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Temperature dependence of spin relaxation in quasi-one-dimensional organic metals

Yaffa Tomkiewicz
IBM Thomas J. Watson Research Center, P. O. Box 218, Yorktown Heights, New York 10598

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A study of the temperature dependence of the spin-relaxation rate is presented for various organic conductors in which the spin flip occurs via spin-orbit coupling during an electron-phonon scattering process. The temperature dependence is in no way universal; some compounds such as TTF-TCNQ, TSeF-TCNQ, and HMTTF-TCNQ exhibit an increasing linewidth with decreasing temperature, while others such as TMTTF-TCNQ and TMTSeF-DMTCNQ (the last one over most of the temperature range) exhibit a decreasing linewidth with decreasing temperature. The existence of these very different temperature dependences is interpreted in terms of the existence of at least two competitive processes: (i) Peierls fluctuations on one hand tending to increase the rate of spin-flip scattering with the increase in the amplitude of fluctuations. This effect will tend to increase the linewidth with decreasing temperature, and (ii) the decrease of the number of available states into which the electron can be scattered (as evidenced by the decreasing magnetic susceptibility with decreasing temperature) which tends to reduce the rate of spin flip with decreasing temperature. The actual temperature dependence of the spin relaxation rate depends on which of these two competing mechanisms prevails. The supportive experimental evidence in favor of the role of Peierls fluctuations in spin relaxation is the following: (a) The temperature at which the linewidth reaches its maximum value, for all the compounds for which the linewidth increases with decreasing temperature, is the temperature at which the phase transition occurs. (b) The effects due to doping either the donor or acceptor stack on the temperature dependence of the linewidth are consistent with the effects of doping on the growth of the correlation lengths.

I. INTRODUCTION

Organic metals[1] consist of segregated stacks of cations and anions. It is not necessary for both kinds of stacks to be composed of organic molecules in order to achieve metallic conductivity. A characteristic example of a family of compounds in which only one kind of stack comprises organic molecules is the tetrathiafulvalene (TTF) halides[2,3] family. In all the known cases, however, the conduction is achieved by overlap of the π orbitals of the organic molecules. The planarity of the constituent molecules, combined with the high anisotropy of the π orbitals, gives rise to a highly anisotropic band structure, which is reflected in a highly anisotropic conductivity. Typical ratios of the longitudinal and transverse conductivities, as measured for the most prominent member of the family, tetrathiafulvalenium-tetracyanoquinodimethanide (TTF-TCNQ), are[4,5]: $\sigma_b/\sigma_a = 10^3$; $\sigma_b/\sigma_c^* = 60$. The quasi-one-dimensional nature of the band structures of these compounds makes them interesting in terms of studying the effects of dimensionality on various physical properties.

The subject of this paper is one of the physical properties that depends crucially on the dimensionality: the electron spin relaxation rate. It has been shown previously[6,7] that the relative importance of the dominant processes causing spin relaxation, the spin-spin and the spin-phonon interactions, depends strongly on the dimensionality of the band structure. In isotropic metals, for example, the dominant relaxation process was shown[8-10] to be the spin-lattice relaxation caused by the scattering of conduction electrons by acoustical phonons. Thus both the resistivity and the spin-resonance linewidth are determined by the electron-phonon scattering rate. It was also shown previously[11,12] that for a given scattering rate as measured by resistivity and for a given spin-orbit coupling strength, the rate of spin-flip scattering is much smaller in electronically one-dimensional systems than in three-dimensional systems. One can summarize the detailed discussion in Refs. 11 and 12 in the following way. For systems with flat energy surfaces, there exist two possible kinds of scatterings in terms of their effect on the longitudinal component of the electron wave vector: (a) Scattering in which the change in the longitudinal component of the wave vector, $k_{\parallel}$, is small. We shall refer to this scattering as "forward" scattering despite the fact that Δk is not necessarily forwarded since $k_{\perp}$ does not have to be conserved. (b) Scattering in which the change in $k_{\parallel}$ is large, $\sim 2k_F$. This scattering we shall refer to as "backward" scattering. Both the "forward" and "backward" scatterings are sharply reduced from their values in three-dimensional systems, but the reduction of their contribution to the linewidth is much greater than to the resistivity. The longitudinal component of the phonon wave vector is confined, in the case of one-dimensional forward scattering, to small values because of energy conservation. This limitation significantly reduces the probability of a spin flip in a forward-scattering process since the spin-flip matrix element is proportional[9,12] to $\Delta k_{\parallel}$. The contribution of backward scattering with spin flip to the linewidth is also greatly reduced in electronically one-dimensional systems, because the matrix element for strictly backward spin-flip scattering is zero,[9] the respective states between which the scattering occurs being related by time-reversal symmetry.

The high anisotropy of the conductivity has quite an opposite effect on the dipolar contribution to the linewidth. In those compounds in which the longitudinal conductivity is diffusive, the anisotropy can significantly increase the dipolar linewidth; i.e., motional narrowing, when spin diffusion is confined to one dimension, is much less effective than for a three-dimensional spin diffusion path having the same correlation time.[13-16]

The quasi-one-dimensional nature of the organic conductors has, therefore, two opposing effects on the effective linewidth: reduction of the rate of spin-phonon relaxation and enhancement of the dipolar contribution. Which mechanism dominates the linewidth will depend on the deviation of the Fermi surface from planarity and on the magnitude of the spin-orbit coupling.

