Three-dimensional ordering of charge-density waves in quasi-one-dimensional and layered crystals

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The tunnel-Hamiltonian method is used to obtain the free interaction energy of charge-density waves (CDW) in quasi-one-dimensional and layered crystals as a function of the phase difference of the CDW of individual chains or layers. It is shown that a contribution to this interaction is made by tunneling of the electrons between the chains (layers) and by the Coulomb interaction of the CDW, and that the first of these mechanisms predominates in all cases. The experimental data for quasi-one-dimensional crystals are discussed on the basis of the results. For layered crystals, the three-dimensional ordering is determined from the condition that the free energy of the interaction of the layers be a minimum, with account taken of the commensurability effects. This approach explains the experimentally observed types of three-dimensional ordering of CDW in layered crystals.

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1. INTRODUCTION

Structural investigations show that charge-density waves (CDW) appear in layered crystals of dichalcogenides of transition metals and in quasi-one-dimensional compounds when the temperature is lowered (see also the reviews1). In all the investigated layered crystals, the appearance of a CDW superstructure is connected with the appearance of a superstructure of the lattice within the chains (layers). We shall similarly, in quasi-one-dimensional compounds, the period of the lattice within the chains is altered. In most cases the appearance of a superstructure within layers or chains is accompanied by three-dimensional ordering of the CDW in the crystal, owing to the interaction of the CDW of different layers or chains. Such a distinct three-dimensional periodicity of the CDW was observed in the T and 2H modification of the purely layered crystals TaS₃, NbSe₃, and NbS₃ in the entire region of the existence of the two-dimensional superstructure.1-4 It was also observed in the quasi-one-dimensional TTF-TCNQ crystals below 54 K and in TTF-TCNQ below 29 K.5-6

In a number of disordered quasi-one-dimensional and layered crystals, however, no long-range three-dimensional order of the CDW is observed, and only the appearance of correations of the CDW of different layers or chains has been noted. This situation takes place in KCP below 120 K17 and in the 17-Ta₆₅-Zr₆₅ alloys at x > 0.015.8-11 Finally, both possibilities are realized in 4H-TaSe₂ crystals—the CDW of the octahedral layers are ordered in the crystal at those temperatures at which investigations of the superstructure were carried out (10 and 300 K), while the CDW of the trigonal layers remain disordered at 10 K.12

The present article deals with three-dimensional ordering of CDW in similar systems. Within the framework of the microscopic theory based on the use of the Fröhlich Hamiltonian, we derive an expression for the free energy of the interaction of the CDW in different layers (chains) as a function of the phase difference of the CDW of the individual layers (chains). We shall show, that this free energy consists of two contributions, one from the Coulomb interaction of the CDW and the other from transitions of the electrons between the layers (chains), with the second effect predominating. In the absence of a commensurability energy, both contributions tend to establish in neighboring layers CDW that are in antiphase. This result was qualitatively arrived at earlier by Barisch (who considered only the Coulomb interaction of the CDW) and one of us (see9). In the present article we have obtained the explicit of the corresponding terms of the interaction as a function of the phase difference of the CDW of layers. This form has enabled us to determine the type of the three-dimensional ordering with allowance for the commensurability effects.

We note that the possible types of the three-dimensional ordering were predicted earlier within the framework of the phenomenological Ginzburg-Landau theory,13,14 with allowance for commensurabilities for layered compounds, in our short paper,10 and by McMillan.15 The proposed types of three-dimensional ordering are different in these papers. We shall show that both types of solutions can exist in disordered crystals (KCP, 17-Ta₆₅-Zr₆₅ alloys at x > 0.015). The proposed types of three-dimensional ordering are different in these papers.

