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THEORY OF INFRARED CONDUCTIVITY FROM DENSITY WAVES: $(TMTSF)_2X$

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Abstract It is argued that the infrared conductivity due to a spin density wave (SDW) in $(TMTSF)_2X$ may in some cases be of a semiconductor form for a strongly pinned density wave or in other cases be of a more complicated form with phonon resonances due to charge density wave harmonics of a weakly pinned SDW.

Infrared conductivity due to a charge density wave (CDW) or spin density wave (SDW) may include contributions from single-particle excitations of the electrons, $\sigma_{s.p.}$, and from collective-mode motion (vibration) of the density wave, $\sigma_{c.m.}$.[1-4] We will argue that for the SDW states of the $(TMTSF)_2X$ superconductors, there may be some cases where the SDW is strongly pinned and other cases where it is very weakly pinned. By strong pinning of the SDW, we mean that the conductivity is similar to that of a semiconductor, arising almost entirely from $\sigma_{s.p.}$. In this case there is a conductivity edge and peak at the SDW gap 2Δ. By very weak pinning we mean that $\sigma_{c.m.}$ contributes significantly to σ, and in this case according to our theory: (a) the single-particle conductivity $\sigma_{s.p.}$ commencing at 2Δ is almost entirely cancelled by $\sigma_{c.m.}$ and no conductivity edge should occur at 2Δ; (b) due to interaction with the lattice of a 2Q CDW harmonic of the SDW, phonon resonance peaks appear in σ for phonons with twice the SDW wave vector $\underline{Q}$; and (c) a peak near or overlapping zero frequency occurs, shifted from zero (as for the CDW) by weak commensurability, impurities, or by a three-dimensional ordering effect acting weakly through a 2Q CDW

harmonic of the SDW. This peak will be broadened by impurities so that if the frequency shift is small or negligible, it may appear as the usual low-frequency form of σ for a normal metal but with a different transport lifetime τ. This description applies for a quasi-one-dimensional part of the electron Fermi surface gapped by the SDW.

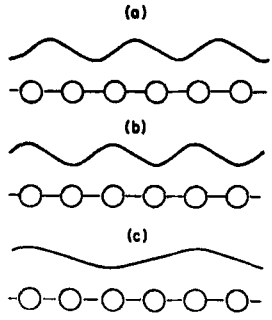

FIGURE 1 Density wave in a solid with one atom in each unit cell.

Consider now a simple solid with one atom in each unit cell as in Figure 1. Lee, Rice and Anderson[1] noted that for $2Q = G$, the $2Q$ and $q - 2Q$ phonons must be the same phonon and in this case the phase-phonon collective-mode motion of the CDW, represented by $\sigma_{c.m.}$, does not occur. This is illustrated in Figures 1(a) and (b). In Figure 1(a), every atom sees an electron density gradient due to the CDW and through the electron-phonon interaction of the Frohlich hamiltonian odd-numbered atoms move rightward and even-numbered atoms move leftward. In Figure 1(b) the atoms do not move and the CDW does not exist. Changing the position (phase) of the CDW from Figure 1(a) or equivalent positions is equivalent to just reducing the electron-phonon coupling constant and the CDW amplitude toward zero. Formally, for this case the phase degree of freedom does not exist and only the infrared non-active amplitude

mode of the Lee, Rice and Anderson theory exists.[1] For this simple solid the same reasoning applies to the SDW in the Hubbard hamiltonian, where the SDW occurs for $2Q = G$ only when antinodes are centred at atoms. For higher order commensurability such as $4Q = G$ in Figure 1(c), some atoms see an electron density gradient for any position and phase of the CDW so that distortion of the host lattice and a new lattice period four times longer always occurs. In this case the phase degree of freedom and $\sigma_{c.m.}$ definitely exist.

