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Lattice dynamics and electrical properties of commensurate one-dimensional charge-density-wave systems

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The ground-state properties, the phonon dispersion, and the electrical properties of systems with a commensurate superstructure are calculated. The superstructure leads to the appearance of a gap at the Fermi energy. Phonon branches representing oscillations of the phase and amplitude of the superstructure show strong anomalies at $q = 0$. The smaller the electronic energy gap, the stronger these anomalies are. For general commensurate cases the phase mode of finite frequency ω_{ph} couples to an external field leading to a δ singularity in the electrical conductivity at $\omega = \omega_{ph}$. This is in contrast to the incommensurate case, where, due to the translational invariance, the phase-mode frequency vanishes, resulting in metallic electrical properties. In the special case of a half-filled band the phase and amplitude of the superstructure have the same degree of freedom in the system. In this case the corresponding phonon mode does not couple to an external field. However, the lower symmetry of the state with superstructure leads to a coupling of usually infrared-inactive intramolecular modes to an external field, and, correspondingly, these modes lead to peaks in the frequency-dependent conductivity.

I. INTRODUCTION

Quasi-one-dimensional conductors like TTF-TCNQ (tetrathiofulvalinium-tetracyanoquinodimethanide) and KCP (potassium-tetracyanoplatinate) exhibit at low temperatures a metal-insulator transition connected to a lattice superstructure.[1-4] The properties of these systems have been treated theoretically using a one-dimensional jellium model with electron-phonon interaction.[5,6] This theory predicts at $T = 0$ a periodic lattice deformation and a charge-density wave (CDW) of period $2k_F$ leading to a gap in the spectrum of one-electron states at the Fermi energy (Peierls instability). The resulting system is, however, no real insulator as, due to the inherent translational invariance of the jellium model, the phase of the CDW is not fixed. Allowing for the motion of this phase one obtains metallike collective conduction in addition to the one-electron excitations across the gap.[6,7] This model does not agree with the experimental results which show a mode of large oscillator strength at extremely low frequency but not at $\omega = 0$ as predicted.[8,9] Lee *et al.*[7] pointed out that this discrepancy might be explained assuming that the CDW and the underlying lattice are commensurate, i.e., the ratio of the periods of the lattice to the CDW is a (small) integer.

However, experiments show that the CDW in TTF-TCNQ and KCP is incommensurate with the lattice.[2,4] Therefore the low-frequency mode is now generally attributed to impurity-pinned oscillations of the CDW.[7,10]

Commensurate CDW's and the associated lattice superstructure exist in many semiconducting quasi-one-dimensional substances. For instance the alkali-TCNQ salts show a dimerization of the TCNQ stacks, i.e., the superstructure has twice the period of the underlying lattice.[11,12] TEA-$(TCNQ)_2$ (triethylammonium-ditetracyanoquinodimethanide) shows a superstructure with the fourfold period of the underlying lattice.[13] These superstructures may be understood in terms of the Peierls instability as the conduction band is half-filled in the alkali-TCNQ salts and $\frac{1}{4}$-filled in TEA-$(TCNQ)_2$. Current interest in these substances is especially due to the fact that in the state with superstructure usually infrared-inactive intramolecular vibrations of the TCNQ molecule are coupled to the electrons and therefore are infrared active.[14,15] This makes an experimental determination of the coupling of the electrons to the intramolecular vibrations possible.[16-18]

Another interesting development is the discovery of a commensurate superstructure of the TCNQ stacks in TTF-TCNQ at high pressure,[19] while at ambient pressure the superstructure is incommensurate. This has been interpreted as a change of the charge transfer from the TTF to the TCNQ molecules. At ambient pressure the charge transfer is 0.59, i.e., the TCNQ electron band is 0.295 filled and the Peierls instability leads to an incommensurate superstructure. At high pressure the charge transfer is 0.66, so that the TCNQ band is $\frac{1}{3}$-filled and the superstructure has the threefold period of the underlying lattice.

In the present paper we treat the lattice dynamics and the electrical properties of commensurate systems. It turns out that the properties of the system depend strongly on the ratio of the

reciprocal-lattice wave number G to the Fermi wave number k_F. For small-integer values of the commensurability index $m = G/2k_F$,[20] the phase of the superstructure and the CDW relative to the underlying lattice is not free and the jellium model is thus inadequate in this case. Taking account of this fact we have used a tight-binding model which is described in Sec. II. In Sec. III we use mean-field theory to obtain the energy bands and lattice configuration of the CDW ground state for a $\frac{1}{2}$-, $\frac{1}{3}$-, and $\frac{1}{4}$-filled band.[21] The Peierls instability leads to a superstructure with the twofold, threefold, and fourfold period of the original lattice, respectively. These types of superstructure are commonly found experimentally.[11-13,19] Using the band structures and the corresponding eigenvectors we calculate in Sec. IV the phonon dispersions of the coupled electron-phonon system in the CDW ground state. These dispersions show at $q = 0$ strong anomalies of some optical-phonon branches which represent oscillations of the phase and amplitude of the CDW and the superstructure about their ground-state values. The influence of the coupled electron-lattice modes and especially of the phase mode on the electrical properties is investigated in Sec. V. For a $\frac{1}{2}$-filled band in the undeformed state ($m = 2$) the CDW does not couple to an homogeneous external field. However the superstructure leads to a coupling of usually infrared-inactive intramolecular modes to an homogeneous external field, so that these modes become infrared active. This effect has been used by Rice *et al.*[18] for the determination of the coupling of the electrons to the intramolecular vibrations of TCNQ molecules. For $m = 3$ and $m = 4$ the coupling of an external field to the phase mode leads to the appearance of a δ-function peak in the electrical conductivity at very low frequency.

The essential results given in this paper are not restricted to a system with an instability against the formation of a CDW due to the Peierls mechanism but should equally be valid for a system with a CDW due to the direct electron-electron interaction.[22]

II. THE MODEL

The presently known substances which show quasi-one-dimensional behavior are structurally rather complicated molecular systems. The characteristic properties of a one-dimensional system with a commensurate CDW may however be shown using a linear chain of harmonically interacting ions which may be thought to represent the TCNQ molecules in the quasi-one-dimensional TCNQ compounds. The electrons are treated in the tight-binding approximation and we take only account of nearest-neighbor overlap integrals.