2. GENERAL EXPRESSION FOR THE INTERACTION ENERGY OF THE CDW OF DIFFERENT LAYERS (CHAINS)

The interaction of CDW of different layers or chains in a three-dimensional crystal with strong anisotropy is due to two effects: transitions of the electrons between the layers (chains), and Coulomb interaction of the CDW. The interactions due to the tunneling of the electrons between the layers (chains) is in effect similar to the Josephson interaction of superconductors, and particularly with the Josephson interaction of layers in layered...
superconductors. To calculate this effect, we shall use in the greater part of this paper the tunnel-Hamiltonian method, which was developed for the solution of analogous problems in the superconductivity region.

We describe the CDW transitions within the framework of the Frijhlich model for a system of electrons and phonons (see, e.g., ). We consider two layers: 1 and 2. The Hamiltonian of this subsystem, without allowance for the Coulomb interaction of the electrons, is given by

\[ H = \sum \epsilon_n \hat{c}^\dagger_n \hat{c}_n + U N \sum \hat{a}_n^\dagger \hat{a}_n + \text{h.c.} \]

and \( H \) has a similar form. \( \hat{c}_n^\dagger, \hat{c}_n \) are the operators for the production of the electrons with spin \( s \) on the sites \( n \) of layers 1 and 2, and \( t, \) is the matrix element of the electron transition between the sites \( n \) of layers 1 and 2 (we use the strong-coupling approximation to describe the motion of the electrons between layers, and assume for simplicity that the lattices of layers 1 and 2 are equivalent). We designate the electron energy in layer 1 by \( \epsilon_{l1} \); \( b(Q) \) is the operator of the production of a phonon with quasimomentum \( Q \) and energy \( a, \) where \( k \) is the wave vector of the CDW. We assume that the vectors \( Q \) are identical to layers 1 and 2, for otherwise there is no interaction of the CDW of layers 1 and 2 in first-order approximation. The interaction of the electrons with the \( Q \) phonons, which determine the instability, is described by the parameters \( g_{n1} \) for layers 1 and 2; \( N \) is the density of the atoms (molecules) in the layer or chain. All the vectors \( n, k, \) and \( Q \) in (1) are two-dimensional for layered crystals and one-dimensional for the quasi-one-dimensional systems. Since the phonons with quasimomentum \( Q \) which condense in the CDW transition correspond to longitudinal acoustic oscillations or to fully symmetrical intramolecular oscillations, there is no direct interaction of phonons with quasimomentum \( Q \) in different layers (chains) in the linear approximation.

We take into account the influence of the tunnel Hamiltonian \( H_t \) on the interaction of the CDW of layers 1 and 2 by using perturbation theory in \( H_t \). The limits of applicability of this approach to quasi-one-dimensional systems are discussed below. To use perturbation theory we must know the solution for CDW of individual layers 1 and 2. We introduce the order parameters

\[ \Delta_{l1} = \sum_n \epsilon_n \hat{c}_n^\dagger \hat{c}_n \]

To describe the electron system, we use the Nambu representation

\[ \psi_{l1} = \sum_n \epsilon_n \hat{c}_n^\dagger \hat{c}_n + \text{h.c.} \]

In (2) and hereafter we reckon all the energies from the Fermi level \( \epsilon_F \).

For the free energy of an individual layer we have

\[ F_{l1} = -T \sum_{\delta} \left[ n(\epsilon_F + Q) \right] + \tilde{G}(\delta) \left( W_{l1} / 2 \right) \]

and the gap \( |\Delta| \) is determined from the equation

\[ 1 = \sum_{\delta} \left\{ \left[ \tilde{G}(\delta) \right] \left[ \epsilon_F - \epsilon(\delta) \right] / \left( \delta + \epsilon(\delta) \right) \right\} \]

which has a nontrivial solution at \( T < T_0 \) where \( T_0 \) is the temperature at which the CDW appears in the self-consistent field approximation for an isolated layer or chain.

