth but not the resistivity. The linewidth is therefore much smaller relative to resistivity than predicted by the Elliott relation.

Deviations from this very small linewidth can arise from a relatively thick Fermi shell (high temperature or narrow bands) and/or from appreciable departures from one-dimensionality ("interchain hybridization") associated with wave-function overlaps in the c and/or a directions.

The increase of γ_D with x at room temperature by a factor of 16 in going from TTF-TCNQ to TSeF-TCNQ is an indication of interchain hybridization, not of a thicker Fermi shell, because the bandwidth of TSeF appears to be wider,[16] not narrower, than that of TTF. Furthermore, the hybridization is more likely to be along the a direction[17] than the c direction for the following reasons:

(1) Although both a and c increase[6] slightly with x, tending to reduce overlaps, the chalcogens are so situated that the increase of their average size with x can overcome the increase in a but not in c.

(2) In $(\text{TSeF})_{0.94}(\text{TTF})_{0.06}\text{TCNQ}$, g value studies for $T \lesssim 20$°K indicate about 50% hybridization between donor and acceptor states at the Fermi energy. For example, g_{c^*} was found to be 2.022 in this alloy, while the calculated g_{c^*} for the donor chain, assuming equal amplitudes on the TTF and TSeF sites of the Fermi-energy wave function, is 2.039 and on the TCNQ sites it is believed to be 2.0025. This contrasts with TTF-TCNQ, where it was shown[8] that the isotropic component of the g value arises solely from the TTF chain, and agrees with that found[18] in TTF-Cl and for the free TTF cation in solution.

(3) The difference between the EPR measured in TTF-TCNQ and in TSeF-TCNQ at low temperatures provides additional evidence for hybridization in the latter but not in the former. In both systems, the magnetic excitations observed at higher temperatures are frozen out. However a Curie tail in the susceptibility, observed between 4 and 10°K, indicates a low concentration of unpaired spins, possibly due to segments of the two kinds of stacks containing odd numbers of sites. Such segments could be produced by occasional imperfections. In TTF-TCNQ Walsh *et al.*[19] performed an extensive study of these unpaired spins in this imperfection-dominated regime and found three resonance lines, two having the g tensor of a free TTF cation, with different orientations, and one having that of a free TCNQ anion; i.e., there was no indication of hybridization. In TSeF-TCNQ at 4°K, by contrast, we find two absorption lines whose g values in the a-c plane as a function of the angle between H_{dc} and the a axis are given in Fig. 3. It is clearly seen that the two absorption lines represent symmetry-related species whose g values correspond to neither TCNQ anions nor TSeF cations. The mixed g values are, therefore, further evidence for hybridization of the wave functions on the donor and acceptor chains in TSeF-TCNQ.

In conclusion, we have argued that electron-phonon coupling plays a major role in the spin relaxation of the isostructural family of organic metals, $(\text{TSeF})_x(\text{TTF})_{1-x}\text{TCNQ}$. The dependence of this relaxation on the fraction of TSeF in the donor chain suggests a picture of hybridized donor-acceptor bands for TSeF-TCNQ in contrast to the nonhybridized bands of TTF-TCNQ.

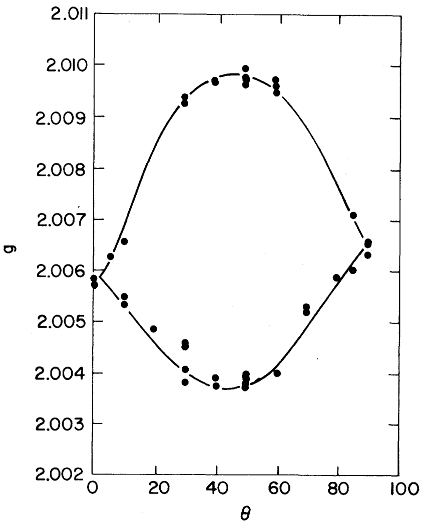

FIG. 3. g anisotropy of TSeF-TCNQ measured at 4°K. The measurement was done on five aligned single crystals.

Finally, we note that this hybridization might be related to the lower metal-insulator transition temperature measured[4] for TSeF-TCNQ than for TTF-TCNQ.[3] Hybridized chains are expected to be less susceptible to a Peierls instability, because the hybridization gap makes it more difficult to achieve a good match between the Fermi surface in the absence of the distortion and the planes in $\vec{k}$ space along which a Peierls distortion creates energy gaps. In addition, the mean-field temperature for a Peierls transition is considerably lower[20] for the TTF chain than for the TCNQ chain in TTF-TCNQ. Since the metal-insulator transition at 54°K in TTF-TCNQ is apparently driven by the TCNQ chain,[20,21] a lower transition temperature in TSeF-TCNQ, where there is interchain hybridization, is expected.

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[13] No intrinsic g values for the donor chain could be measured for TSeF-TCNQ. The value used for evaluation of γ_D is the value extrapolated from the measured one for $(\mathrm{TSeF})_{0.94}(\mathrm{TTF})_{0.06}\mathrm{TCNQ}$.

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[15] Mode softening will tend to increase the measured linewidth; therefore it cannot explain why the linewidths in 1D are narrower than expected from Elliott's relationship. A detailed paper by us and A. N. Bloch, on the theory of the spin-orbit contribution to the linewidth, including the role of mode softening and interchain hybridization, is in preparation.

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