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## Magnetic Studies of Tetrathiofulvalinium Tetracyanoquinodimethanide (TTF-TCNQ)

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EPR and magnetic-susceptibility studies of TTF-TCNQ indicate that in the temperature region  $T \geq 60^\circ\text{K}$  this compound consists of a metallic  $(\text{TTF})^+$  chain and a  $(\text{TCNQ})^-$  chain with localized spins. The metal-insulator transition at  $\sim 60^\circ\text{K}$  is accompanied by a strong interchain interaction.

The magnetic properties of a large number of TCNQ salts have previously been studied.<sup>1</sup> Most of the low- and intermediate-conductivity TCNQ complexes [conductivities below  $10 (\Omega \text{ cm})^{-1}$ ] exhibit a temperature-activated susceptibility, whereas the susceptibility of the highly conductive TCNQ complexes shows a very weak temperature dependence. In TTF-TCNQ, however, despite the unusually high conductivity<sup>2,3</sup> the magnetic susceptibility behavior<sup>2</sup> resembles that of low-conductivity salts.

In order to understand this unusual behavior, we have made an extensive EPR investigation of TTF-TCNQ single crystals as well as static magnetic-susceptibility studies of polycrystalline samples. The EPR measurements were performed at X and K bands. (In the following, whenever the frequency is not specified the related experiment was performed at X band.) Two different types of single crystals were used: Solution-grown<sup>4</sup> crystals, in which the  $b$  axis is the needle axis [conductivity along the  $b$  axis  $\sim (3.3-10) \times 10^2/\Omega \text{ cm}$ ],<sup>5</sup> were used for the  $\vec{H}_1 \parallel \vec{b}$  orientation, while vapor-grown<sup>6</sup> crystals, in which the  $b$  axis

is almost perpendicular to the needle axis [conductivity along the  $b$  axis  $\sim (2-6.7) \times 10^2/\Omega \text{ cm}$ ],<sup>5</sup> were used for the  $\vec{H}_1 \perp \vec{b}$  orientation. Crystals of highest conductivity exhibited Dyson-Bloembergen line shapes at the  $\vec{H}_1 \perp \vec{b}$  orientation. No significant variations of line widths or  $g$  values, for a common orientation, were found between samples grown by these two different methods. The static susceptibility of polycrystalline TTF-TCNQ crystals was measured by the Faraday method in a helium gas atmosphere in the temperature range 2–400°K.

In solutions the reported  $g$  values of  $(\text{TTF})^+$  and  $(\text{TCNQ})^-$  are, respectively, 2.00838<sup>7</sup> and 2.0025.<sup>8</sup> In view of this large difference between the  $g$  values one might expect to observe two distinct absorptions in the solid TTF-TCNQ (actually four because there are two molecules per unit cell<sup>9</sup>). However, over the entire temperature range 20–300°K,<sup>10</sup> in which the susceptibility was found to be temperature activated, only a single line was observed. The principal values of  $g$  at room temperature are  $g_{zz} = 2.0026 \pm 0.0003$ ,  $g_{xx} = 2.0065 \pm 0.0003$ , and  $g_{yy} = 2.0086 \pm 0.0003$ . The  $z$

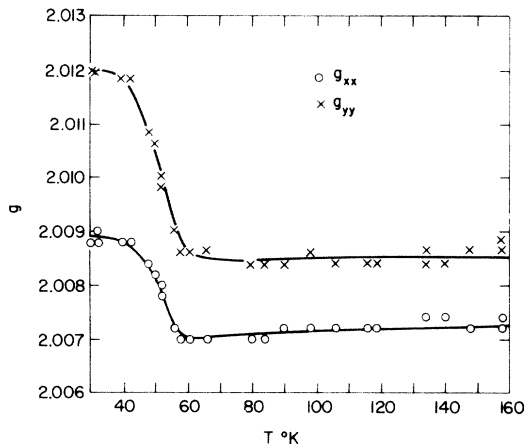


FIG. 1. The principal  $g$  values  $g_{xx}$  and  $g_{yy}$  as a function of temperature.

direction coincides with the  $b$  axis, the  $x$  with the  $a$ , and the  $y$  with the  $c^*$ . The fact that the measured values are indeed  $g$  values was confirmed by measuring the same values at two different frequencies, 9 and 35 GHz. There are two possible explanations for the existence of only a single absorption line. Either the coupling between the stacks exceeds the differences between the respective Larmor frequencies, or one of the absorptions is not detectable experimentally because of the existence of a very fast relaxation on the corresponding chain. (The trivial possibility of an overlap of two absorption lines of comparable intensities and relaxation times and of different  $g$  values was eliminated by comparing the resonance linewidths at 9 and 35 GHz. The linewidths were found to be identical at both frequencies.)