In this paper we shall concentrate on those compounds in which, despite their quasi-one-dimensional nature, the spin-phonon mechanism is the dominant relaxation process. The subject of the paper is the temperature dependence of the spin relaxation rate. We shall present several observed trends. The most unusual one is an increasing relaxation rate with decreasing temperature observed for some of the compounds, TTF-TCNQ, diselenadithiafulvalene-tetracyanoquinodimethane (DSeDTF-TCNQ), hexamethyltetrathiafulvalene-tetracyanoquinodimethane (HMTTF-TCNQ), tetraselenafulvalene-tetracyanoquinodimethane (TSeF-TCNQ), *in the regime of metallic conductivity*, i.e., in a temperature range where the conductivity increases with decreasing temperature. The temperature dependence of the conductivity implies that the rate of electron scattering is *decreasing* with *decreasing* temperature, while the temperature dependence of the linewidth suggests that the rate of electron scattering with spin flip is *increasing* with *decreasing* temperature. Since the two scattering processes are normally (at least in a situation in which the origin of the resistivity is the electron-phonon interaction) proportional to each other, this unusual behavior requires explanation. We shall also show that the previously described linewidth variation with temperature is not universal for all the organic conductors. Some of them, such as tetramethyltetrathiafulvalene-tetracyanoquinodimethane (TMTTF-TCNQ), exhibit a decreasing linewidth with decreasing temperature over the whole range of metallic conductivity. Others, such as tetramethytetraselenafulvalene-dimethyltetracyanoquinodimethane (TMTSeF-DMTCNQ), have a decreasing linewidth over part of the metallic temperature range and an increasing linewidth over the rest.

In this paper we shall show these experimental results. We shall also offer a tentative explanation according to which the observed temperature dependence of the linewidth depends on which of the following two competitive processes is dominant: phonon softening, on the one hand, which increases the $2k_F$ phonon population with decreasing temperature, and a decreasing number of available electronic states at the Fermi level, on the other hand, which decreases the probability of electron scattering. The latter situation can occur as a consequence of either one of two possibilities, the opening of a gap in the density of states caused by interstack banding[17] or the opening of a pseudogap by Peierls fluctuations. We shall also present the effects of isostructural doping on the temperature dependence of the linewidth and show that these results are consistent with the expected effects of impurities on phonon softening. Finally, detailed study of the temperature dependence of the linewidth of TTF-TCNQ will be presented and compared with the detailed x-ray scattering results obtained for this compound by Khanna *et al.*[18]

II. EXPERIMENTAL

The EPR absorption spectra were measured at 10^{10} Hz. In some cases the broadness of the signal and the small size of the available single crystals required alignment of several single crystals. Only for TTF-TCNQ and TMTTF-TCNQ was it possible to perform an EPR study on one single crystal. In all the other cases a multitude of aligned crystals was used, at least of the order of ten. The temperature was controlled and varied by an Air Products Heli-Tran Dewar and Scientific Instruments temperature controller. The derivative of the EPR absorption line was digitized. At least 400 points for each spectrum were fitted with a model Lorentzian derivative line. In most cases we report the linewidths of the model Lorentzian lines.

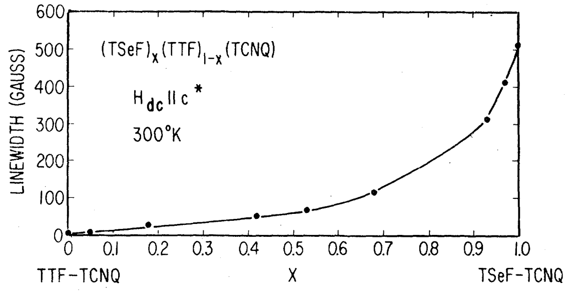

FIG. 1. Linewidth of $(\mathrm{TSeF})_x(\mathrm{TTF})_{1-x}(\mathrm{TCNQ})$ $0 \leqslant x \leqslant 1$ as a function of the concentration, x, of TSeF in the donor stack. The measurements were taken at 300 K for $\vec{H}_{dc} \| \vec{c}^*$ orientation.

III. RESULTS AND DISCUSSION

As was mentioned in Sec. I, and as was discussed extensively before,[11,12] the quasi-one-dimensional band structure of the organic conductors causes a reduction of the spin-flip scattering rate caused by the spin-phonon interaction. Extreme anisotropy can so reduce this scattering rate that the dominant spin relaxation will be of a different character altogether, as was found to be the case for the TTF halides,[7] where dipolar broadening was shown to dominate. Therefore, the first requirement in any linewidth analysis is to determine the dominant relaxation mechanism. This was done for the isostructural[19] family $(\mathrm{TSeF})_x(\mathrm{TTF})_{1-x}(\mathrm{TCNQ})$, $0 \leqslant x \leqslant 1$, in the following way: a characteristic feature of the spin-phonon relaxation mechanism is that, other things being equal, the linewidth should vary as $(\Delta g)^2$, where Δg is the deviation of the g value from the free-electron g value of 2.0023, because Δg is a measure of the spin-orbit coupling strength. Since the spin-orbit coupling of TSeF is significantly larger than that of TTF,[11] a continuous variation of the average g value in the isostructural family can be achieved by doping TTF-TCNQ with varying amounts of TSeF-TCNQ. As the concentration of TSeF-TCNQ in TTF-TCNQ is increased, one would expect an increasing linewidth, which is indeed observed (Fig. 1, curve a). This increase of linewidth with doping, however, could also be due to the growth of another relaxation mechanism different from that which dominates the relaxation in the pure compound. To check if this is indeed the case, we measured the angular dependence of the linewidth in the pure and doped compounds. If the relaxation mechanisms were different, one would expect a different angular dependence of the linewidth for each mechanism. The angular dependence of the linewidth in the $\vec{a}$-$\vec{c}$ crystallographic plane is illustrated in Fig. 2 for TTF-TCNQ, $(\mathrm{TTF})_{0.18}(\mathrm{TSeF})_{0.82}(\mathrm{TCNQ})$, and TSeF-TCNQ. In spite of the big variation in the magnitude of the linewidth, the angular dependences obtained for all three compounds look strikingly similar, indicating a similar relaxation mechanism over the whole range of solid solutions.