The instability against the formation of a CDW and a superstructure is induced by the electron-phonon interaction. The electron-electron interaction may lead to different ground states.[22] Further the electron-electron interaction has a quantitative effect on the one-electron excitations of the CDW ground state and is important for the magnetic properties of the system.[23] In the present paper we consider however a system with a superstructure and a CDW in its ground state, in accord with experiments on almost all quasi-one-dimensional compounds. As we are mainly interested in the qualitative effects of the CDW and the superstructure on the lattice dynamics and on the electrical properties we can neglect the electron-electron interaction in our model.

The Hamiltonian is

$$H = \sum_k \epsilon_k a_k^\dagger a_k + \sum_{k,q} g(k,q) a_{k+q}^\dagger a_k (b_q + b_{-q}^\dagger) + \sum_q \omega_q b_q^\dagger b_q , \tag{2.1}$$

with

$$\epsilon_k = -W \cos ka . \tag{2.2}$$

The a_k and b_q are destruction operators for electrons and phonons, respectively. The summations are over the first Brillouin zone, i.e., from $-\frac{1}{2}G$ to $\frac{1}{2}G$.

In the main part of this paper we shall assume that the electrons interact with acoustical phonons of the chain. The effect of these phonons is a modulation of the electronic overlap integrals and one obtains[24]

$$\omega_q = \omega_a \sin|\tfrac{1}{2}qa| ,$$

$$g(k,q) = 2iJ(2NM\omega_q)^{-1/2} \times [\sin ka - \sin(k+q)a] , \tag{2.3}$$

where J is the first derivative of the overlap integral with respect to the interionic distance, M is the ionic mass, and N is the number of ions in the chain.

In Sec. V we shall also consider the interaction with symmetric intramolecular vibrations, which may be assumed to be dispersionless. The effect of these vibrations is to modulate the local-energy integrals, and we have

$$\omega_q = \omega_0, \quad g(k,q) = \frac{\text{const}}{\sqrt{N}} . \tag{2.4}$$

For a $1/m$-filled band the Peierls instability

leads to a superstructure and a CDW of wave number G/m. The reciprocal-lattice wave number of the deformed system is therefore $Q=G/m$ so that the new unit cell consists of m cells of the undeformed system. The superstructure breaks the symmetry and may be described by a macroscopic occupation of phonons of wave numbers νQ (ν integer), i.e., by nonzero expectation values $\langle b_{\nu Q}\rangle$.[25] These expectation values are the order parameters of the Peierls transition and are determined by minimizing the ground-state energy.

We introduce new phonon operators[26]

$$c_q = b_q - \langle b_q\rangle , \tag{2.5}$$

which describe displacements of the lattice relative to the superstructure ground state and obtain from Eq. (2.1)

$$H = \sum_k \epsilon_k a_k^\dagger a_k + \sum_{\nu,k} g(k,\nu Q) a_{k+\nu Q}^\dagger a_k (\langle b_{\nu Q}\rangle + \langle b_{-\nu Q}^\dagger\rangle)$$

$$+ \sum_{k,q} g(k,q) a_{k+q}^\dagger a_k (c_q + c_{-q}^\dagger) + H_{\rm ph} , \tag{2.6a}$$

with

$$H_{\rm ph} = \sum_q \omega_q (c_q^\dagger + \langle b_q^\dagger\rangle)(c_q + \langle b_q\rangle) . \tag{2.6b}$$

The first two terms in Eq. (2.6a) describe electrons interacting with the superstructure potential. This interaction leads to a splitting of the band ϵ_k of the undistorted state into m bands B_{kn} which are determined by the eigenvalue equation

$$\sum_m M_{lm}(k) f_{mn}(k) = E_{kn} f_{ln}(k) , \tag{2.7}$$

with

$$M_{lm}(k) = \delta_{lm}\epsilon_{k+lQ} + (1-\delta_{lm}) g(k+mQ, (l-m)Q)$$

$$\times \langle b_{(l-m)Q} + b_{-(l-m)Q}^\dagger\rangle . \tag{2.8}$$

The electron operators corresponding to the eigenvalues E_{kn} are given by

$$A_{kn}^\dagger = \sum_l f_{ln}(k) a_{k+lQ}^\dagger . \tag{2.9}$$

With these operators we obtain

$$H = \sum_{k,n} E_{kn} A_{kn}^\dagger A_{kn} + \sum_{\substack{k,q\\ \nu,l,n}} V_{\nu ln}(k,q) A_{k+q,l}^\dagger A_{kn}$$

$$\times (c_{q+\nu Q} + c_{-q-\nu Q}^\dagger) + H_{\rm ph} . \tag{2.10}$$

This Hamiltonian describes the Bloch electrons of the system with superstructure interacting with the phonons of the periodically deformed lattice. The electron-phonon coupling factors now read

$$V_{\nu ln}(k,q) = \sum_\mu g(k+\mu Q, q+\nu Q)$$

$$\times f_{\mu+\nu,l}(k+q) f_{\nu n}(k) . \tag{2.11}$$

The interaction conserves wave number as Q is a reciprocal-lattice wave number.

III. GROUND STATE

In the mean-field approximation the ground-state wave function is a product of electron and phonon wave functions. As the expectation values $\langle c_q\rangle$ vanish [Eq. (2.5)] we obtain from Eq. (2.10) for the ground-state energy

$$E_g = 2\sum_k E_{k1} + \sum_\nu \omega_{\nu Q} |\langle b_{\nu Q}\rangle|^2 . \tag{3.1}$$

The factor of 2 in front of the sum of the one-electron energies results from the spin summation.

In order to show the origin of the Peierls superstructure we consider first small amplitudes of the superstructure. In this case the gap Δ between the highest occupied state and the lowest empty state is proportional to the amplitude of the superstructure:

$$\Delta \propto J |\langle b_{2k_F}\rangle| , \tag{3.2}$$

where J is the electron-phonon coupling constant. Further for small Δ the electronic part of the energy is given by

$$E_g^e(\Delta=0) - E_g^e(\Delta) \propto \Delta^2 \ln\Delta . \tag{3.3}$$

The singular behavior for $\Delta \to 0$ stems from the divergent density of states near the band edge. From Eq. (3.1) we obtain

$$E_g - E_g(\Delta=0) \propto \Delta^2 (pJ^{-2} + \ln\Delta) , \tag{3.4}$$

where p is a positive proportionality factor independent of Δ and J. This equation shows that for arbitrarily small electron-phonon coupling the state with a superstructure is energetically favored with respect to the metallic state with $\Delta = 0$.