Just as for the conductivity, two distinct temperature ranges emerge for the magnetic data:  $T > 60^\circ\text{K}$  and  $T < 60^\circ\text{K}$ . We will try to determine for each of these temperature ranges which of the two above mentioned mechanisms is responsible for the appearance of a single absorption line. The "metallic" region,  $T > 60^\circ\text{K}$ , is characterized by three distinct features: (1) The measured principal  $g$  values are temperature independent (Fig. 1); (2) the line broadens with decreasing temperature (Fig. 2); (3) the susceptibility is strongly temperature dependent (Fig. 3). Since the line shape of the resonance is Lorentzian the interaction rate between the  $(\text{TTF})^+$  stack ( $F$  stack) and the  $(\text{TCNQ})^-$  stack ( $Q$  stack) is in either the fast or the slow limit compared to the differences between the respective Larmor fre-

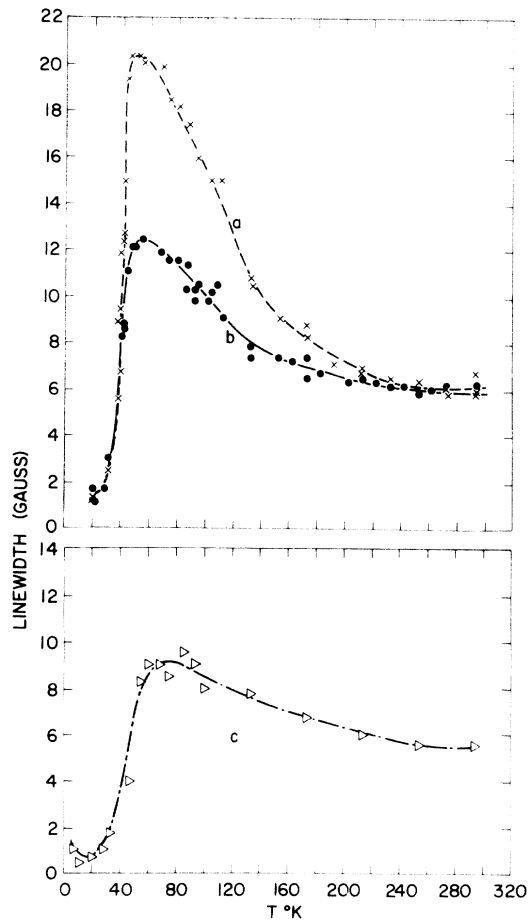


FIG. 2. Variations of EPR linewidth with temperature with the magnetic field parallel to the principal axes. Curves  $a$  and  $b$  are for  $\vec{H}_1 \parallel \vec{b}$  while curve  $c$  is for  $\vec{H}_1 \perp \vec{b}$ .

quencies.

Consider first the strong-coupling limit. The single line is centered at

$$g = g_Q \alpha_Q + g_F \alpha_F, \tag{1}$$

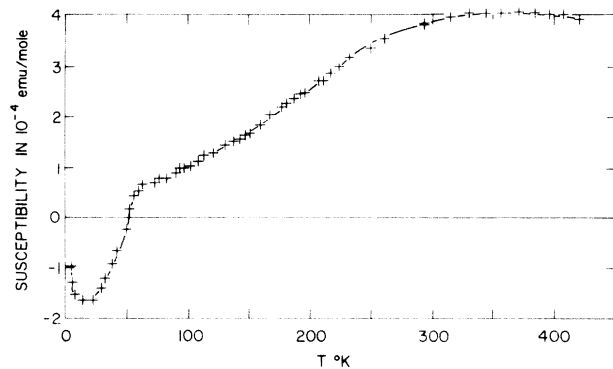


FIG. 3. Static susceptibility as a function of temperature.