For the single-electron Green's function \( G(k, \omega) \) we have in the temperature technique (\( i\omega_m - \epsilon_{l1} \)) and

\[ G(k, \omega) = \left[ \frac{i\omega_m - \epsilon_{l1}}{2} \right] \frac{1}{\left[ i\omega_m - \epsilon_{l1} - \epsilon_0 \right]} \left[ \frac{\epsilon_0}{\omega_m} \right] \]

where \( N(0) \) is the state density on the Fermi surface, \( \rho_0 \) and \( M \) are the density and mass of the ions and \( u \) stands for their displacements in the CDW transition.

We can now obtain an expression for the free-energy density of the interaction of the CDW of layers 1 and 2. We are interested here only in that part of the free energy which depends on the phase differences \( \varphi_1 \) and \( \varphi_2 \) of the CDW of layers 1 and 2. For the density of the Coulomb interaction of the CDW we obtain from (6)

\[ F_{c12} = -2T \sum_{\delta} \frac{N(0)}{2 \pi} \left[ \tilde{G}(\delta) \right] \sum_{\delta} \frac{1}{\left[ \epsilon_F - \epsilon(\delta) \right]} \left[ \frac{\epsilon_0}{\omega_m} \right] \left[ \frac{\epsilon_0}{\omega_m} \right] \]

where \( R \) is the distance between the layers (chains) and \( K_o(\epsilon) \) is a Bessel function. The tunnel Hamiltonian makes a contribution to the free energy of the interaction in second-order perturbation theory and this contribution is determined by

\[ F_{t12} = -2T \sum_{\delta} \frac{N(0)}{2 \pi} \left[ \tilde{G}(\delta) \right] \sum_{\delta} \frac{1}{\left[ \epsilon_F - \epsilon(\delta) \right]} \left[ \frac{\epsilon_0}{\omega_m} \right] \left[ \frac{\epsilon_0}{\omega_m} \right] \]

where \( F_{t12} \) is that part of the interaction free energy which does not depend on the phases of the phases of the CDW.
The free energy (3) of the layer 1 the commensurability effects can be disregarded, since they yield small corrections to the expressions obtained by us.

In the expressions for $F_{c}(p_{l})$ and $F_{c}(q_{l})$, the commensurability effects can be disregarded, since they yield small corrections to the expressions obtained by us.

We now take into account the influence of the disorder of the lattice on the CDW interaction. According to the theory and the experimental data obtained by us, however, the effect of the disorder of the crystal on the values of the matrix elements $t_{q}$ is so small that its influence on the values of $I_{q}$ is negligible.

In the case of identical chains, the "tunnel" interaction of the CDW takes the form

$$F_{c}(p_{l}) = \sum_{q_{l}, q_{l}'} \left[ \frac{1}{2} \left( 1 - \exp\left(-\frac{2k_{F}q_{l}}{\hbar v_{F}}\right) \right) - \frac{1}{2} \right] \delta(p_{l} - q_{l})$$

In the limit of a system without impurities, $\Gamma = 0$, the tunnel interaction can be reduced to the form

$$F_{c}(p_{l}) = \sum_{q_{l}, q_{l}'} \left[ \frac{1}{2} \left( 1 - \exp\left(-\frac{2k_{F}q_{l}}{\hbar v_{F}}\right) \right) - \frac{1}{2} \right] \delta(p_{l} - q_{l})$$

where $\delta$ is the Riemann delta function.

An analysis of equations (12) and (13) for $F_{c}$ shows that the disorder leads to a considerable decrease of the CDW tunnel interaction. At $I = R(1 + p_{l})^{1/2}(\hbar)$ the values of $F_{c}$ decreases in proportion to $I$ with decreasing $I$. If $(\hbar)$ remains unchanged, $F_{c}$ decreases by an approximant factor $\exp(-\frac{1}{2}R)$, when $I$ decreases from $\Gamma$ to distances on the order of interatomic. However, a comparison of $F_{c}$ and $F_{c}$ even in the most disordered system (when $F_{c}$ is minimal) shows that $F_{c}$ is smaller than $F_{c}$ by at least a factor of $\exp(-\frac{1}{2}R)$ with increasing $R$.