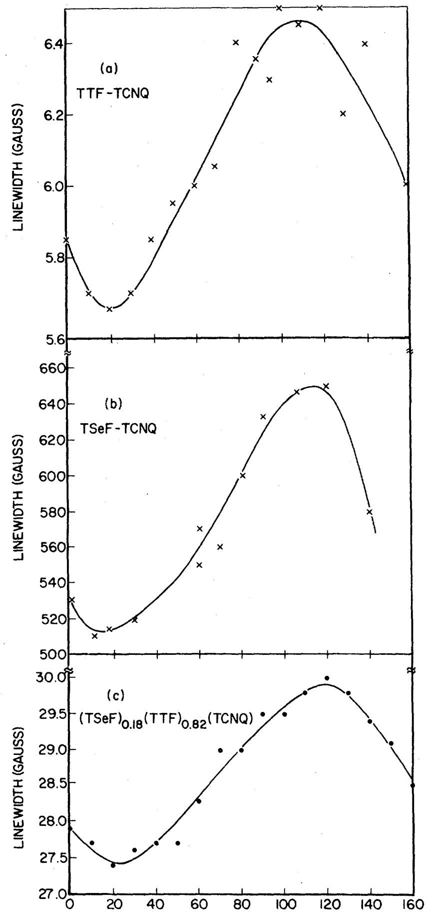

FIG. 2. Angular dependence of the linewidth in $\vec{a}$-$\vec{c}^*$ crystallographic plane for (a) TTF-TCNQ, (b) TSeF-TCNQ, and (c) $(\mathrm{TSeF})_{0.18}(\mathrm{TTF})_{0.82}(\mathrm{TCNQ})$.

To see if the single spin-relaxation mechanism is indeed the spin-phonon interaction via spin-orbit coupling, we have normalized the measured linewidth to $(\Delta g_F)^2$, where Δg_F is the g shift measured for the donor stack.[20] The results are shown in Fig. 3. Two concentration ranges emerge, which we discuss separately:

(i) $0 \leqslant x \leqslant 0.68$. In this range of x, the strong dependence of the linewidth on dopant concentration is appreciably reduced by the $(\Delta g)^2$ normalization. For example, comparison of the unnormalized linewidths for $x = 0$ and $x = 0.68$ shows a dramatic increase by a factor of 25 in going to the latter

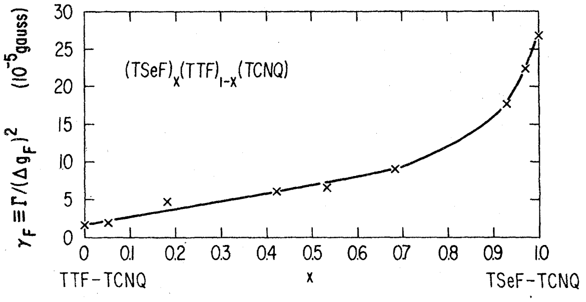

FIG. 3. Linewidth of $(\mathrm{TSeF})_x(\mathrm{TTF})_{1-x}(\mathrm{TCNQ})$ $0 \leqslant x \leqslant 1$ at 300 K normalized to $(\Delta g_F)^2$, where Δg_F is the deviation of the donor stack g value from the free-electron value. g_F was obtained by measuring the corresponding g value of the single EPR absorption line in a temperature range in which all the spin excitations reside on the donor stack. Since no such measurements could be performed on compounds with $x > 0.94$, the g values for these particular compounds were extrapolated from lower values of x.

concentration, while a comparison of the normalized linewidths shows an increase by only a factor of 3. The behavior in this concentration regime is thus consistent with the origin of the linewidth being the spin-phonon interaction. The slow increase of the normalized linewidth with x observed in this concentration regime can be residue of the phenomenon observed in the second concentration regime.

A linewidth proportional to $(\Delta g_F)^2$ can also result if there is incomplete averaging between the donor and acceptor stacks. The different stacks, on which coherent one-dimensional motion occurs, are coupled by diffusive hopping of the electrons. Since the donor and acceptor stacks have different g values, the linewidth of the absorption of the motionally averaged line has a term proportional to $(\omega_F - \omega_Q)^2/\nu_{FQ}$ where ω_F and ω_Q are the Larmor frequencies of the donor and acceptor stacks and ν_{FQ} is the interstack hopping rate. Since the g value of the TCNQ is very close[21] to the free-electron g value, this term will be proportional to $(\Delta g_F)^2$. There is, however, a difference between this contribution to the linewidth, resulting from incomplete averaging, and the linewidth derived solely from the spin-phonon mechanism. In the latter case the linewidth would be field independent, since it depends on only the spin-orbit coupling, while in the contribution of incomplete averaging, the linewidth would vary with the square of the magnetic field. Thus the field dependence of the measured linewidth can distinguish between these two mechanisms. The linewidth of TTF-TCNQ was found to be field independent[22] for fields ranging between and 10 and 14 000 G. Although the field dependence of the linewidth was measured only for TTF-TCNQ, we shall conclude that incomplete motional averaging has no significant contribution to the linewidth, because the mechanism of the spin relaxation is the same for all the members of the solid solution series as we discussed above.

(ii) $0.68 \leqslant x \leqslant 1$. In this range of x, there is still a strong dependence on x, even for the normalized linewidth. For example, the normalized linewidth is 16 times larger at $x = 1$ than at $x = 0$. This difference is attributed[11,12] to a smaller anisotropy in the band structure of TSeF-TCNQ than in that of TTF-TCNQ. The difference in anisotropy was confirmed by transverse conductivity measurements[23] in TSeF-TCNQ, which indicate that the conductivity in the direction corresponding to the overlap of the donor and acceptor wave functions is about five times greater than its value in TTF-TCNQ while the longitudinal conductivities are comparable. The hybridization between donor- and acceptor-stack wave functions causing banding in the $\vec{a}$ direction is expected to be affected by the introduction of impurities, the reason being that impurities cause a smearing of the k values (since the electrons no longer see a periodic potential). k smearing of energy eigenstates is equivalent to energy smearing of states of definite k and therefore the energy degeneracy, which is essential for transverse banding, is less sharp. A reduction in transverse banding upon doping is expected to affect the magnitude of the linewidth in agreement with the experimental observation. A detailed discussion on this subject will be found in Ref. 11.

Having established that the spin relaxation occurs via the spin-phonon interaction, let us turn to the temperature dependence of this process, which is the subject of this paper. Curves a, b, and c, of Fig. 4 describe the temperature dependence of the EPR linewidth of TTF-TCNQ, TSeF-TCNQ, and DSeDTF-TCNQ, respectively. The measurements were taken with the magnetic field parallel to the $\vec{c}^*$ direction. All three compounds exhibit an increasing linewidth with decreasing temperature in the metallic regime. In the relaxation mechanism commonly accepted for three-dimensional metals, an increase in conductivity, with decreasing temperature, should be accompanied by a *decrease* in linewidth. The reason for this is that the decrease in the rate of electron-phonon scattering, which is predominantly without spin-flip, implied by the increase in the conductivity, should also reduce the rate of the spin-flip scattering. However, in these materials this is clearly not the situation.

