

Finally we contrast the localized excitations underlying the phenomena discussed in this Letter with the spin-flip Raman scattering associated with free and bound electrons (holes).⁸ In $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ and $\text{Cd}_{1-x}\text{Mn}_x\text{S}$ such transitions are characterized by large g factors arising from the band-electron- Mn^{++} exchange interaction.⁹ In $\text{Cd}_{1-x}\text{Mn}_x\text{Te}$ we have observed a spin-flip Raman line with effective g factors in excess of 80.

The work reported in this Letter has been supported in part by the National Science Foundation Grant No. DMR81-06144 and the National Science Foundation—Materials Research Laboratory Program No. DMR80-20249. We wish to thank R. L. Aggarwal and J. K. Furdyna for stimulating discussions and help. A. P. is a David Ross Fellow and D. L. P. is a Kodak Fellow.

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¹R. R. Galazka, in *Physics of Semiconductors*, 1978,

edited by B. L. H. Wilson (Institute of Physics, Bristol, 1979), p. 133.

²R. R. Galazka, S. Nagata, and P. H. Keesom, *Phys. Rev. B* **22**, 3344 (1980).

³S. Venugopalan, A. Petrou, R. R. Galazka, A. K. Ramdas, and S. Rodriguez, *Phys. Rev.* **25**, 2681 (1982).

⁴J. Lambe and C. Kikuchi, *Phys. Rev.* **119**, 1256 (1960).

⁵S. A. Al'tshuler, Y. Nazarov, and A. K. Khasanov, *Pis'ma Zh. Eksp. Teor. Fiz.* **33**, 525 (1981) [*JETP Lett.* **33**, 508 (1981)].

⁶P. A. Fleury and R. Loudon, *Phys. Rev.* **166**, 514 (1968).

⁷T. Giebultowicz, H. Kepa, B. Buras, K. Klausen, and R. R. Galazka, *Solid State Commun.* **40**, 499 (1981); T. M. Holden, G. Dolling, V. F. Sears, J. K. Furdyna, and W. Giriat, *Solid State Commun.* **49**, 281 (1981).

⁸D. G. Thomas and J. J. Hopfield, *Phys. Rev.* **175**, 1021 (1968); R. E. Slusher, C. K. N. Patel, and P. A. Fleury, *Phys. Rev. Lett.* **18**, 77 (1967); J. F. Scott, *Rep. Prog. Phys.* **43**, 951 (1980); R. L. Hollis, J. F. Ryan, and J. F. Scott, *Phys. Rev. Lett.* **34**, 209 (1975).

⁹M. Nawrocki, R. Planel, G. Fishman, and R. Galazka, *Phys. Rev. Lett.* **46**, 735 (1981); D. D. Alov, S. I. Gubarev, V. B. Timofeer, and B. N. Shepel', *Pis'ma Zh. Eksp. Teor. Fiz.* **34**, 76 (1981) [*JETP Lett.* **34**, 71 (1981)].

Electron-Electron Umklapp Scattering in Organic Superconductors

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(Received 23 December 1981)

A theory of the tetramethyltetraselenafulvalene (TMTSF) salts and their sulfur analogs is developed. It is shown that the phase diagram is controlled by electron-electron umklapp scattering. The theory accounts for differences between the sulfur and selenium series, and the absence of Peierls transitions. Predictions of the pressure dependence of the spin-density-wave critical temperature and correlations of the dimerization of the organic stacks with critical pressures and temperatures are verified experimentally.

PACS numbers: 61.65.+d, 72.15.Nj, 74.10.+v, 75.25.+z

Much of the recent interest in the study of organic metals has been focused upon the tetramethyltetraselenafulvalene salts $(\text{TMTSF})_2\text{X}$ where X is AsF_6 , PF_6 , TaF_6 , ClO_4 , BF_4 , etc. These materials are structurally anisotropic and, by the standards of organic metals, are very good conductors. At low temperatures they undergo transitions to states which are insulating at low pressure but superconducting at higher pressure.¹

Attempts to observe a Peierls distortion have so far been unsuccessful² and, quite early on, there were speculations that the metal-insulator transition might be brought about by the formation of a spin-density-wave (SDW) state.³ Recent experiments¹ strongly support this idea.