We return now to $(TMTSF)_2X$. Each atom in Figure 1 is replaced by two TMTSF molecules. If the TMTSF are internally rigid, the $2Q = G$ case is similar to Figure 1(c) but with bond lengths alternating with less than one percent bond length difference. For any position of a CDW, not all atoms see zero gradient of electron density, atoms move, and the period of the host lattice is changed from two spacings to four spacings. The phase degree of freedom exists for this case, even with $2Q = G$. Analogous argument applies for the SDW. Intramolecular distortions of charge and spin in the TMTSF ions leads to similar complexity of the phase degree of freedom in the collective mode motion as has been described theoretically with apparent success for the CDW in $TEA(TCNQ)_2$.[5]

A SDW always has $n\underline{Q}$ harmonics because when an electron state at wavevector $\underline{k}$ is correlated with another state at wavevector $\underline{k} + \underline{Q}$, then an electron state at wavevector $\underline{k} - \underline{Q}$ is also correlated with the $\underline{k}$ state.[3,4] States at $\underline{k} - \underline{Q}$ and $\underline{k} + \underline{Q}$ are therefore correlated with correlation vector $2Q$, and so on. The even-order harmonics of the SDW are charge density waves.[3,4] The SDW is therefore coupled by electron-phonon interaction to lattice distortions and phonons through its even-order CDW harmonics. We take an electron dispersion with $0 < |k| < 4k_f$, which represents the $4k_f$ cutoff for $(TMTSF)_2X$ before dimerization and then include the $2\pi/a$ dimerization-and-X-ion potential explicitly in the hamiltonian. For $|k| > 4k_f$, we will take $\varepsilon_k \to \infty$ in equations of motion for the

electron Green function, as we did earlier for the incommensurate case.[3,4] We linearize the electron dispersion near E_f with the nesting condition $\varepsilon_{k+\frac{Q}{2}} = -\varepsilon_{-\frac{Q}{2}} = v_f k$ for $Q = 2k_f$, and also for wavevector near $3k_f$ with $\varepsilon_{k\pm\frac{3Q}{2}} \equiv \varepsilon_{k\pm\frac{Q}{2}} + \varepsilon_Q$ where ε_Q is comparable to $2E_f$. The hamiltonian is

$$H = \sum_{k,\alpha} \varepsilon_k c^+_{k\alpha} c_{k\alpha} - \frac{V_{SDW}}{2N} \sum_{\substack{k,k',q \\ \alpha,\beta}} c^+_{k-\frac{q}{2}\beta} c_{k+\frac{q}{2}\alpha} c^+_{k'+\frac{q}{2}\alpha} c_{k'-\frac{q}{2}\beta}$$

$$+ \sum_{q,u} \omega^{(u)}_q b^+_{uq} b_{uq} + \sum_{q,k,\alpha,u} \frac{ig_u}{N^{\frac{1}{2}}} c^+_{k+q\alpha} c_{k\alpha} (b_{uq} + b^+_{u-q})$$

$$+ V_X \sum_k \left(c^+_{k+\frac{2\pi}{a}} c_k + c^+_k c_{k+\frac{2\pi}{a}} \right) \qquad (1)$$

where N is the number of atoms; k, k' and q are wavevector components parallel to the highly-conducting axis; α and β denote spin states; and u is the index of the phonon band. The direct coulomb interaction appears in screening of the exchange potential V_{SDW}, averaged over k and k', and in renormalization of coupling g_u and frequency $\omega^{(u)}_q$ for the phonons, which include the a_g symmetric modes discussed by Michael Rice.[2] V_X represents the $2\pi/a$ potential seen by the electrons. For a SDW state, there is a mean-field part of H given by

$$H_{m.f.} = -\sum_{k,\alpha,\beta} M(\underline{\sigma}\cdot\underline{n})_{\alpha\beta} c^+_{k-\frac{Q}{2}\alpha} c_{k+\frac{Q}{2}\beta} + \text{h.c.}$$