Before we proceed to an interpretation of the experimental data, let us discuss the conditions of the applicability of the perturbation theory for the tunnel Hamiltonian in the case of quasi-one-dimensional crystals. We
consider a system of identical chains and start from a three-dimensional band structure with a spectrum \( \varepsilon(k) = (k_0)^2/2m + (\cos k_x + \cos k_y + \cos k_z)\), where \( k_0 \) is the momentum along the chain and \( k_x, k_y, k_z \) is the transverse momentum. The Hamiltonian of the system takes the same form as in (1), but all the vectors must be regarded as three-dimensional (including the superstructure wave vector \( \mathbf{Q} \)). By a procedure similar to that used in Sec. 2, we obtain next expression (3) for the free energy and the self-consistency equation (4) for the order parameter \( \Delta \).

We consider antiferromagnetically ordered systems with \( t \ll t_c \). The vector \( \mathbf{Q} \), which determines the three-dimensional period of the superstructure, has a component \( Q_x = 2m \mathbf{t}_c \mathbf{t}_c \), and its transverse component \( \mathbf{Q}_y = \{0, \mathbf{t}_c, \mathbf{t}_c \} \) should be determined from the condition that the free energy is a minimum. In real systems in which \( t/t_c \) is not linear, the transition of the CDW takes place if \( t/t_c < T_0 \) (see (3)), and we shall consider below separately systems for which \( t < T_0 \) or \( t/t_c < T_0 \).

In crystals with \( t < T_0 \), the self-consistency equation (4) for \( \Delta \) has a solution for all values of \( \mathbf{Q} \). The free energy takes in the self-consistent-field approximation the form

\[
F(\Delta, Q, Q_y) = \frac{1}{2} \sum_{\sigma} \left[ (\sigma + \frac{t}{2}) + (\sigma - \frac{t}{2}) \right] \left[ \frac{1}{2} \left( \frac{1}{4} \frac{Q}{2} \right) \right] + \alpha Q \left[ \frac{1}{2} \left( \frac{1}{4} \frac{Q}{2} \right) \right],
\]

and the first nonvanishing term of the expansion of \( F \) in \( t \) yields expression (43), the expansion parameter being \( t/t_c \) at \( T = 0 \) or \( t/T_0 \) near \( T_0 \).

Similar results are valid also at \( T < t/t_c T_0 \), except that in the weak-coupling limit \( \lambda \ll 1 \) a solution with \( \Delta = 0 \) exists only when the phase difference \( \phi_1 - \phi_2 \) satisfies the condition \( \cos(\phi_1 - \phi_2)/2 = \cos(\Delta/2) \). This inequality determines the limits within which deviations of \( \phi_1 - \phi_2 \) from \( \lambda \) as a result of the commensurability effects are permissible.

Adding now to the chain interaction energy the commensurability energy (which is significant if \( \lambda \ll 1 \) and \( t < t_c \)), the expansion parameter being \( t/t_c \) at \( T = 0 \) or \( t/T_0 \) near \( T_0 \).