It is interesting to contrast these properties with those of the closely related tetramethyltetrafulvalene salts, $(\text{TMTTF})_2\text{X}$, in which seleni-

um is replaced by sulfur. At atmospheric pressure and temperatures of a few hundred kelvins⁴ they undergo a metal-insulator transition with no anomaly in the magnetic susceptibility, yet at least one compound, (TMTTF)₂PF₆, shows² a Peierls-like transition at about 10 K. Until recently,⁵ no member of this series had been made superconducting.

The purpose of this Letter is to analyze the existing experiments by means of a slight extension of the theory of quasi one-dimensional materials. Any theory should encompass all of the features—the absence of Peierls distortions, the transition from SDW to superconductive behavior, and the differences between the selenium- and sulfur-based compounds. It is known⁶ that such phase diagrams are characteristic of one-dimensional systems with electron-electron umklapp coupling, and Barišić and Brazovskii⁷ have pointed out that precisely this interaction is produced by the anion lattice. Once these ideas are extended to take account of the crossover from one-dimensional behavior to a regime in which transverse motion of the electrons becomes significant as the temperature is lowered, it proves possible to understand the main features of the experiments, and to show how they are correlated with the observed dimerization of the organic stacks. Recently, Horovitz, Gutfreund, and Weger⁸ have considered the effects of *electron-phonon* umklapp scattering in mean-field theory. They suggested that the *electron-electron* umklapp scattering, upon which our theory is based, vanishes because of a symmetry of the anion lattice. There is no such symmetry in the structure of these materials and, if it existed, it would affect both umklapp processes and remove the observed dimerization of the organic stacks.

Structurally⁹ both the sulfur and selenium series have a triclinic space group $P\bar{1}$ with an inversion center at X ; there is no glide-plane symmetry. The TMTSF or TMTTF molecules are arranged in stacks, lying in planes separated one from another by a plane of anions. Complete charge transfer to the anions leaves a conduction band comprised of one hole for every two TMTSF or TMTTF molecules. With this structure, there are distinct transfer integrals along the stacking direction (t_a), from stack to stack (t_b), and perpendicular to the organic planes (t_c). They satisfy $t_c < t_b < t_a$ and, in particular,¹⁰ for (TMTSF)₂PF₆, $t_a \approx 300$ meV, $t_b \approx 3.3$ meV, and $t_c \approx 0.3$ meV. This anisotropy implies that the materials are quasi one-dimensional at high temperature but they

cross over to an anisotropic three-dimensional behavior when $T < t_b$.

The reciprocal lattice vector of the anion lattice has a component along the stacking direction equal to $4k_F$, where k_F is the Fermi wave vector of the holes when transverse hopping is neglected. Consequently, electron-electron umklapp scattering, generated by the Coulomb potential of the anions, may transfer two holes across the Fermi surface. This process is known to be singular in the one-dimensional region.^{6,11} Thus the standard weak-coupling model contains three coupling constants^{6,11}: g_1 and g_2 for small and large momentum transfer, respectively, and g_3 for electron-electron umklapp scattering. Their bare values may be expressed in terms of the on-site coupling U and the near-neighbor coupling V of an extended Hubbard model⁶ as $g_1 = U - 2V$ and $g_2 = U + 2V$.