$$- \sum_{k,\alpha} (\Gamma + V_X) \left(c^+_{k-\frac{3Q}{2}\alpha} c_{k+\frac{Q}{2}\alpha} + c^+_{k-\frac{Q}{2}\alpha} c_{k+\frac{3Q}{2}\alpha} \right) + \text{h.c.} \qquad (2)$$

where

$$M = \frac{V_{SDW}}{2N} \sum_{k',\alpha,\beta} (\underline{\sigma}\cdot\underline{n})_{\alpha\beta} \langle c^+_{k'+\frac{Q}{2}\alpha} c_{k'-\frac{Q}{2}\beta} \rangle \qquad (3)$$

and

$$\Gamma = \frac{1}{N} \sum_{k',\alpha,u} \frac{g_u^2}{\omega_{2Q}^{(u)}} \langle (c^+_{k'} + \frac{3Q}{2} \alpha \, c_{k'} - \frac{Q}{2} \alpha + c^+_{k'} + \frac{Q}{2} \alpha \, c_{k'} - \frac{3Q}{2} \alpha) \rangle \tag{4}$$

The electron Green functions and the gap equations obtained are the same as we have earlier obtained for the incommensurate SDW[3,4] except that $\Gamma \to \Gamma + V_X$ in Eq. 2. Γ carries twice the phase of the SDW fundamental measured relative to the host crystal, whereas V_X as part of the crystal potential has relative phase fixed at zero.

The SDW gap function with harmonics present is

$$\Delta \equiv M\left(1 + \frac{2(|\Gamma| + V_X)}{\varepsilon_Q}\right)\left(1 + \frac{|M|^2}{\varepsilon_Q^2}\right)^{-1}$$

$$= \left(V_{SDW} + \sum_u \frac{2g_u^2 a^2}{\omega_{2Q}^{(u)}}\right) \frac{k_B T}{\left(1 + \frac{a^2}{4}\right)^2} \sum_{\omega_n} \frac{\Delta}{(i\omega_n - \omega_{k-k_f})(i\omega_n + \varepsilon_{k-k_f}) + |\Delta|^2}$$

$$+ \frac{aV_X}{\left(1 + \frac{a^2}{4}\right)} \tag{5}$$

where M is the magnitude of Δ in the limit $\varepsilon_Q \to \infty$ where the 2Q amplitude would be zero.[1] To first order in ε_Q^{-1}, the ratio $\langle 2Q \rangle_{CDW} / \langle 1Q \rangle$ is $a = \frac{2|M|}{\varepsilon_Q} \approx \frac{|M|}{E_f}$. At T = 0 the gap equation becomes

$$1 - \frac{V_X}{\Delta} \left(\frac{a}{1 + \frac{a^2}{4}}\right) = \lambda \ln \frac{2E_f}{|\Delta|} \qquad (2E_f \gg |\Delta|) \tag{6}$$

where

$$\lambda = \left(1 + \frac{a^2}{4}\right)^{-2} \left(N(0)V_{SDW} + N(0) \sum_u \frac{2g_u^2 a^2}{\omega_{2Q}^{(u)}}\right)$$

$$\equiv \lambda_{SDW} + \sum_u \lambda_u \quad ; \quad \lambda_u = a^2 \lambda^{ph}_{u,2Q} / \left(1 + \frac{a^2}{4}\right)^2 \tag{7}$$

N(0) is the one-spin density of states at the Fermi surface (for the part gapped by the SDW).

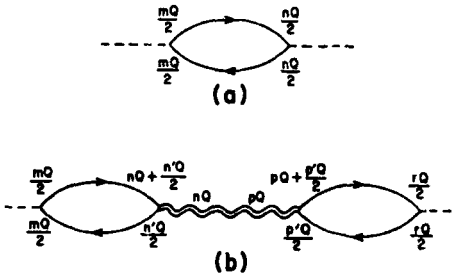

FIGURE 2 Response diagrams important in the infrared conductivity due to a density wave with harmonics.