In order to understand this unusual temperature

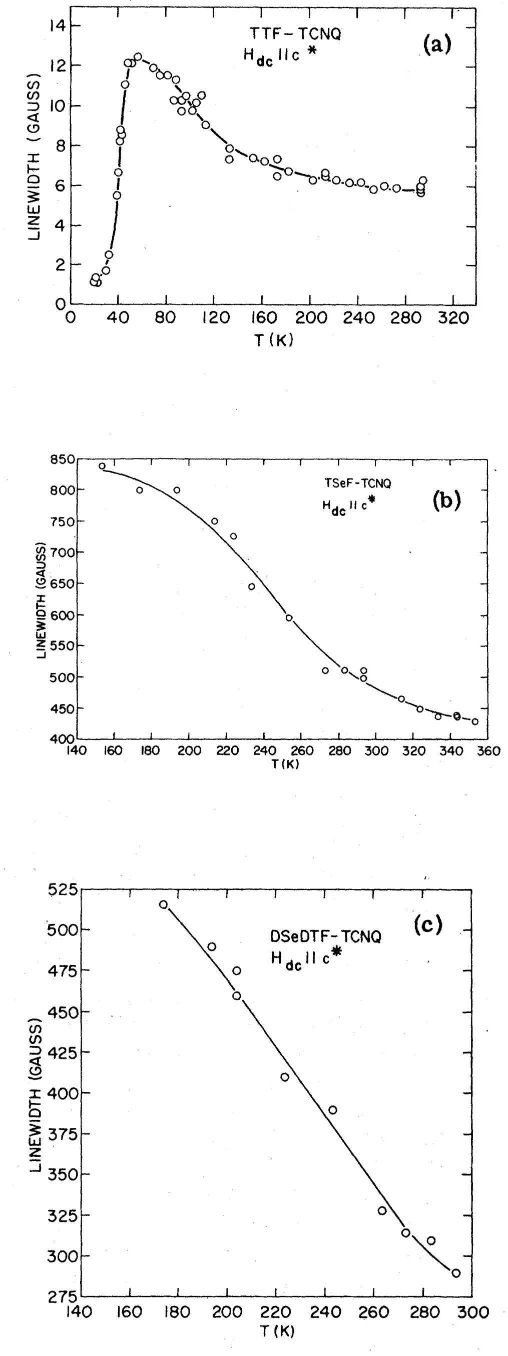

FIG. 4. Temperature dependence of the linewidth for $\vec{H}_{dc} \| \vec{c}^*$ orientation for (a) TTF-TCNQ, (b) TSeF-TCNQ, and (c) DSeDTF-TCNQ.

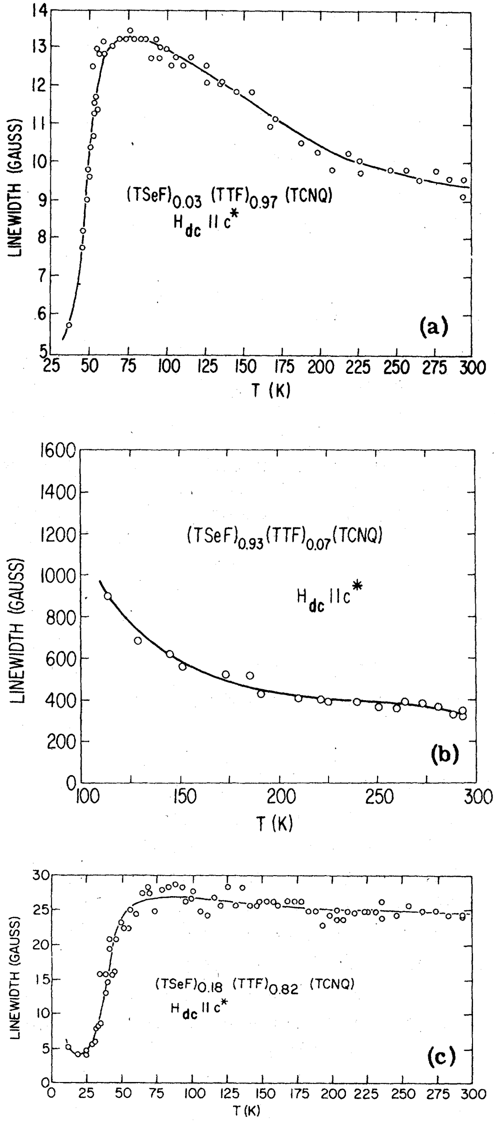

FIG. 5. Temperature dependence of the linewidth for several members of the family $(TSeF)_x(TTF)_{1-x}(TCNQ)$, $0 \leq x \leq 1$. (a) $(TSeF)_{0.03}(TTF)_{0.97}(TCNQ)$, (b) $(TSeF)_{0.93}(TTF)_{0.07}(TCNQ)$, and (c) $(TSeF)_{0.18}(TTF)_{0.82}(TCNQ)$. All the measurements were taken in the $H_{dc} \| \vec{c}^*$ orientation.

dependence of the linewidth in "pure" materials, we have studied the temperature dependence of the EPR linewidths measured for various other members of the series of solid solutions $(TSeF)_x(TTF)_{1-x}(TCNQ)$, $0 \leq x \leq 1$. Representative curves are shown in Fig. 5 for $x = 0.03$, $x = 0.18$, and $x = 0.93$. Comparison of the temperature dependence of the linewidth of TTF-TCNQ [4(a)] with the corresponding curve for $(TSeF)_{0.03}(TTF)_{0.97}(TCNQ)$ [5(a)] and that of TSeF-TCNQ [4(b)] with the corresponding curves for $(TSeF)_{0.93}(TTF)_{0.07}(TCNQ)$ [5(b)] clearly indicates that the temperature dependence of the linewidth in the metallic regime is greatly reduced by doping. Particularly interesting is the curve for