The dimensionless renormalized coupling constants $\bar{g}_i \equiv g_i/2\pi t_a$ satisfy renormalization-group (RG) equations which are, in lowest order,

$$\bar{g}_1' = -a\bar{g}_1\bar{g}_2 - b(\bar{g}_1^2 - \bar{g}_1\bar{g}_2), \quad (1a)$$

$$\bar{g}_2' = -\frac{1}{2}a(\bar{g}_1^2 + \bar{g}_2^2) + \frac{1}{2}b(\bar{g}_2^2 + \bar{g}_3^2), \quad (1b)$$

$$\bar{g}_3' = \bar{g}_3(2c\bar{g}_2 - d\bar{g}_1), \quad (1c)$$

where the prime denotes differentiation with respect to $l \equiv \ln(t_a/T)$. These equations encompass the well-known RG equations for the one-dimensional electron gas^{6,11} ($a = b = c = d = 1$), which are valid at high temperatures, as well as the separate equations for particle-particle ($b = c = d = 0$) or particle-hole ($a = 0$) scattering which are appropriate when $T < t_b$. The one-dimensional region will be considered first and, in view of the existence of extensive reviews,^{6,11} we shall simply state the principal results and show how they may be applied to the materials under consideration.

In the continuum limit, which is suitable for a discussion of long-ranged correlations, the charge-density and spin-density degrees of freedom are decoupled, and each may be studied by combining solutions of Eqs. (1) with various exact results. The spin waves are controlled by \bar{g}_1 : When $\bar{g}_1 < 0$, there is a gap in their energy spectrum and the magnetic susceptibility is exponentially activated. Since this is not found to be true in the TMTSF or the TMTTF salts at high temperatures, it follows that $\bar{g}_1 > 0$, and, from Eq. (1a) with $a = b = 1$, it can be seen that $\bar{g}_1 \rightarrow 0$ as T decreases. On the other hand, the charge-density degrees of freedom are governed by the combination ($2\bar{g}_2 - \bar{g}_1, \bar{g}_3$) for which the flow lines

$$\bar{g}_3^2 - (2\bar{g}_2 - \bar{g}_1)^2 = \tau, \quad (2)$$

where τ is a constant, divide into two regions with quite different physical properties. When $2\bar{g}_2 - \bar{g}_1 < -|\bar{g}_3|$, the umklapp coupling constant \bar{g}_3 is an irrelevant variable; correlations in the hole gas are such that the response to umklapp scattering is small. A consequence is that the singlet and triplet superconductive correlation functions diverge algebraically as frequency ω and wave vector q tend to zero; but there is no pairing gap without three-dimensional order. On the other hand, if $2\bar{g}_2 - \bar{g}_1 \gtrsim -|\bar{g}_3|$, then \bar{g}_3 is a relevant variable, and there is a finite correlation length¹² $\xi \approx \exp(\pi/\tau^{1/2})$. In this region, there is a gap in the charge-density spectrum proportional to ξ^{-1} , the conductivity is activated, and the hole gas develops a charge-density wave (CDW) with wave vector $4k_F$. The latter is essentially a CDW form of a Wigner crystal, and it enhances the effects of umklapp scattering. For $q = \pm 2k_F$, the SDW correlation function is proportional to ω^{-1} as $\omega \rightarrow 0$ but the CDW correlation function remains finite.^{6,13}

As the temperature is lowered, three-dimensional effects modify this behavior in a variety of ways. When g_3 is relevant, the $4k_F$ CDW will be strongly enhanced¹⁴ near some temperature T_0 , and interstack hopping will stabilize a SDW state with long-ranged order: Coupling to the lattice will produce associated distortions at $4k_F$ (dimerization) and $2k_F$ (spin-Peierls transition), respectively. The absence of an ordinary Peierls transition in this case is an important consequence of the one-dimensional theory.^{6,13} Given this picture, it seems reasonable to associate the metal-insulator transition in the TMTTF salts with an enhancement of the $4k_F$ CDW, and the $2k_F$ distortion seen² in (TMTTF)₂PF₆ with a spin-Peierls transition. The dimerization should increase rapidly for T near T_0 , and Table I shows that this is consistent with existing experiments (the quoted values of the dimerization were measured at room temperature). In order to have $T_0 > t_b$, it is necessary either that g_3 be large or that $2g_2 - g_1 = U + 6V > 0$ in the sulfur compounds.