To obtain the ground-state expectation values $\langle b_{\nu Q}\rangle$ we first calculate the electronic part of the energy for arbitrary $\langle b_{\nu Q}\rangle$ and then minimize the resulting energy, i.e., we solve the set of equations

$$\omega_{\nu Q}\langle b_{\nu Q}\rangle^* + \frac{\partial}{\partial\langle b_{\nu Q}\rangle} \sum_k E_{k1} = 0 . \tag{3.5}$$

In the $\frac{1}{2}$-filled-band case the superstructure leads to a dimerization of the chain. The displacement of the lth ion is given by

$$\langle u_l \rangle = u_0 \cos(\pi l + \varphi) = (-1)^l u_0 \cos\varphi \,. \tag{3.6}$$

Hence the ground state depends only on the product $u_0 \cos\varphi$. Correspondingly it exists only one real order parameter and the electron bands are given by the well-known expression[27]

$$E_{kn} = \pm [W^2 \cos^2 ka + \tfrac{1}{4}(\Delta \sin ka)^2]^{1/2} \,. \tag{3.7}$$

For a $\frac{1}{3}$-filled band ($m = 3$) we have a superstructure given by

$$\langle u_l \rangle = u_0 [\cos(2\pi l/3)\cos\varphi - \sin(2\pi l/3)\sin\varphi] \,. \tag{3.8}$$

Correspondingly, the order parameter

$$\delta e^{i\varphi} = 2\sqrt{3}\, J \langle b_Q + b_{-Q}^{\dagger} \rangle (2NMW^2\omega_Q)^{-1/2}$$

$$(\delta, \varphi \text{ real};\ \delta \geq 0) \tag{3.9}$$

is complex, the phase and amplitude of the order parameter representing the phase and amplitude of the superstructure. The electron bands are

$$E_{kn} = -W(1 + 2\delta^2)\cos\{\tfrac{1}{3}[\arccos(C\cos 3ka) - 2\pi(n-1)]\} \quad (n = 1, 2, 3) \,, \tag{3.10}$$

with

$$C = (1 - 3\delta^2 + 2\delta^3 \sin 3\varphi)(1 + 2\delta^2)^{-3/2} \,. \tag{3.11}$$

As can be easily shown the elastic energy of a statically deformed lattice is independent of φ for $m \neq 2$. Thus the phase dependence of the energy of the system is only due to the phase dependence of the electronic energy [Eqs. (3.10) and (3.11)]. In the present case ($m = 3$) the electronic energy decreases with decreasing C so that in the ground state we have $\sin 3\varphi = -1$.

From Eq. (3.5) δ is given by

$$\pi(1 + 2\delta^2) = 4\lambda(y_0 - y_2)^{1/2} \left[4E(k) + \frac{4y_2 - 1}{y_0 - y_2} K(k) - \frac{2 + \delta + \delta^2}{1 - 3\delta^2 - 2\delta^3} \times \left(4E(k) + \frac{4y_2 - 3}{y_0 - y_2} K(k)\right)\right] \,, \tag{3.12}$$

with

$$y_n = \cos^2[\tfrac{1}{3}(\arccos C - n\pi)] \,,$$

$$k^2 = (y_0 - y_1)/(y_0 - y_2) \,, \tag{3.13}$$

$$\lambda = 2J^2/MW\omega_a^2 \,.$$

K and E are the complete elliptic integrals of the first and second kind, respectively.[28]

The energy bands in the ground state and the lattice configuration for some values of φ are shown in Fig. 1. The ground-state lattice configuration is given by $\varphi = \frac{1}{2}\pi$ or $\varphi = \frac{7}{6}\pi$ which differ only by a primitive translation of the lattice. The $\varphi = \frac{5}{6}\pi$ structure corresponds to a maximum of the energy.

In the $\frac{1}{4}$-filled band case ($m = 4$) a similar calculation as for $m = 3$ gives a phase dependence of the energy of the form

$$E(\varphi) - E(0) \propto \delta^4(\cos 4\varphi - 1) \,, \tag{3.14}$$

where δ is proportional to the amplitude of the superstructure.

In the ground state the electronic energy bands are

$$E_{kn} = \pm W\{\tfrac{1}{2} + 2\delta^2 \pm [\cos^2 2ka(\tfrac{1}{2} - 2\delta^2)^2 + 4\delta^2]^{1/2}\}^{1/2} \,. \tag{3.15}$$

The phase dependence of the energy of the system [Eqs. (3.10) and (3.14)] agrees with the general considerations of Lee *et al.*[7]

If the interaction with the intramolecular vibrations [Eq. (2.4)] is taken into account, the results given here remain essentially unchanged, however in general the ground state is no more inversion symmetric. This is in contrast to the case of interaction with the acoustic phonons alone which we have treated above.

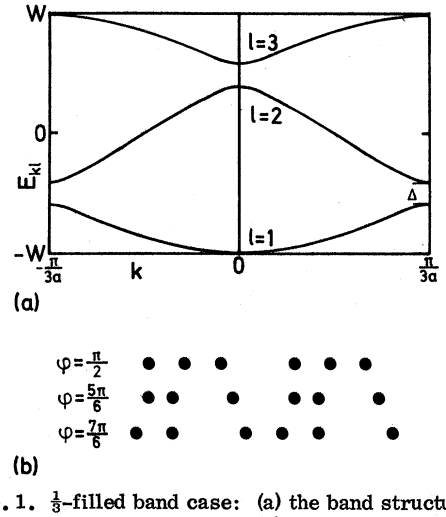

FIG. 1. $\frac{1}{3}$-filled band case: (a) the band structure in the the state with superstructure; (b) the lattice configuration for some values of the phase.

IV. PHONONS

A. General

In the mean-field approximation the appearance of the Peierls superstructure is due to the logarithmic divergence of the electronic susceptibility $\chi(2k_F, \omega = 0)$ for $T \to 0$ in the metallic state.[27] Because of this divergence the frequency of the $2k_F$ phonons goes to zero for some $T = T_P$ [Fig. 2(a)]. The resulting superstructure leads to a reduction of the first Brillouin zone by a factor $1/m$ for a $1/m$-filled band, so that each phonon branch is split up into m branches. The points $q = 0$ and $q = 2k_F$ are transformed into equivalent points of the zone scheme of the distorted lattice. In Fig. 2(b) the dispersion of an acoustical-phonon branch is drawn in the first Brillouin zone of the distorted state for $T = T_P$ and $m = 3$. For $T < T_P$ only the frequency of the acoustical mode of the distorted lattice is zero, the frequencies of the two other modes being considerably lowered with respect to the usual phonon dispersion of a linear triatomic chain [Fig. 2(c)]. This lowering is due to the small energy gap in the electronic spectrum which leads to a sharp maximum of the electronic susceptibility at $q = 0$.