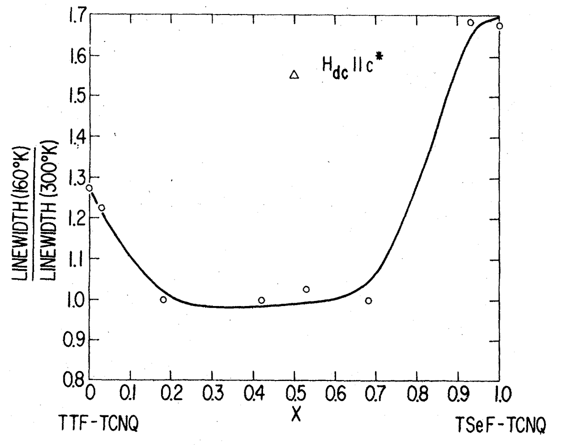

FIG. 6. Dependence of the ratio of the EPR linewidth measured at 160 K to the linewidth measured at 300 K on x, the fraction of TSeF in the donor stack. These data points are the open circles while the corresponding ratio for DSeDTF-TCNQ appears as an open triangle.

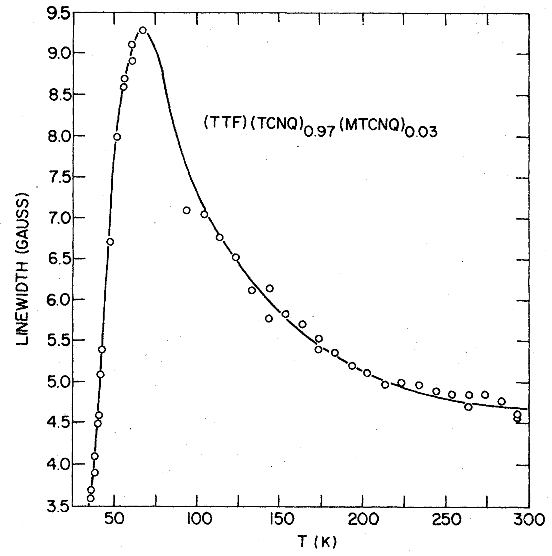

FIG. 7. EPR linewidth of $(TTF)(MTCNQ)_{0.03}(TCNQ)_{0.97}$ as a function of temperature. The measurements were taken in the $\vec{H}_{dc} \parallel \vec{c}^*$ orientation.

$(TSeF)_{0.18}(TTF)_{0.82}(TCNQ)$ [5(c)]. As is seen from this curve, the linewidth is approximately temperature independent over the whole metallic regime. The effect of dopants on the temperature dependence of the linewidth is brought out very clearly in Fig. 6, where the ratio of the linewidth at 160 K to the linewidth at 300 K is shown as function of x, the fraction of TSeF in the donor stack. The reason for the choice of 160 K as the lower limit for the range of study is the fact that the excessive broadening of the linewidth of TSeF-TCNQ (800 G at 160 K) combined with its decreasing susceptibility[24] limits our measurements, because of sensitivity considerations, to $T > 160$ K.

It should be pointed out that not only doping of the donor stacks but also doping of the acceptor stacks has a pronounced effect on the increase in the linewidth as a function of decreasing temperature. The effect on the linewidth of doping the acceptor stacks of TTF-TCNQ with about 3% methytetracyanoquinodimethane (MTCNQ) is shown in Fig. 7. While the doping of the donor stacks was performed with a dopant having a different g value than that of the original stack (either TSeF doping in a TTF stack or TTF doping in a TSeF stack) the doping of the acceptor stacks was done with a dopant of a very similar g value (MTCNQ into a TCNQ stack). Since the effects of both kinds of doping on the temperature dependence of the linewidth are very similar, it seems that these effects are not related to the difference between the spin-orbit coupling of the dopant and the parent compound.

What, then, is the origin of the doping effect, and how do the results of doping help to explain the unexpected temperature dependence of the linewidth? The x-ray spectra of both TTF-TCNQ and TSeF-TCNQ show precursors of superstructure well above their respective phase transitions,[18,25,26] namely, Peierls fluctuations occur well above the temperature corresponding to the onset of three-dimensional ordering. In principle, dopants introduced into systems that manifest Kohn-anomalous phonons and Peierls fluctuations can reduce the softening of the phonons and inhibit the growth of both the amplitude and correlation length of the related Peierls fluctuations. The phonon softening is reduced because of the smearing of electron wave functions in k space; Peierls fluctuations are inhibited by the tendency of the dopants to pin the phase at random values, thereby preventing the growth of correlations both along and between stacks. Indeed, we have evidence that the same specific doping that affects the temperature dependence of the linewidth also has pronounced effects on the phase transitions.[27-29] For example, donor-stack doping in TTF-TCNQ by 3% TSeF affects[27] both the acceptor- and donor-ordering temperatures 53 and 49 K, respectively, and the transition at 38 K, having a much more pronounced effect on the transitions in which the donor stack is involved directly (at 49 and 38 K) than on the transition in which the donor stack is not involved (at 53 K). On the other hand all the transitions seemed to be affected considerably by acceptor-stack doping.[27] Doping of

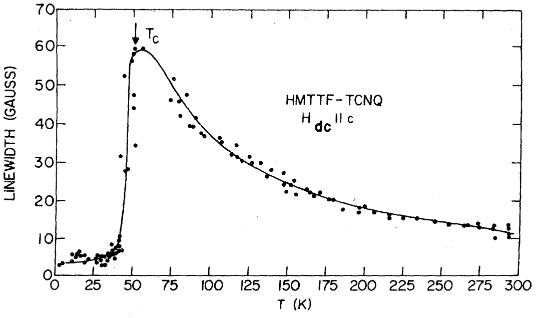

FIG. 8. EPR linewidth of HMTTF-TCNQ, measured in the $\vec{H}_{dc} \parallel \vec{c}$ orientation, as a function of temperature.

the donor stacks in TSeF-TCNQ by TTF also has pronounced effects—what appears to be a single phase transition in TSeF-TCNQ[29,30] splits, as a consequence of doping, into two transitions.[28] Thus we can observe that in both the investigated cases (TTF-TCNQ and TSeF-TCNQ), doping that was found to affect the temperature dependence of the linewidth was also found to affect the respective Peierls transitions. This coincidence suggests that there might be a connection between the existence of Peierls fluctuations and the observed increase of linewidth with decreasing temperature.