On the other hand, in the TMTSF series, the $4k_F$ CDW does not develop strongly at low pressure, and the metal-insulator transition is related to the formation of a SDW state. The dimerization should be smaller than in the sulfur compounds. Table I shows that this is indeed the case, with the exception of (TMTSF)₂FSO₃ which has a large dimerization and $T_{MI} > t_b$. It is therefore qualitatively similar to the sulfur compounds, and should not have a magnetic anomaly at T_{MI} .

TABLE I. Table of the dimerization Δ , the metal-insulator transition temperature T_{MI} (K) and the critical pressure for superconductivity P_c (kbar) for the TMTTF and TMTSF salts. $\Delta \equiv (d_1 - d_2)/(d_1 + d_2) \times 10^{-3}$, with d_1 and d_2 nearest-neighbor distances, was measured at room temperature. Values of $\Delta < 4$ may not be experimentally significant. Values are from Ref. 1 and 9 and references therein, and from F. Wudl (private communication).

TMTTF	Δ	T_{MI}	P_c	TMTSF	Δ	T_{MI}	P_c
Br	0	100	25	CIO ₄	(1)	None	0
BF ₄	(3)	190	...	PF ₆	4	12	7
I	6	AsF ₆	4	12	10
NO ₃	9	NO ₃	...	12	10
CIO ₄	10	230	...	SbF ₆	...	15	11
SCN	10	240	...	TaF ₆	11
PF ₆	14	245	>30	FSO ₃	10	86	...

This picture implies that \bar{g}_3 is almost marginal at low pressure, and this is consistent with the fact that \bar{g}_3 becomes irrelevant when the pressure P exceeds a critical value P_c at which a superconducting state becomes stabilized. Dimerization is a measure of the relevance of g_3 and should be correlated with P_c . Table I shows that it is. Our interpretation of the experiments requires that $2g_2 - g_1 = U + 6V < 0$ in the selenium compounds.

In order to give a more quantitative description of the low-temperature behavior it is necessary to take account of the fact that, for $T < t_b$, the distortion of the Fermi surface removes the logarithmic singularities in particle-hole (p-h) diagrams,¹⁵ except for particular values of the momentum transfer,¹⁶ corresponding to perfect nesting^{16,17} of the Fermi surface. Since particle-particle (p-p) ladder diagrams are most divergent for total momentum zero, it follows that singularities in the two channels occur for different ranges of values of incoming and outgoing momenta (with small overlap) and that the singularities no longer interfere, as they do in a one-dimensional system. If we set $b = 0$, $a = 1$, the resulting Eqs. (1a) and (1b) constitute the RG method of summing p-p ladder diagrams, which diverge at the transition temperature T_c for superconductivity. The boundary conditions for these equations are obtained (apart from factors of order unity) by setting \bar{g}_i equal to the solution \bar{g}_i of the one-dimensional equations when $T = t_b$. It is straightforward to show that the resulting val-

ue of T_c for singlet superconductivity is given by

$$T_c \approx t_b \exp[2/(\tilde{g}_1 + \tilde{g}_2)] \quad (3)$$

when $\tilde{g}_1 + \tilde{g}_2 < 0$. This should exceed the transition temperature for triplet superconductivity when retardation of \tilde{g}_2 is included.

To consider the question of SDW or CDW order, it is necessary to omit p-p and nonlogarithmic p-h contributions to Eqs. (1) by setting $a = 0$, $b = c = 1$, $d = 0$ for the SDW channel or $a = 0$, $b = d = 1$, $c = \frac{1}{2}$ for the CDW channel. The solutions of the resulting equations are sums of p-h ladder diagrams which diverge at the SDW or CDW transition temperatures. With the same matching procedure as before, the SDW transition temperature is

$$T_{SDW} \approx t_b \exp[-2/(\tilde{g}_2 + |\tilde{g}_3|)] \quad (4)$$

when $\tilde{g}_2 + |\tilde{g}_3| > 0$. The corresponding expression for T_{CDW} is given by Eq. (4) with $\tilde{g}_2 + |\tilde{g}_3|$ replaced by $-2\tilde{g}_1 + \tilde{g}_3 + |\tilde{g}_3|$. Since $\tilde{g}_1 > 0$, $T_{SDW} > T_{CDW}$. Equations (3) and (4) are reminiscent of the mean-field expressions for the transition temperatures but significant one-dimensional effects reside in the renormalized coupling constants and energy scale.