where  $g_Q$  and  $g_F$  are the respective  $g$  values of  $(\text{TTF})^+$  and  $(\text{TCNQ})^-$  and  $\alpha_Q$  and  $\alpha_F$  are the respective fractions of the total measured susceptibility on each type of stack. The width of the line is

$$\frac{1}{T_2} = \frac{\alpha_Q}{T_{2Q}} + \frac{\alpha_F}{T_{2F}} + \beta_{FQ}(\nu_Q - \nu_F)^2, \quad (2)$$

where  $T_{2Q}$  and  $T_{2F}$  are the transverse relaxation times for the respective stacks,  $\nu_F$  and  $\nu_Q$  are the Larmor frequencies, and  $\beta_{FQ}$  includes the interaction terms between the different stacks. If this coupling regime were applicable to the "metallic" range, one would have to assume that the term  $\beta_{FQ}(\nu_Q - \nu_F)^2$  due to incomplete averaging of the two resonance frequencies is negligible, since as mentioned earlier the measured linewidth was found to be field independent. An estimate of  $\alpha_Q$  and  $\alpha_F$  can be made from Eq. (1) and the measured  $g$  values.  $\alpha_Q$  is found to be 0.4 while  $\alpha_F$  is 0.6. The temperature-independent values of the measured  $g$  therefore indicate that  $\alpha_Q$  and  $\alpha_F$  are temperature independent. Therefore the temperature dependence of the measured linewidth occurs through  $T_{2Q}$  and  $T_{2F}$ . For simple metals, or even for an organic metal such as N-methyl-phenazinium TCNQ,<sup>11</sup>  $T_2$  has been found to increase with decreasing temperature, and therefore in the strong-coupling limit one expects a decreasing linewidth with decreasing temperature. This is in contrast to the experimental observations. In addition, the temperature independence of  $\alpha_Q$  and  $\alpha_F$  seems to be very strange in view of the strong temperature dependence of the susceptibility. Moreover, a temperature-dependent susceptibility is very unusual again in comparison to other organic metals.<sup>1</sup>

In view of the foregoing we believe that the correct description in the region  $T > 60^\circ\text{K}$  is provided by the weak-coupling limit under the assumption that one of the resonance lines is not observed because of extensive broadening. This assumption is not unreasonable since according to Elliott's formalism<sup>12</sup> the expected resonance linewidth of a metallic  $F$  stack will be almost 3 orders of magnitude larger than that of a metallic  $Q$  stack for comparable scattering times. The detected line has a width of

$$1/T_2 = 1/T_2^0 + P_{QF} \quad (3)$$

where  $1/T_2^0$  is the linewidth in the absence of interchain coupling and  $P_{QF}$  is the interaction term between the  $Q$  and  $F$  stacks. The tempera-

ture dependence of this linewidth is due to the temperature dependence of  $T_2^0$  and  $P_{QF}$ . A comparison of the measured static and spin susceptibilities indicates that most of the susceptibility at  $300^\circ\text{K}$  is seen in the relatively narrow EPR line and that the temperature dependence of the susceptibility is due to the temperature dependence of the intensity of this line. From linewidth considerations it seems that this line is associated with the  $Q$  stack. The temperature-dependent susceptibility can be explained by assuming that in the measured temperature range there is already an energy gap on this stack and the spins are localized. The  $F$  stack on the other hand gives rise to the metallic conductivity.

The most interesting feature of the "insulating" region,  $T < 60^\circ\text{K}$ , is the temperature dependence of the  $g$  values (Fig. 1). The measured  $g$  value shifts gradually toward  $g_F$  and coincides with it at  $20^\circ\text{K}$ . At  $20^\circ\text{K}$ , the average  $g$  value is  $2.0082 \pm 0.0003$  (the measured principal values are 2.012, 2.009, and 2.0036), which is very close to the reported isotropic  $g$  value of 2.00838 for  $(\text{TTF})^+$ . Since in this temperature region both the  $Q$  and  $F$  stacks are expected to be seen, the direction of the  $g$  shift toward  $g_F$  indicates that indeed  $F$  is the conducting chain in the region  $T > 60^\circ\text{K}$ . In addition the temperature dependence of  $g$  and the linewidth indicate that for  $T < 60^\circ\text{K}$  the strong-coupling limit is applicable.