An additional experimental finding indicating that the existence of Peierls fluctuations has a bearing on the increase of the linewidth with decreasing temperature is the following: the temperature at which the linewidth peaks corresponds to the temperature at which the phase transition occurs. The effect of the phase transition on other physical properties such as the dc conductivity and magnetic susceptibility is less dramatic—it is seen in their first temperature derivatives. The peak in the conductivity occurs typically as a higher temperature than the metal-insulator transition. The example that best demonstrates the difference between the temperature dependence of the linewidth and conductivity in relation to the phase transition is HMTTF-TCNQ. The conductivity of this compound peaks at 80 K,[31] while the linewidth, as seen in Fig. 8, peaks at 50 K. The latter temperature corresponds[31] to the metal-insulator transition. In TTF-TCNQ a similar situation occurs, although it is less striking than in HMTTF-TCNQ. The linewidth, as seen in Fig. 9, is temperature independent between 60 and 53 K. In this particular compound the actual phase transition occurs at 53 K while the conductivity reaches its maximum value at 60 K. Both examples demonstrate that the scattering time as reflected in the conductivity does not seem to affect the linewidth which seems to follow the same trend (namely, increases with decreasing temperature) until the phase transition occurs. If indeed dynamic Peierls fluctuations are the cause of the increase in linewidth, this result is expected, since as the three-dimensional ordering of the charge-density waves occurs, the fluctuations begin to decrease and the linewidth should cease to increase.

We can further check the correlation between Peierls fluctuations and the temperature dependence of the linewidth by comparing the results of very detailed x-ray and neutron diffraction work performed on TTF-TCNQ[18,25,32-37] and recent more-refined dc conductivity studies[38] with a detailed linewidth study in this compound. Figure 9 describes the temperature dependence of the linewidth of TTF-TCNQ for $\vec{H}_{dc} \parallel \vec{a}$. An interesting feature of this figure is the sudden increase of the linewidth occurring in the vicinity of 170 K. This feature is brought out in a more detailed fashion in Fig. 10 describing the derivative of the linewidth as a function of temperature for $T > 100$ K. It is clearly seen that the slope of the derivative

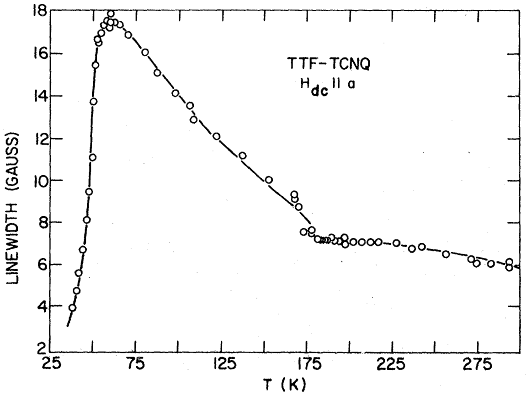

FIG. 9. EPR linewidth of TTF-TCNQ as a function of temperature in the orientation $\vec{H}_{dc} \parallel \vec{a}$.

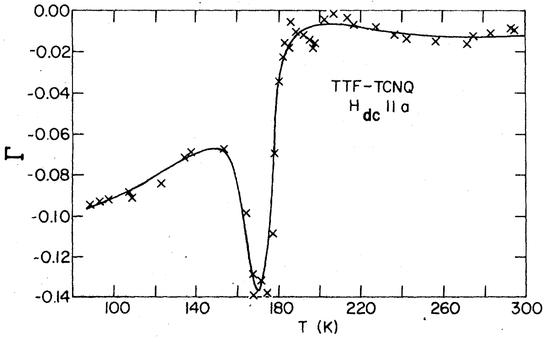

FIG. 10. Derivative of the EPR linewidth of TTF-TCNQ as a function of temperature for $T > 100$ K. The linewidth was measured at $\vec{H}_{dc} \parallel \vec{a}$.

changes in the vicinity of 170 K—it is bigger for the lower temperatures. At roughly the same temperature, the intensity of the diffuse x-ray scattering on the $2k_F$ sheets starts to increase[18] and there is a discontinuous increase in the conductivity.[38]

An additional interesting feature of the temperature dependence of the linewidth is shown in Fig. 11, which exhibits the derivative of the linewidth as a function of temperature for $T < 140$ K for the two crystallographic orientations $\vec{H}_{dc}\parallel\vec{a}$, [Fig. 11(a)] and $\vec{H}_{dc}\parallel\vec{c}^*$ [Fig. 11(b)]. The derivative peaks at 49 ± 1 K. Phase transition at this temperature was predicted[39] and later confirmed experimentally[25,35] to be the ordering temperature of the TTF stacks. At this temperature the transverse periodicity of the lattice starts to shift from $2a$. Recently the $2k_F$ phonons with longitudinal polarization were found[18] to condense at this temperature. Since most of the magnetic susceptibility resides on the TTF stacks[40] in the temperature range $T < 54$ K, the spin relaxation rate is expected to be sensitive to the charge-density-wave condensation occurring on this stack.

The conclusion of the experimental results presented above is that it seems plausible, but by no means definite, that the source of the unusual temperature dependence of the linewidth is related to Peierls fluctuations. Why should either Peierls fluctuations or Kohn anomalous phonons increase the spin-flip rate? In principle the population of the $2k_F$ phonons increases with decreasing temperature as one approaches the transition temperature. Since the spin relaxation rate is proportional to the phonon population, it should increase with decreasing temperature.[41] Phonon softening should affect the linewidth, however, only if $2k_F$ phonons have a nonzero matrix element for spin-flip scattering, i.e., if the system does not have a strictly one-dimensional band structure. Peierls fluctuations, on the other hand, can by the disorder which they introduce relax the selection rule causing the matrix element for strict backward scattering to be zero.