Since $\tilde{g}_2 + |\tilde{g}_3|$ must vanish at the critical pressure P_c where $T_{SDW}(P)$ vanishes, it is possible to linearize near P_c and rewrite Eq. (4) in the form

$$T_{SDW} \sim \exp[-\text{const}/(P_c - P)] \quad (5)$$

which accounts for the rapid drop in T_{MI} as P_c is approached from below, and gives a good representation of the measured values¹⁸ of T_{SDW} in $(\text{TMTSF})_2\text{PF}_6$. For the TMTTF salts, which have $T_{MI} > t_b$, the one-dimensional recursion relations give $T_{MI} \sim \exp[-\text{const}/(P_c - P)^{1/2}]$.

Perhaps the most striking confirmation of these ideas is provided by the discovery⁵ of superconductivity in $(\text{TMTTF})_2\text{Br}$ above 25 kbar. This is the least dimerized of the sulfur series and hence, from our point of view, the most likely to show superconductivity under pressure. It is the only member of the sulfur series in which superconductivity has been found so far. The transition temperature⁵ is 4.5 K.

A number of questions are raised by the above analysis. Experimentally, it would be of value to make a more accurate and extensive investigation of the dimerization of various materials as functions of temperature and pressure, and to search for spin-Peierls distortions. The most interesting theoretical question is the source of the interactions leading to the observed behavior.

Generally speaking, $2g_2 - g_1$ appears to be positive in the sulfur series, as it is¹⁹ in tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ). However, the crossover to superconducting behavior in the selenium series requires that $2g_2 - g_1 < 0$. The difference may be related to virtual excitation to the second hole levels of the organic molecules, which are spread into a band by hopping. In the selenium series, the level spacing is relatively small and the bandwidth large, so that such a mechanism leads quite naturally to a stronger attraction. Its pressure dependence may account for the shape of the phase diagram.

A preliminary account of this work was given at the meeting of the French Physical Society, Clermont-Ferrand, France, June 1981, and at the Boulder Conference.¹

We acknowledge discussions with S. Brazovskii, and thank B. Horowitz for helpful comments on the low-temperature theory. We are grateful to D. Jerome for showing us that our prediction of $T_{SDW}(P)$ is consistent with his experiments, and to him and to J.-P. Pouget for a number of discussions.

This work was supported by U. S. Department of Energy Contract No. DE-AC-02-76CH00016.

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¹D. Jerome, A. Mazaud, and M. Ribault, *J. Phys. (Paris)*, Lett. **41**, 95 (1980). For a summary of recent experimental results see Proceedings of the International Conference on Low-Dimensional Conductors, Boulder, 1981 (to be published).

²J. P. Pouget *et al.*, in Ref. 1.

³W. M. Walsh *et al.*, *Phys. Rev. Lett.* **45**, 829 (1980); J. C. Scott, H. J. Pedersen, and K. Bechgaard, *Phys. Rev. Lett.* **45**, 2125 (1980).

⁴D. Delhaes *et al.*, *Mol. Cryst. Liq. Cryst.* **50**, 43 (1979).

⁵S. S. P. Parkin, D. Jerome, and K. Bechgaard, in Ref. 1.

⁶V. J. Emery, in *Highly Conducting One-Dimensional Solids*, edited by J. T. Devreese, R. P. Evrard, and V. E. van Doren (Plenum, New York, 1979).

⁷S. Barišić and S. Brazovskii, in *Recent Developments in Condensed Matter Physics*, edited by J. T. Devreese (Plenum, New York, 1981), Vol. 1.

⁸B. Horowitz, H. Gutfreund, and M. Weger, *Solid State Commun.* **39**, 541 (1981).

⁹N. Thorup *et al.*, *Acta Crystallogr. Sec. B* **37**, 1236 (1981).

¹⁰C. S. Jacobsen, D. B. Tanner, and K. Bechgaard, *Phys. Rev. Lett.* **46**, 1142 (1981).