From the displacement patterns of the two low-lying optical modes at $q = 0$ one can see that the lowest mode represents a shift of the phase of the superstructure out of its equilibrium position (the phase mode), while the second mode corresponds to a change of the amplitude (amplitude mode). Especially the frequency of the phase mode is very low due to the independence of the elastic energy of the lattice on the phase of the superstructure. Therefore a restoring force against displacements of the phase is only due to the weak phase dependence of the electronic part of the ground-state energy [Eqs. (3.10) and (3.14)]. As the phase independence of the lattice energy results essentially from the harmonic interaction between the ions, anharmonic interactions are expected to have an important influence on the phase-mode frequencies. In the model considered here the finite frequency of the phase mode is however entirely due to the phase dependence of the electronic part of the energy.

As shown in Sec. III, in the special case of a $\frac{1}{2}$-filled band the phase and amplitude of the system are the same degree of freedom of the system. Therefore the phase and amplitude modes are identical in this case. As will be shown the behavior of this mode is similar to that of the amplitude mode for $m \neq 2$ and thus we will call this mode the amplitude mode for $m = 2$ as well.

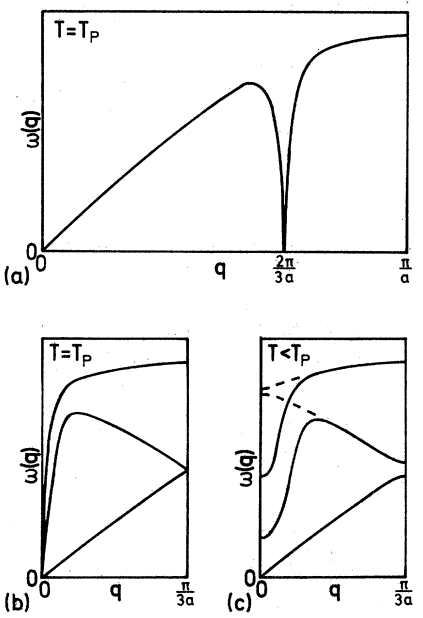

FIG. 2. Schematic drawing of the phonon dispersion of a system with a $\frac{1}{3}$-filled band ($m = 3$): (a) at the Peierls transition temperature in the Brillouin zone of the undistorted system; (b) same as (a), however, in the Brillouin zone of the distorted system; (c) below the Peierls transition, the dashed line is the usual dispersion of a linear chain with three atoms in the unit cell.

B. Green's functions

The phonon dispersions are calculated by means of the retarded Green's function

$$D_{\mu\nu}(q,t) = \langle\langle c_{q+\mu Q}(t) + c^{\dagger}_{-q-\mu Q}(t), c_{-q-\nu Q} + c^{\dagger}_{q+\nu Q}\rangle\rangle_r . \quad (4.1)$$

Umklapp processes in the deformed lattice lead to the appearance of off-diagonal elements of $D_{\mu\nu}(q,t)$. The equations of motion give for the Fourier transform of $D_{\mu\nu}(q,t)$

$$D_{\mu\nu}(q,\omega) = 2D^0(q,\omega)\left(\delta_{\mu\nu} + \sum_{\substack{l,n \\ k}} V^*_{\mu ln}(k-q,q) G_{nl\nu}(k,q,\omega)\right), \quad (4.2)$$

where $G_{nl\nu}(k,q,\omega)$ is the Fourier transform of

$$G_{nl\nu}(k,q,t) = \langle\langle A^{\dagger}_{k-q,n}(t) A_{kl}(t), c_{-q-\nu Q} + c^{\dagger}_{q+\nu Q}\rangle\rangle . \quad (4.3)$$

and

$$D^0_{\mu}(q,\omega) = \omega_{q+\mu Q}/[(\omega + i\delta)^2 - \omega^2_{q+\mu Q}] \quad (4.4)$$

is the phonon Green's function of the noninteracting system. The equation of motion for $G_{nl\nu}(k,q,t)$

leads to higher-order Green's functions. Corresponding to the RPA approximation we replace the electron-density operators by their ground-state expectation values in these higher Green's functions:

$$\langle\langle A^{\dagger}_{k-q,n}(t)A_{k-p,l}(t)[c_{p+\mu Q}(t) + c^{\dagger}_{-p-\mu Q}(t)], c_{-q-\nu Q} + c^{\dagger}_{q+\nu Q}\rangle\rangle = \delta_{qp}\delta_{nl}n_{k-q,l}D_{\mu\nu}(q,t)\,. \quad (4.5)$$

This leads to a closed system of equations for the phonon Green's functions:

$$\sum_{\mu}[\delta_{l\mu} - 2D^{0}_{l}(q,\omega)T_{l\mu}(q,\omega)]\,D_{\mu m}(q,\omega) = 2\delta_{lm}D^{0}_{l}(q,\omega)\,, \quad (4.6)$$

where the electronic susceptibilities $T_{\mu\nu}(q,\omega)$ are

$$T_{\mu\nu}(q,\omega) = 4\sum_{k,n} V^{*}_{\mu 1n}(k,q)V_{\nu 1n}(k,q) \times \frac{E_{kn} - E_{k+q,1}}{(\omega + i\delta)^2 - (E_{kn} - E_{k+q,1})^2}\,. \quad (4.7)$$

Here the time-inversion symmetry of the Bloch states has been taken into account. The phonon frequencies are obtained from the poles of $D_{\mu\nu}(q,\omega)$. The diagonal elements of the electronic susceptibility $T_{\mu\nu}(q,\omega)$ lead to a renormalization of the phonon frequencies whilst the primary effect of the off-diagonal elements, which are generally much smaller than the diagonal elements, is to split the dispersions at the zone center and at the zone boundary where otherwise some branches would be degenerate.