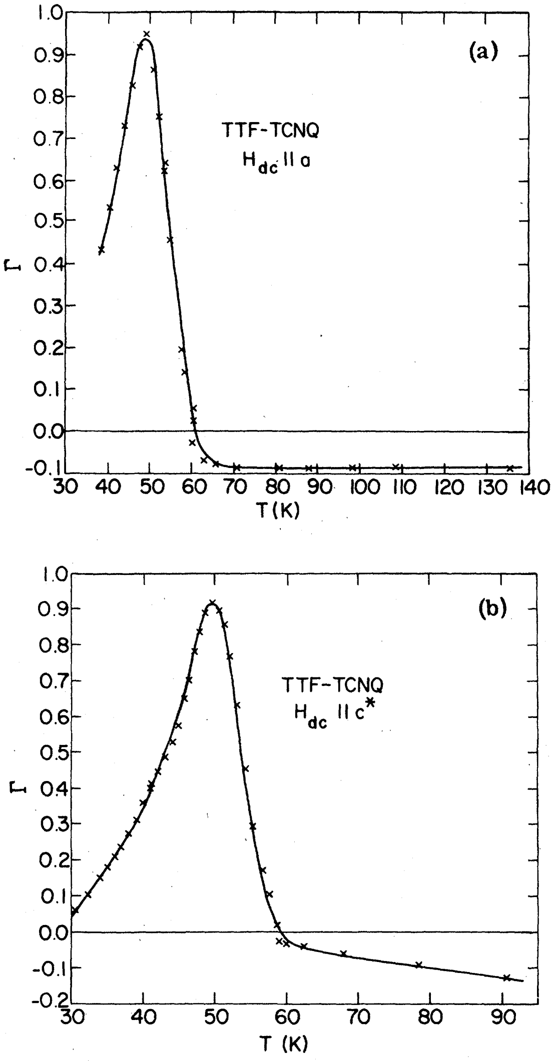

FIG. 11. Derivative of the linewidth of TTF-TCNQ as a function of temperature for $T < 100$ K, at different orientations of the magnetic field with respect to the crystallographic axes. (a) $\vec{H}_{dc}\parallel\vec{a}$. (b) $\vec{H}_{dc}\parallel\vec{c}^*$.

In the spin-phonon mechanism, the spin relaxation rate is proportional not only to the phonon population but also to the density of states at the Fermi level. In the noninteracting-electron picture[42] an experimental measure of the density of states at the Fermi level is the magnetic susceptibility. A characteristic feature of the organic metals of interest is their decreasing susceptibility as a function of decreasing temperature in the range of metallic conductivity.[43] This decrease suggests the existence of either a gap or a pseudogap in the density of states. The origin of this gap is controversial.[44] However independent of its origin, the observed decrease of the density of states as a function of decreasing temperature should decrease the magnitude of the measured linewidth, thus providing a competing mechanism to the previously described effect of fluctuations which increases the linewidth.

In principle there can be situations in which this competing mechanism wins, as can be seen in Fig. 12, where the linewidth of TMTTF-TCNQ is displayed as a function of temperature for crystallographic orientations in which the static magnetic field is both parallel and perpendicular to the stacking axis. The linewidth of this compound decreases as a function of decreasing temperature

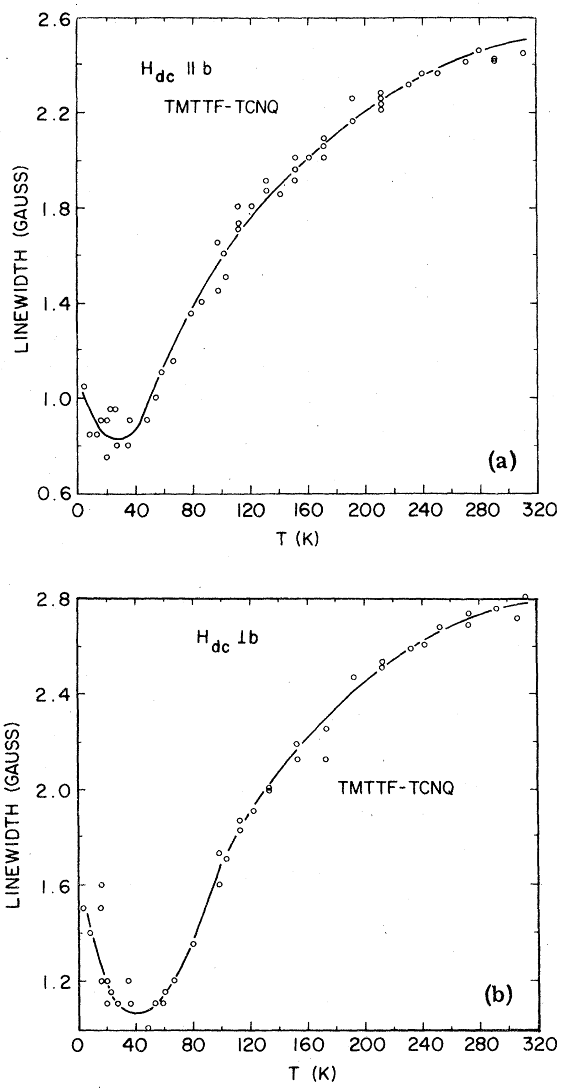

FIG. 12. Linewidth of TMTTF-TCNQ as a function of temperature. (a) Orientation in which the static field is parallel to the stacking axis. (b) Orientation in which the static field is perpendicular to the stacking axis.

over the whole temperature range of the metallic conductivity. Another example in which the actual temperature dependence of the linewidth could be determined by the competition between different processes is demonstrated in Fig. 13, where the temperature dependence of the linewidth of TMTSeF-DMTCNQ is shown. As is seen in this figure, down to a temperature of about 70 K the linewidth decreases with decreasing temperature. At lower temperatures, it increases with decreasing temperature until the phase transition[45] at 42.5 K. At this temperature the slope of the linewidth versus temperature changes again as the linewidth starts decreasing with decreasing temperature. A possible interpretation of this behavior is the following: as the temperature decreases below 300 K, the process that determines the temperature dependence of the linewidth is the decrease of density of states, which was observed in the magnetic susceptibility measurements.[44] However, as one approaches the phase transition temperature the fluctuation effects become important and the linewidth begins to increase despite the continuing decrease in the density of states.