The contribution of $\sigma_{c.m.}(q = 0, \omega)$ to σ arising from the phase oscillation of the SDW and its harmonics is calculated exactly in the same manner as we have described in detail earlier for the incommensurate phase with no commensurability potential, evaluating the response diagram of Figure 2(b). The result is

$$\sigma_{c.m.}(\omega) = \frac{-ne^2}{i\omega m} \left(\frac{\omega}{2\Delta}\right)^2 f\left(\frac{\omega}{2\Delta}\right)^2 \lambda D_\phi(\omega) \tag{8}$$

where

$$D_\phi^{-1}(\omega) = D_o^{-1}(\omega) + 1 - \frac{V_X}{\Delta} \left(\frac{a}{1 + \frac{a^2}{4}}\right) + \frac{\lambda\omega^2}{4\Delta^2} f\left(\frac{\omega}{2\Delta}\right) \tag{9}$$

with

$$D_o(\omega) = -\frac{\lambda_{SDW}}{\lambda} - \sum_u \frac{(\lambda_u/\lambda)\omega_u^2(2Q)}{\omega_u^2(2Q) - \omega^2 - i\omega\gamma_u} \tag{10}$$

The γ_u are the widths of the phonon states for the solid including

effects of all interactions except those expressed explicitly in the hamiltonian of Eq. 1. The function f is

$$f(x) = \{\pi i + \ln\left[\frac{1 - (1 - x^{-2})^{\frac{1}{2}}}{1 + (1 - x^{-2})^{\frac{1}{2}}}\right]\}/2x^2(1 - x^{-2})^{\frac{1}{2}}$$

and the single-particle conductivity evaluating Figure 2(a) is

$$\sigma_{s.p.}(\omega) = \frac{ne^2}{i\omega m}\left[f\left(\frac{\omega}{2\Delta}\right) - f(0)\right] \qquad (11)$$

which is exactly the same as $\sigma_{s.p.}$ for the usual theory with no harmonics.[1]

The hamiltonian of Eq. 1 assumes that the electron conduction band width is much greater than the coulomb interaction, i.e. $\lambda << 1$ in Eqs. 6 and 7 is required. We now make a second assumption for the SDW state in $(TMTSF)_2X$ compounds: the SDW is a mean field system, with the SDW gap 2Δ comparable to $3.5k_BT_c$, or $2\Delta \approx 20$ to 40 cm^{-1}. $2\Delta << E_f \approx 0.25$ eV[7] and with $M \approx \Delta$ in this case, $a \approx \langle 2Q\rangle_{CDW}/\langle 1Q\rangle \approx \frac{\Delta}{E_f} \approx 0.02$ for $T_c \approx 15$ K. The dimerization-and-X-ion potential V_X appears in the gap equation and in the conductivity, Eqs. 6, 8 and 9, multiplied by $a/\left(1 + \frac{a^2}{4}\right)$. If we take V_X as comparable to the dimerization difference for the electron transfer integral along the TMTSF stack, roughly 50 meV according to Grant,[7] then $V_X a/\left(1 + \frac{a^2}{4}\right)$ is less than 1 meV and comparable to or less than the lifetime broadening of the collective mode frequency near $\omega = 0$. Displacement of this mode from zero is probably not observable. From Eqs. 6 and 7 and with $T_c \lesssim 15$ K, $\lambda \lesssim 0.2$.

Ng, Timusk and Bechgaard[8] have observed at 2 K an asymmetric peak in Reσ similar to Figure 2(d) of ref. 3 for the quenched state of $(TMTSF)_2ClO_4$ where a SDW is known to occur below a T_c comparable to 5 K. In the quenched state the ClO_4 anions are disordered and probably constitute a strong pinning field for the SDW, in which

case we expect that $\sigma = \sigma_{s.p.}$ as in Figure 2(d) of ref. 3. The observed peak begins at 20 cm^{-1}, which for $2\Delta = 3.5k_BT_c$ means that $T_c = 8$ K. For the slowly cooled state of $(TMTSF)_2X$ the anions are ordered and Ng et al observe a sharp peak at 7 cm^{-1} and a broader peak at 25 cm^{-1}. For this state no SDW occurs and it appears that these peaks may be associated with the $2\pi/a$ charge transfer mechanism of Rice, Yartsev, and Jacobsen[6] but also including effects of the anion ordering which occurs at roughly 25 K. No theory for this situation exists at present.