The susceptibilities [Eq. (4.7)] have been calculated numerically using the analytically given eigenvalues and eigenvectors of Eq. (2.7). $T_{\mu\nu}(q,\omega)$ has been approximated by $T_{\mu\nu}(q,0)$. A test of this approximation showed that it results in negligible errors as long as the maximum phonon energy given by ω_a is smaller than half the electronic energy gap. This is a reasonable assumption as the optical data of TTF-TCNQ and KCP indicate a gap of the order of 0.1 eV at low temperature while the phonon frequencies are of the order of some meV. For larger ω_a the phonon frequencies must be determined self-consistently from Eq. (4.6).

C. Dispersions

The phonon dispersions for a $\frac{1}{2}$-, $\frac{1}{3}$-, and $\frac{1}{4}$-filled bands are shown in Figs. 3, 5, and 6. Also

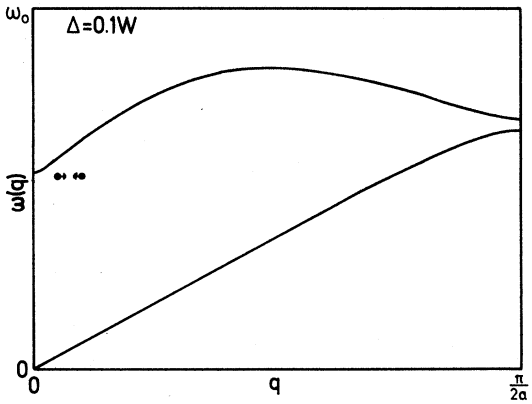

FIG. 3. Phonon dispersion for $m=2$ and the displacement pattern of the optical mode at $q=0$. This optical branch is the amplitude mode.

shown are the displacement patterns of the ions of the unit cell of the deformed system corresponding to the optical modes at $q=0$. These patterns can be calculated from the residues of the Green's functions at the corresponding poles.

half-filled band. In this case we have two phonon branches (Fig. 3) which are the acoustical and optical branch of a dimerized chain, the optical branch being the amplitude mode. The most interesting feature is the strong lowering of the frequency of this mode at small wave numbers with respect to the usual dispersion of a diatomic chain. This lowering is due to the fact that the denominator of $T_{11}(q,0)$ becomes very small for $q=0$, $k=Q$, and $T_{11}(q,0)$ has therefore a sharp maximum for $q=0$ (Fig. 4). In the Brillouin zone of the undeformed system $T_{11}(q,0)$ is the electronic susceptibility $\chi(2k_F+q,0)$. The low frequency of the amplitude mode is therefore the low-temperature analog of the soft $2k_F$ phonon for $T>T_P$ (giant Kohn anomaly). The effect is the larger the smaller the electronic gap and therefore the

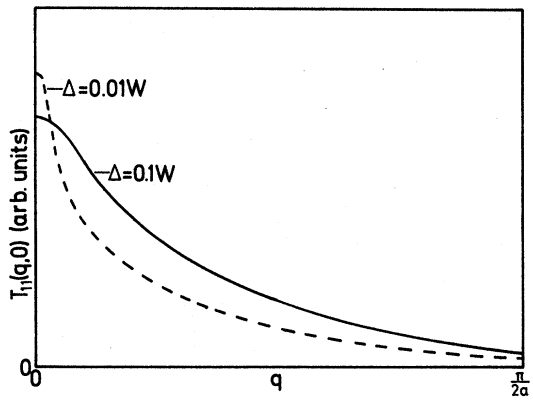

FIG. 4. Electronic susceptibility $T_{11}(q,0)$ for $m=2$ and two values of the energy gap.

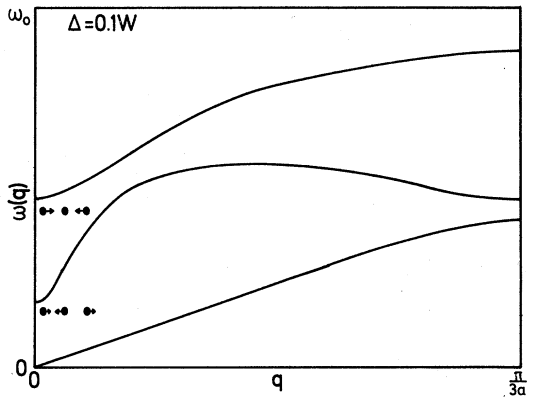

FIG. 5. Phonon dispersion and the displacement patterns of the two optical modes at $q=0$ for $m=3$. The lowest optical mode is the phase mode, the second-lowest optical mode is the amplitude mode.

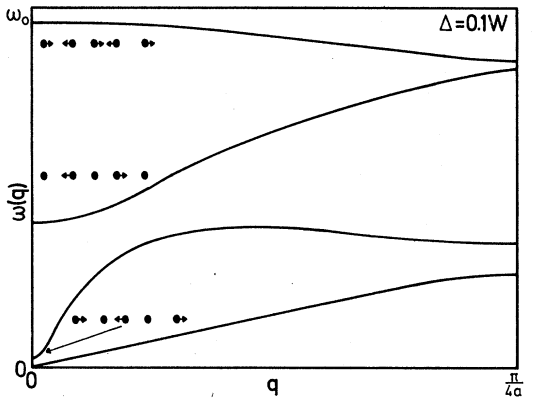

FIG. 6. Phonon dispersion and the displacement patterns of the optical modes at $q=0$ for $m=4$. As for $m=3$ the two lowest optical modes are the phase and amplitude modes, respectively.

weaker the electron-phonon coupling. For $\nu \neq 1$ or $\nu \neq 1$ $T_{\mu\nu}(q, 0)$ has no peak as in this case the matrix elements vanish for $q=0$. For large wave numbers we obtain the usual dispersion of a diatomic linear chain. The splitting between the acoustical and optical modes at the zone boundary grows with increasing electron-phonon coupling.

$\frac{1}{3}$-filled band. In Fig. 5 the phonon dispersion for $m=3$ is shown. In addition to the strongly lowered amplitude mode there is another optical mode of still smaller frequency. The displacement pattern of this mode represents a shift of the phase of the superstructure and therefore this branch is the phase mode. The very low frequency of the phase mode is due to the independence of the elastic energy on the phase of the superstructure. This is reflected in Eq. (4.7) by the fact that $T_{-1,1}(q, 0)$ has a peak at $q=0$ similar to $T_{11}(q, 0)$, while $T_{\mu\nu}(q, 0)$ vanishes for $q=0$ and $|\mu| \neq 1$ or $|\nu| \neq 1$. The peaks of $T_{11}(q, 0)$ and $T_{-1,1}(q, 0)$ are the sharper the smaller the energy gap Δ. Correspondingly the phonon anomalies are strongest for small Δ.