The free energy must be regarded as a function of the phases of the Landau functional that depends on the phases of the chains, and all the thermodynamic characteristics of the system are determined by averaging over the phases. Within the framework of this analysis, the long-range three-dimensional order, which corresponds to the maximum value of the free energy of test chain interaction (11) and (13), appears at a temperature \( T_0 \leq T_0 \), and the value of \( T_0 \) can be obtained in the self-consistent-field approximation from the chain interaction (32). If in the region \( T_0 < T \) there is no correlation of the Peierls distortions between the chains, a three-dimensional structure appears below \( T_0 \), but the fluctuations remain strong also at temperatures \( T < T_0 \), i.e., \( \langle \Delta^2 \rangle \ll \langle \Delta \rangle \) (at low temperatures it is necessary to take the quantum fluctuations into account) (32). It appears that the situation \( T > T_0 \) is not encountered in all those quasi-one-dimensional compounds in which a superstructure has by now been observed. In fact, in crystals containing chains of two types with isocoupled charge transfer, the hybridization gap at \( T > T_0 \) is large in comparison with the Peierls gap, so that the CDW transition cannot be energy favored. In addition, at \( T > T_0 \), the three-dimensional order is determined by the form of the three-dimensional Fermi surface, and the latter must of necessity affect directly the entire system. It is difficult to reconcile this conclusion with the fact that in TTF-TCNQ, in the interval 49–55 K, three-dimensional ordering is observed only in TCNQ chains (32). At the same time, in all the quasi-one-dimensional compounds with the exception of KCP, abrupt changes of the magnetic susceptibility and of the resistivity are observed at the three-dimensional-ordering temperature. Experiment has revealed in TTF-TCNQ at 55 K a specific-heat discontinuity of the same order as that given by the SCF approximation. None of these facts are possible in the \( t < t_c \) situation. As a most probable situation in TCNQ salts is therefore \( t_c < T_0 \) to which the SCF approximation is applicable (the case \( t < t_c \) is not excluded for KCP).

At \( t < t_c \), the SCF approximation is not valid. In this region, the free energy must be regarded as a Ginzburg-Landau functional that depends on the phases of the chains, and all the thermodynamic characteristics are determined by averaging over the phases. However, with the SCF approximation, a solution with \( \Delta = 0 \) exists at any phase difference \( \phi_1 - \phi_2 \), and the three-dimensional ordering is determined in this range of parameters by the usual procedure for minimizing the free energy with respect to the phase.

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Thus, the form of the three-dimensional ordering is determined from the minimization condition of the free-energy density (13)-(15):

$$F = \sum_{n} h_{n} \cos(q_{n} \cdot \mathbf{a}) = \sum_{n} h_{n} \cos(q_{n} \cdot \mathbf{a}) = \sum_{n} h_{n} \cos(q_{n} \cdot \mathbf{a})$$

where $n$ and $m$ are the numbers of the chains in the crystal. We do not take into account here the commensurability effect, inasmuch as in all the quasi-one-dimensional crystals investigated to date the CDW is not commensurate with the period of the host lattice. The interaction of the chains falls off rapidly when they move apart, so that we need retain in (16) only the interaction of the nearest neighboring chains if the crystal is made up of chains of the same type, and the interaction with the nearest and next-nearest neighbors in complicated crystals with chains of two types, for the directions in which the different chains alternate.

It follows from (16) that in a crystal made up of identical chains there should be observed a superstructure with a doubled transverse period. In crystals with internal disorder or with impurities, there may be no phase transition with appearance of three-dimensional long-range order. In fact, according to the results, the disorder greatly weakens the CDW interaction of different chains. In the case of weak CDW interaction of the chains, the structure defects cause loss of phase coherence of the CDW within the chains, and no long-range order is established either along or across the chains even at zero temperature, $T_{0}$. Under these conditions, only a correlation (in the antiphase) of CDW of different chains should occur. This is precisely the situation observed in KCP crystals. In these crystals, constructed of chains of the same type, the internal disorder is due to the random disposition of the Br ions among the conducting chains of the Pt atoms. A disorder of this type leads to a maximum suppression of the tunnel interaction ($I_{c} = 0$), and as a result, a tendency to a doubling of the transverse period is observed in these crystals below 120 K, whereas the "one-dimensional" superstructure with period $I_{c} = 6.70$ is observed already at 300 K.