Below  $20^\circ\text{K}$ , the Curie-type behavior of the EPR intensity is typical of many TCNQ salts.<sup>1</sup> It has been<sup>13</sup> attributed to the presence of lattice irregularities which might lead to a finite-chain behavior. Our data indicate that the concentration of the chain-interrupting species is  $\sim 2.5 \times 10^{-3}$  per mole of host.

In conclusion our picture is the following: The "metallic" phase consists of a conducting chain,  $(\text{TTF})^+$ , and a chain with localized spins,  $(\text{TCNQ})^-$ . The coupling between the chains is weak and the system is one-dimensional. In the "insulating" phase there is a strong coupling between the chains and therefore a three-dimensional representation will be more suitable for this phase.

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<sup>5</sup>S. von Molnar, private communication.

<sup>6</sup>Crystals were grown by vapor-phase transport of TTF ( $90^\circ\text{C}$ ) and TCNQ ( $150^\circ\text{C}$ ) in a temperature gradi-

ent  $5\text{--}10^\circ/\text{cm}$  at pressures between  $10^{-3}\text{--}10^{-5}$  Torr. Alternatively, crystals were grown by direct sublimation of TTF-TCNQ powder in the above gradients at source temperatures between  $100\text{--}150^\circ\text{C}$ .

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## Spin-Orbit Splitting at the $\Gamma$ Point in $\text{ZnSe}_x\text{Te}_{1-x}$ Alloys

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Electroreflectance spectra were measured at room temperature to determine the energies of the lowest gap,  $E_0$ , and its spin-orbit-splitting gap,  $E_0 + \Delta_0$ , in  $\text{ZnSe}_x\text{Te}_{1-x}$  alloys as a function of composition  $x$ . The variation with  $x$  of the spin-orbit splitting at the  $\Gamma$  point,  $\Delta_0$ , was found to show convex behavior, confirming our preliminary results deduced from reflectivity measurements. The deviation from linearity of  $\Delta_0$  is  $0.146\text{ eV}$  at  $x = 0.5$ . The bowing parameters of the  $E_0$  and  $E_0 + \Delta_0$  gaps were determined to be  $1.266 \pm 0.023$  and  $0.681 \pm 0.040\text{ eV}$ , respectively.

The composition dependence of spin-orbit splitting in semiconductor alloys is of considerable interest, since it can be used to check the predictions of various theoretical models. Two main approaches are used to explain the observed variation with composition of the various energy gaps: One is the virtual crystal approximation (VCA) in which the fluctuations in the crystal potential are negligible<sup>1-3</sup>; the other is the taking into account of the fluctuations on the basis of the dielectric method.<sup>4</sup> It is not conclusive which approach is best, because both have been successful in predicting the nonlinear composition dependence of the energy gaps. Also both approaches<sup>5-8</sup> may explain the concave variation with composition of the spin-orbit splitting  $\Delta_0$  observed in several III-V alloy systems and in one or two II-VI alloy systems,<sup>5,9</sup> except for

$\text{ZnSe}_x\text{Te}_{1-x}$ .<sup>10</sup> In  $\text{ZnSe}_x\text{Te}_{1-x}$  a convex variation has been suggested.<sup>10</sup> While Hill<sup>5</sup> predicted very recently a concave variation for this system and also for other alloy systems on the basis of the VCA, Van Vechten, Berolo, and Woolley<sup>6,7</sup> have suggested that either a convex or a concave variation may occur.

We measured the electroreflectance (ER) spectra of the  $E_0$  and  $E_0 + \Delta_0$  gaps for  $\text{ZnSe}_x\text{Te}_{1-x}$  alloys using an electrolyte technique with Potentiostat control in a KCl solution. Melt-grown crystals were used for ZnTe, ZnSe, and alloys of  $x = 0.12$  and  $0.20$ , and vapor-phase-grown crystals<sup>11</sup> for  $x = 0.48, 0.79, 0.87$ , and  $0.97$ . They are single crystals except for  $x = 0.12, 0.79$ , and  $0.87$ , which are polycrystals. The inhomogeneities of  $x$  in samples of the alloys are less than  $\pm 0.2\%$  for the vapor-phase-grown crystals and