$\frac{1}{4}$-filled band. For a $\frac{1}{4}$-filled band we obtain a phonon dispersion similar to the case $m=3$ (Fig. 6). However, the phase-mode frequency is lower as the phase dependence of the ground-state energy is weaker than for $m=3$. Corresponding to the smaller Brillouin zone there is an additional optical mode at high frequency.

The results for $m=2, 3, 4$ show the existence of strong anomalies for optical-phonon branches representing oscillations of the phase and amplitude of the superstructure. These anomalies are due to the nearly singular behavior of $T_{\mu\nu}(q=0, 0)$ for $|\mu|=1$ and $|\nu|=1$ which is caused by the small energy gap in the electron spectrum. Therefore the anomalies are strongest if the electron-phonon coupling is small. As the appearance of the anomalies is due to the small energy gap they should be essentially independent of the special form of the band structure and of the electron-phonon coupling used here.

If the period of the superstructure is not commensurate with the lattice, the phase of the superstructure is not fixed with respect to the lattice. Therefore this case is generally treated by a jellium mode.[7] In that model the frequency of the phase mode vanishes due to the translational invariance so that besides the usual acoustical mode there is another mode with $\omega(q=0)=0$. This mode represents long-wavelength variations of the phase of the superstructure. Similar to the commensurate case treated here the frequency of this mode should grow with increasing q much more steeply than the acoustical mode.

V. ELECTRICAL PROPERTIES

A. Linear-response theory

The electrical properties are calculated by means of the retarded current-current correlation function

$$J(\omega) = \int \langle\langle j(t), j(0)\rangle\rangle_r e^{i\omega t}\, dt\,. \tag{5.1}$$

From the equation of motion of this function we obtain with an approximation analogous to Eq. (4.5)

$$J(\omega) = \sum_{\substack{l,n \\ k}} |P_{ln}(k)|^2 \frac{n_{kl} - n_{kn}}{\omega + E_{kn} - E_{kl} + i\delta} + \sum_{\mu,\nu} I_\mu(\omega) D_{\mu\nu}(q=0, \omega) I_\nu(\omega)\,, \tag{5.2}$$

with

$$I_\mu(\omega)=\sum_{\substack{l,n\\k}} P_{nl}(k)\,V_{\mu ln}(k,0)\,\frac{n_{kl}-n_{kn}}{\omega+E_{kn}-E_{kl}+i\delta}\,. \tag{5.3}$$

$P_{ln}(k)$ is the matrix element of the current operator between states of wave number k in the lth and nth band and describes the coupling of the electrons to an homogeneous external field. Using the equation for the expectation value of the current in a Bloch state

$$\langle k|j|k\rangle=\frac{e}{m}\langle k|p|k\rangle=e\,\frac{\partial E_k}{\partial k}\,, \tag{5.4}$$

we obtain from Eq. (2.9)

$$P_{ln}(k)=e\sum_\mu f^*_{\mu l}(k)f_{\mu n}(k)\,\frac{\partial \epsilon_{k+\mu Q}}{\partial k}\,. \tag{5.5}$$

The first term in Eq. (5.2) gives the contribution of the one-electron excitations of a one-dimensional insulator. The second term stems from the collective excitations of the coupled electron-phonon system.

The frequency-dependent electrical conductivity and dielectric constant are given in terms of $J(\omega)$ by

$$\sigma(\omega)=\frac{i}{\omega}\left(J(\omega)-\frac{ne^2}{m}\right),\quad \epsilon(\omega)=1+\frac{4\pi i}{\omega}\,\sigma(\omega)\,, \tag{5.6}$$

where n and m are the electron density and mass.

B. Results

In the following we consider first the case of coupling of the electrons to the acoustical phonons only. In this case the unit cell of the distorted state is inversion symmetric (see Sec. III).

In the special case of a $\frac{1}{2}$-filled-band ($m=2$) phase and amplitude motions of the superstructure are equivalent, as may be seen from Eq. (3.6). Correspondingly a change of the phase of the superstructure is only connected to a change in the amplitude of the CDW and no dipole moment is generated in the unit cell [Fig. 7(a)]. Consequently none of the collective modes of the $m=2$ system couples to an homogeneous external field and we have in this case a regular one-dimensional insulator. It should be emphasized that this is not an artifact of the special model used here but is due to the symmetry of the amplitude mode. Due to this symmetry $V_{\nu ln}(k,0)$ is an even function of k while $P_{ln}(k)$ is an odd function of k. Therefore the functions $I_\nu(\omega)$ which describe the coupling of the external field to the amplitude mode, vanish for arbitrary ω.

The remaining sums in Eq. (5.2) can be evaluated analytically in terms of elliptic integrals and we obtain (Fig. 8)

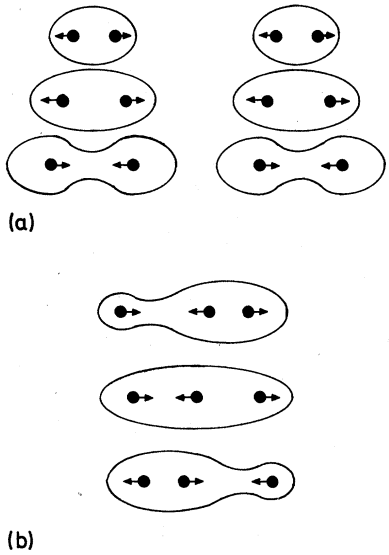

FIG. 7. Deformation of the charge cloud around the ions which is connected to (a) the amplitude mode for $m=2$ and (b) the phase mode for $m=3$.

$$\sigma(\omega)=\frac{\omega_p^2 W\Delta^2}{2\pi(4W^2-\Delta^2)^2}\,\frac{1}{\omega^2}\left(\frac{(4W^2-\omega^2)^3}{\omega^2-\Delta^2}\right)^{1/2}, \tag{5.7a}$$

$$\epsilon(\omega)=1-\frac{\omega_p^2}{\omega^2}\,\frac{8W^3\Delta^2}{(4W^2-\Delta^2)^2}\times\left[\frac{4W^2}{\Delta^2}E(k)-\left(1-\frac{\omega^2}{4W^2}\right)\Pi\left(\frac{4W^2-\Delta^2}{4W^2-\omega^2},k\right)-\frac{\omega^2}{4W^2}K(k)\right],$$

$$k^2=1-\Delta^2/4W^2\,, \tag{5.7b}$$

where ω_p is the electronic plasma frequency and

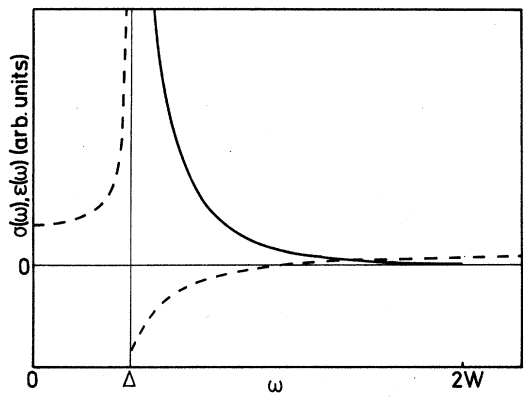

FIG. 8. Frequency-dependent conductivity (full line) and the dielectric constant (dashed line) for $m=2$.