¹¹J. Solyom, *Adv. Phys.* **28**, 201 (1979).

¹²J. M. Kosterlitz, *J. Phys. C* **7**, 1046 (1979); I. E. Dzyaloshinskii and A. I. Larkin, *Zh. Eksp. Teor. Fiz.* **61**, 791 (1971) [*Sov. Phys. JETP* **34**, 422 (1972)].

¹³This follows from a critical discussion of the field-theory models and from the strong coupling (Ref. 10). Some authors have reached a different conclusion (Ref. 11).

¹⁴The value of T_0 depends upon the one-dimensional scale energy $2\pi t_a/\xi$ and interstack Coulomb forces.

Note that this cannot be a second-order phase transition since a $4k_F$ CDW does not break the lattice symmetry.

¹⁵L. P. Gor'kov and I. E. Dzyaloshinskii, *Zh. Eksp. Teor. Fiz.* **67**, 397 (1974) [*Sov. Phys. JETP* **40**, 198 (1975)].

¹⁶V. N. Prigodin and Yu. A. Firsov, *Zh. Eksp. Teor. Fiz.* **76**, 1602 (1979) [*Sov. Phys. JETP* **49**, 813 (1979)].

¹⁷B. Horowitz, *Phys. Rev. B* **16**, 3943 (1977).

¹⁸H. J. Schulz *et al.*, *J. Phys. (Paris), Lett.* **42**, L51 (1981); D. Jerome, private communication.

¹⁹V. J. Emery, *Phys. Rev. Lett.* **37**, 107 (1976).

Localization in One-Dimensional Lattices in the Presence of Incommensurate Potentials

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(Received 28 October 1981)

The density of states and the localized or extended nature of the eigenstates is investigated in one-dimensional crystals with a modulation potential incommensurate with that of the underlying lattice. Studies of the transmission coefficient T and of the spatial dependence of the eigenstates show that even in one dimension it is possible to have a mobility edge. The implications of these results on experimentally measured quantities are also discussed.

PACS numbers: 72.10.Bg, 71.50.+t, 71.55.Jv

In recent years there have been many studies of crystals containing a modulating periodic potential of a period different from that of the underlying lattice.^{1,2} Such modulations occur naturally in crystals containing charge-density waves or spin-density waves² as well as in ionic conductors³ and finally it has become possible to grow crystals with such modulation by molecular-beam epitaxy⁴ (superlattices). Such periodic modulations can be either commensurate or incommensurate with the underlying lattice. Both cases are of considerable interest theoretically and experimentally.

A crystal with an incommensurate modulation presents an interesting case, in that, strictly speaking, it does not possess translational order. In this respect it is like a disordered solid. However, unlike a disordered solid, it possesses lengths over which it almost repeats. Thus, an incommensurate crystal presents a case intermediate between an ordered and a disordered solid. It has been argued^{5,7} that, within the one-dimensional (1D) one-band tight-binding model, with incommensurate modulation there exists a "metal-insulator" transition at a critical strength

of the modulation, i.e., all the energy eigenfunctions are localized above the critical value, while all become extended just below it. Such behavior is unlike that of a disordered solid, for which all states are localized in 1D, or that of a commensurate crystal, for which all states are extended. Such a transition in the nature of the eigenfunctions—which may be induced experimentally in the same sample by, for example, external pressure—presents a very interesting theoretical possibility that is worth investigating.

It is the purpose of this Letter to examine the nature of the eigenstates of this model by studying the transmission coefficient T of the 1D system of size N . This technique is employed in the problem of electrical conductance of a 1D disordered crystal with very interesting results.⁸⁻¹⁰ In the course of the present study, a detailed density-of-states (DOS) calculation was made, and the spatial dependence of the eigenstates was examined.

The model we consider is

$$\epsilon_n c_n + t(c_{n+1} + c_{n-1}) = E c_n, \quad (1)$$

where the energy at site n is $\epsilon_n = V_0 \cos(Qn)$, c_n