It is worthwhile mentioning that those particular compounds in which the linewidth was found to decrease with decreasing temperature are those in which the interstack banding is comparatively weak, TMTTF-TCNQ and TMTSeF-DMTCNQ. In both cases the information about the magnitude of the interstack coupling was derived from the magnitude of the linewidth normalized to the appropriate spin-orbit coupling. The normalized value of the linewidth in these compounds is smaller than in any other compound belonging to this particular family of organic conductors, indicating a lower dimensionality. The relatively small magnitude of the interstack hopping rate in these particular compounds can in principle prevent the softening of the $2k_F$ phonons from affecting the linewidth since in a strictly one-dimensional system back scattering does not contribute to spin-flip. This might be the reason that in both TMTTF-TCNQ and TMTSeF-DMTCNQ the mechanisms which determines the spin relaxation rate in most of the metallic range is the decreasing density of

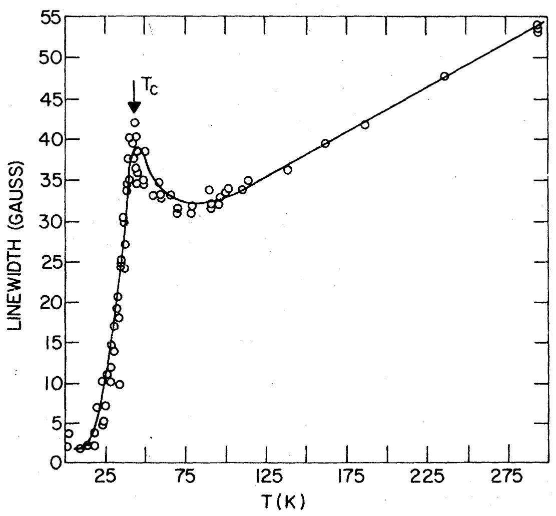

FIG. 13. Linewidth of TMTSeF-DMTCNQ as a function of temperature.

states with decreasing temperature shown to exist by susceptibility measurements. However, since no diffuse x-rays measurements have been performed on these compounds until now, one cannot rule out the possibility that in these compounds phonon softening and the build up of Peierls fluctuations have a very different temperature dependence and that this is the source of the temperature dependence of their linewidths.

IV. SUMMARY AND CONCLUSIONS

In this paper we have presented an experimental study of the temperature dependence of the spin-relaxation rate in several representative organic conductors. We have argued that if indeed spin relaxation is dominated by the spin-phonon mechanism, then the increase of linewidth with decreasing temperature could be related to the existence of Peierls fluctuations above the metal-insulator transition temperature. The supportive experimental evidence for this picture can be summarized in the following fashion: (i) The temperature at which the linewidth reaches its maximum value corresponds to the temperature at which the phase transition occurs. (ii) The effects of doping on the temperature dependence of the linewidth are consistent with the effects of doping on the growth of correlation lengths.

The variety of temperature dependences observed for the various compounds, some of which exhibit increasing linewidth and some of which exhibit decreasing linewidth with decreasing temperature, is understood in terms of having at least two competitive processes determining the actual temperature dependence of the linewidth. On the one hand, scattering off Peierls fluctuations will tend to increase the linewidth with decreasing temperature, while on the other hand, a decreasing density of states with decreasing temperature, whatever its source is, will tend to decrease the linewidth. The effectiveness of the Peierls fluctuations in increasing the linewidth with decreasing temperature is shown experimentally to be dependent on the magnitude of the interstack hopping rate.

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[20] The donor-stack g values were derived in the following fashion. The characteristic temperature dependence, in the $T < T_c$ range (T_c is the metal-insulator transition temperature) of the g values in the family of $(\mathrm{TSeF})_x\,(\mathrm{TTF})_{1-x}\,(\mathrm{TCNQ})$ $0 \leq x \leq 1$, can be described by a strongly increasing g with decreasing temperature until it saturates at a value whose magnitude varies linearly with x. For the particular case of TTF-TCNQ, it was shown [Y. Tomkiewicz, A. R. Taranko, and J. B. Torrance, Phys. Rev. B 15, 1017 (1977); Phys. Rev. Lett. 36, 751 (1976)] that: (i) The gradual increase of g for $T < T_c$ is caused by the existence of gaps of different magnitude in the magnetic excitations spectra on the donor and acceptor stacks, the gap on the donor stack being significantly smaller. (ii) The temperature-independent g value corresponds to the donor-stack g value. Thus the physical meaning of the temperature independence of g is that all the magnetic excitations at the corresponding temperature range reside on the donor stack. By analogy to TTF-TCNQ, the value at which the g value of the alloys saturates is referred to as the donor-stack g value and is used for normalization of the measured linewidth. However, no low-temperature spin resonance could be detected for $x > 0.94$. Thus the appropriate g-values for the donor stack for $x > 0.94$ were determined by extrapolation from lower values of x.

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[41] Although qualitatively phonon softening can explain the increasing linewidth in quasi-one-dimensional systems there exists the following problem (Ref. 12). In principle phonon softening increases the $2k_F$ phonon population but the total number of soft phonons in the vicinity of $2k_F$ can decrease. Since these phonons also contribute to the spin-flip process, a situation in which the softening actually reduces the rate of spin flip can occur. Thus it seems that the actual effect of phonon softening on spin flip depends on the detailed temperature dependence of the softening.

[42] In this stage it is not clear at all whether the noninteracting-electrons model is the right approximation for the various organic metals. For TTF-TCNQ, for example, there exists definite evidence [see, for example, J. B. Torrance, Lecture Notes in Physics, No. 65, edited by L. Pal, G. Grüner, A. Jánossy, and J. Solyom (Academiai Kiado, Budapest, and Springer-Verlag, Berlin, Heidelberg, and New York, 1977); *Chemistry and Physics of One-Dimensional Metals*, *NATO Advanced Study Institutes Series* (*Physics*), Vol. 25, edited by H. J. Keller (Plenum, New York, 1977); J. B. Torrance, Y. Tomkiewicz, and B. D. Silverman, Phys. Rev. B 15, 4738 (1977)] that this model might not be applicable. No similar evidence exists with regard to other compounds, perhaps because of a lack of a similar wealth of experimental information. We shall in this paper use the noninteracting-electrons picture not necessarily because we believe that it describes the investigated compounds in an accurate manner but as a zeroth-order approximation.

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