K, E, and Π are the elliptic integrals of the first, second, and third kind, respectively.[28] These results are typical of a one-dimensional insulator. The singular behavior for $\omega = \Delta$ is due to the divergence of the electronic density of states at the band edge. The zero of $\epsilon(\omega)$ for $\Delta < \omega < 2W$ does not mean a collective excitation of the system since the conductivity and therefore the imaginary part of the dielectric constant have nonzero values.

In a commensurate system with $m \neq 2$ the displacement pattern of the phase mode is connected to a dipole moment in the unit cell of the distorted system [Fig. 7(b) for $m = 3$]. Therefore the phase mode couples to an homogeneous external field for $m \neq 2$. This coupling leads to a δ-function peak in the conductivity at the frequency of the phase mode.[29] The amplitude mode does not generate a dipole moment and therefore does not couple to the external field.

The electrical properties have been calculated numerically from Eq. (5.2) for $m = 3$ and $m = 4$ (Fig. 9 for $m = 3$). The coupling of the phase mode to the external field leads to considerable differences with the case $m = 2$.

(i) The conductivity shows a δ-function maximum at the frequency of the phase mode. Correspondingly there is a pole in the dielectric constant. These singularities are due to collective oscillations of the phase of the CDW and the superstructure about their ground-state values.

(ii) The singularities for $\omega = \Delta$ have disappeared, however conductivity and dielectric constant show still sharp maxima near the band edge. For $\omega = \Delta$ the conductivity vanishes. The disappearance of the singularities is due to the phase mode: the excitation of an electron into a state near the band edge leads to a rigid recoil of the CDW so that the phase of the CDW moves in the direction opposite to that of the excited electron and the resulting current is strongly reduced. This mechanism is most effective if the frequency of the phase mode is very low as in that case the recoil motion is only very weakly inhibited by the restoring force acting against displacements of the phase. Correspondingly the region where the conductivity is considerably lowered compared to the case $m = 2$ is largest for low ω_{ph}.

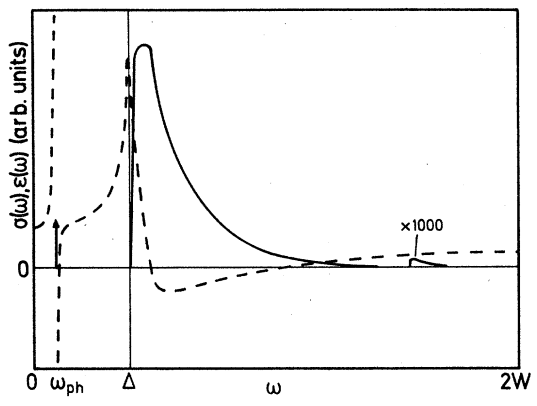

FIG. 9. Frequency-dependent conductivity (full line) and the dielectric constant (dashed line) for $m = 3$. The arrow at ω_{ph} indicates the position of the δ peak of the conductivity.

The cancellation of the singularities at $\omega = \Delta$ can be shown to be exact using the asymptotic form of the sums in Eqs. (5.2) and (5.3) for $\omega \to \Delta$.

Because of the large effective mass of the CDW (M_{eff} is the electron number times the electron mass and goes to infinity in the thermodynamic limit) the probability for tunneling of the CDW from one of the degenerate phase positions to the next is vanishingly small and therefore there is no dc conductivity in a commensurate CDW system.

The amplitude mode is symmetric with respect to the center of the unit cell in all the above considered cases. Therefore this mode is Raman active.

Up to now only the coupling of the electrons to the acoustical phonons has been considered. In addition to this coupling we now take into account the coupling to an intramolecular vibration mode [Eq. (2.4)]. In the state without a superstructure this mode is not infrared active, i.e , it does not lead to any structure in $\sigma(\omega)$. Let us now assume that the band is $\frac{1}{2}$-filled in the metallic state, so that in the ground state the chain is dimerized. In this state the dispersionless intramolecular mode is split into two branches, similar to the splitting of the acoustical modes (Fig. 3). In the limit $q \to 0$ one of these new modes corresponds to an in-phase oscillation of the intramolecular coordinates of the two molecules of the unit cell of the dimerized chain. This mode is symmetric and therefore not infrared active. The $q \to 0$ limit of the second mode represents an antiphase motion of the intramolecular coordinates of the two molecules of the unit cell, i.e., one of the molecules is contracted while the other is expanded. The coupling of the electrons to this mode leads to a concentration of the electrons on the contracted molecule, while the electron density on the expanded molecule is reduced (or inversely, depending on the sign of the electron–intramolecular-vibration coupling). Thus this mode is connected with an oscillating dipole moment in the unit cell and is therefore infrared active, i.e., it will lead to a peak in $\sigma(\omega)$. The superstructure may be said to "activate" the

usually infrared-inactive intramolecular modes. This mechanism has been used by Rice *et al.*[18] for the determination of the coupling of electrons to intramolecular vibrations of TCNQ.

In the above considerations it has been neglected that the electron-intramolecular vibration coupling will also lead to a *static* periodic deformation of the molecules. If this is taken into account the superstructure is composed of two components: (i) the relative displacements of the ions (due to the coupling of the electrons to the acoustic phonons), and (ii) the static displacements of the intramolecular coordinates (due to the coupling to the intramolecular vibrations). The resulting unit cell is no longer inversion symmetric as the two ions' of the cell have different static internal deformations. Therefore also the amplitude mode of the *interionic* displacements is infrared active, in contrast to the inversion symmetric cases treated at the beginning of this section. For commensurate cases with $m \neq 2$ the additional coupling to intramolecular modes has similar effects.