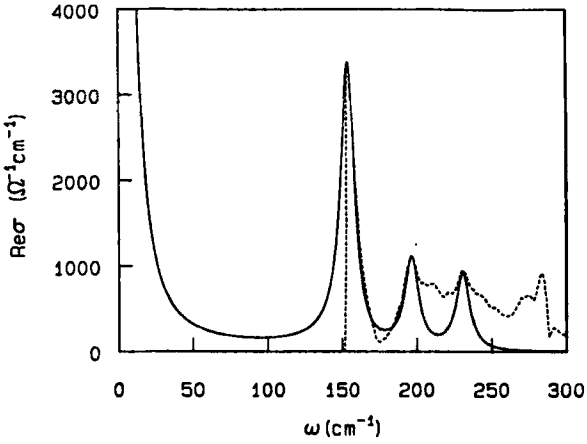

FIGURE 3 Real part of the conductivity versus frequency for $(TMTSF)_2SbF_6$. The solid line is theory and the dotted line represents experimental results by Ng, Timusk, and Bechgaard.[8]

Ng, Timusk and Bechgaard have recently measured the far-infrared spectrum of $(TMTSF)_2SbF_6$.[8] Cooling from 19 K to 2 K, through the SDW $T_c = 17$ K transition, three new and sharp peaks appear between 150 and 250 cm^{-1}. In Figure 3 the dotted line shows $Re\sigma(2\ K) - 0.75\ Re\sigma(19\ K)$, where Ng et al have subtracted part of the normal metal conductivity in an attempt to separate the contribution from the part of the Fermi surface not annihilated by the SDW. The solid line is our theory for $Re\sigma$ adding $\sigma_{c.m.}$ and

$\sigma_{s.p.}$ from Eqs. 8 and 11, with the following parameters: $2\Delta = 40\ cm^{-1}$; $E_f = 0.25$ eV; $\lambda_{SDW} = 0.19$; $a = 0.02$; $aV_X \to 0$; $\omega_1(2Q) = 154\ cm^{-1}$; $\lambda^{ph}_{1\,2Q} = 0.290$; $\omega_2(2Q) = 197\ cm^{-1}$; $\lambda^{ph}_{2,2Q} = 0.148$; $\omega_3(2Q) = 231\ cm^{-1}$; $\lambda^{ph}_{3,2Q} = 0.176$. 2Δ and a are determined using the mean field relation $2\Delta = 3.5k_BT_c$. The value for a is 0.02 only for a linear electron dispersion. If we take $a = 0.05$, then λ_1, λ_2, λ_3 become 0.0464, 0.0237 and 0.0282 for the same solid line conductivity curve in Figure 5. Intramolecular a_g phonon modes of TMTSF observed by Bozio et al in Raman scattering[9] occur at 146 and 265 cm^{-1}. Calculated a_g modes[9] occur at 146, 240, and 299 cm^{-1}. For $TEA(TCNQ)_2$, observed and calculated electron-phonon coupling constants[5] for a_g modes of TCNQ in this frequency range are each comparable to 0.1. The theoretical peak at $\omega = 0$ is orders of magnitude larger than the dc conductivity of $(TMTSF)_2SbF_6$. This occurs because our theoretical σ obeys the conductivity sum rule and at the same time includes only the far-infrared conductivity due to the SDW. Including Holstein and other processes at higher frequencies subtracts spectral weight principally from the $\omega = 0$ conductivity peak in Figure 3.

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