In the incommensurate case as described by the jellium model the frequency of the phase mode vanishes because of the translational invariance. Therefore the coupling of an external field to the phase mode leads to metallic electrical properties at low frequencies (Fröhlich conductivity)[6,7] in contrast to the commensurate case considered here.

VI. SUMMARY AND DISCUSSION

We have calculated the energy bands and ground-state lattice configuration for a one-dimensional coupled electron-phonon system with a $\frac{1}{2}$-, $\frac{1}{3}$-, and $\frac{1}{4}$-filled band. In these cases the period of the superstructure is commensurate with the period of the underlying lattice. Using the band structures we obtain the phonon dispersion relations. They show a strong lowering of some optical branches at $q = 0$ compared to the usual dispersions of a linear chain with an m-atomic unit cell ($m = 2, 3, 4$). These anomalous phonon branches represent oscillations of the phase and amplitude of the superstructure. The anomalies are strongest if the electron-phonon coupling is weak and the electronic energy gap is small. Especially the frequency of the phase mode is strongly lowered. This is due to the independence of the elastic energy of the lattice on the phase of the superstructure, and the finite frequency of the phase mode stems thus only from the weak phase dependence of the electronic part of the ground-state energy. The frequency ω_{ph} of the phase mode decreases with increasing commensurability index m. The incommensurate case may be regarded as the limit $m \to \infty$ and therefore in that case ω_{ph} vanishes.

The highly conducting quasi-one-dimensional compounds like TTF-TCNQ and its derivatives or KCP show an incommensurate superstructure in their low-temperature phases (with the recently discovered exception of TTF-TCNQ at high pressure[19]). It is therefore interesting to investigate whether a system with a band filling which is not just $1/m$ ($m = 2, 3, 4$) but very near to such a commensurate value shows an incommensurate superstructure (with all the electrons below the gap at $T = 0$) or is in a commensurate phase with some electrons above the gap or some holes below it. For a nearly-$\frac{1}{2}$-filled band it has been shown that near the mean-field transition temperature T_P the system is in a commensurate phase if the difference of the chemical potential μ of the metallic state and the chemical potential μ_0 of an exactly half-filled band is smaller than $k_B T_P$.[30] For $|\mu - \mu_0| > k_B T_P$ the system is in an incommensurate state. At $T = 0$ the system is always in the incommensurate state, even if it is in a commensurate state for $T \lesssim T_P$.[31] For a nearly-$\frac{1}{3}$-filled band similar results have been obtained.[32] All these calculations use mean-field theory. Taking account of fluctuation effects it has been shown for a nearly-$\frac{1}{4}$-filled band that in the ground state there is a commensurate superstructure,[33] contrary to the mean-field results. The stabilization of the commensurate phase with respect to the incommensurate state can be easily understood in the light of the results of the present paper, as we have shown that the phase-mode frequency in a commensurate system is nonvanishing, while it vanishes in the incommensurate case due to the translational invariance.[7] The important point is that fluctuations of the phase which tend to inhibit phase transitions at finite temperature in one-dimensional systems[34] are suppressed by the finite frequency of the phase mode in the commensurate state. Consequently the commensurate state is stabilized with respect to the incommensurate state, in accord with the results of Ref. 33. It is known that a weak three-dimensional coupling suppresses the fluctuation effects.[21] Therefore we expect that the incommensurate state is favored compared to the commensurate one if a suitable three-dimensional coupling is taken into account, in agreement with the experimental results.[2,4] However, to our knowledge no theoretical investigations of the effect of such a coupling on the relative stability of the commensurate and incommensurate states have been carried out so far.

The electrical properties have been calculated

by linear-response theory. For $m=3$ and $m=4$ the coupling of an homogeneous external field to the phase mode leads to a δ-function peak in the conductivity at $\omega=\omega_{ph}$. This is in contrast to the incommensurate case where the phase mode has zero frequency resulting in metallic electrical properties. The phase mode leads further to the disappearance of the singularities of the electrical properties near the band edge which are typical for a one-dimensional insulator. This is due to the recoil of the CDW when a single electron is excited across the gap.

In the special case of a $\frac{1}{2}$-filled band in the undeformed state phase and amplitude of the superstructure are equivalent. Therefore there is only one optical-phonon branch with an anomaly at $q=0$. Because of the symmetry of the system this mode does not couple to an homogeneous external field.

If in addition to the coupling to the acoustical phonons also the coupling to intramolecular vibrations is considered, the lower symmetry of the dimerized ground state leads to a coupling of these usually infrared-inactive modes to an homogeneous external field and therefore to a peak in the frequency-dependent conductivity at the frequency of this mode, in agreement with the results of Rice *et al.*[16,18]

The most widely studied quasi-one-dimensional substances are the conducting compounds TTF-TCNQ and KCP. The phase and amplitude modes with low frequency have been found in both substances by infrared[8,9] and Raman[35,36] experiments. The results of the present paper are however not applicable to these systems as they show an incommensurate superstructure at low temperature.[2,4]

A superstructure which is commensurate in the chain direction has recently been found in TTF-TCNQ at high pressure.[19] Further experimental investigations of this state should thus provide data which can be compared with the results presented here. Especially it would be interesting to observe the behavior of the low-frequency infrared- and Raman-active modes in the commensurate state.

Commensurate superstructures are also generally found in quasi-one-dimensional semiconductors like the alkali-TCNQ salts or TEA-$(TCNQ)_2$. Data on the lattice dynamics of these substances are not yet available. Measurements of the frequency-dependent conductivity show strong peaks at the frequencies of usually infrared-inactive intramolecular vibrations of TCNQ,[14,15] in agreement with the arguments given at the end of Sec. V. These data have been used by Rice *et al.*[17,18] to determine the coupling of the electrons to the intramolecular modes of TCNQ. It would be interesting to observe the behavior of the frequency-dependent conductivity in the high-temperature nondimerized phase of K-TCNQ.[12] In the light of the discussion in Sec. V the coupling of the intramolecular modes to the electrons should vanish in this state and consequently there should be no structure in $\sigma(\omega)$ related to the intramolecular modes of the TCNQ molecule.

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filled band. For a n'/n-filled band (n, n' aliquant) one has to define the commensurability index by $m = n$. In the present paper we restrict ourselves to the case $n' = 1$; however, the main results are easily generalized for $n' \neq 1$.

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