In TTF-TCNQ the superstructure $b' = 3.15b$ appears below 250 K. In these crystals, just as in TTF-TCNQ, chains of donor and acceptor molecules alternate along the $a$ direction. The experimental situation with the three-dimensional ordering of the CDW in TSeF-TCNQ is still unclear. According to the experimental data, the superstructure has a doubled period along the $a$ direction ($2b' = 5b$) below 29 K. According to (11) and (12), this period of the superstructure, within the framework of the SCF approximation ($\langle z_{n}^{2} \rangle$), can be observed in the case when the Peierls' displacements are present only on chains of one type ($\langle \Delta z_{n} \rangle = 0$) in the region where the transverse period is doubled. Since most of the scattering by the superstructure is due to Be atoms, it follows that in TSeF-TCNQ the Peierls instability should be due principally to the TSeF chains, if the experimental data of (11) are correct.

In TTF-TCNQ, as shown in (13), the superstructure $b' = 3.4b$ has a period $a' = 5a$ from 54 to 49 K, and below 49 K down to 38 K, the period $a'$ increases with decreasing temperature, becoming jumpwise equal to $4a$ at 38 K. Within the framework of the SCF approximation and of relations (11) and (12), a period $a' = 2a$ corresponds to the appearance of distortions in the TCNQ chains, while the change of $a$ below 49 K is due to the onset and growth of distortions in the TTF chains. In this analysis, however, the jump to $a' = 4a$ has in our opinion not been satisfactorily explained. It is possible that the three-dimensional behavior of the superstructure $b' = 3.4b$ depends on the superstructure $b' = 1.12b$ observed in (10).

4. LAYERED DICHALCOGENIDE CRYSTALS

The total interaction of the CDW of different layers is determined by the form of their Coulomb interaction $F_{0}$, defined by formula (7), and the tunnel interaction $F_{t}$ (relations (8) and (9)). To calculate $F_{t}$ we must know $|\Delta|$ and the electron spectrum of the crystal in the phase without the CDW. The calculations of Matthes' $F_{t}$ yield information on the spectrum, and $F_{t}(\lambda)$ can in principal be calculated for pure crystals. However, even without such calculations we can draw on the basis of (7)-(9) the following qualitative conclusions, which will be needed later on to determine the possible types of three-dimensional CDW ordering of layered compounds.

1. A comparison of $F_{t}$ with $F_{0}$ suggests that $F_{0} < F_{t}$, just as in quasi-one-dimensional crystals. Actually, $F_{0}$ must contain an additional small factor of the type ($\langle z_{n}^{2} \rangle$) in comparison with $F_{t}$, and we have $F_{0} < F_{t}$ even if $|\Delta|$ decreases with decreasing distance $R$ between layers, in analogy with the Coulomb interaction of the CDW, i.e., $|\Delta| = \frac{e^{2}a^{2}}{e^{2}a^{2} + \lambda^{2}}$. In fact, however, the matrix elements $\lambda_{n}$ at least for the nearest neighbors ($\Delta_{n}$), turn out to be larger than $\lambda_{c} = \frac{e^{2}a^{2}}{e^{2}a^{2} + \lambda^{2}}$. The estimate $|\lambda_{c}a_{c}^{2}e^{2}a^{2}|$ would yield $|\Delta_{n}| = 0.02 eV$ and an effective mass anisotropy of the order of 100 (at $e^{2}a^{2} = 2 eV$). According to Matthes' calculations, $|\Delta_{n}|$ is larger by approximately one order of magnitude, and the experimental anisotropy of layered crystals does not exceed $10^{2}$.

2. We shall be interested below in the interaction of the first and second neighboring layers $F_{12}$ and $F_{23}$. Undoubtedly, $F_{12} \propto F_{23}$, but in principle there are no grounds for assuming that $F_{23}$ decreases exponentially with increasing $n$.

3. Just as in the one-dimensional case, the disorder weakens the tunnel interaction between the layers $F_{12}$ and all the more $F_{23}$.

We now write down that part of the free energy which depends on the CDW phases. We recognize first that, owing to the hexagonal symmetry of the layered crystals, there always appear three CDW with vectors $\mathbf{Q}_{i}$ ($i = 1, 2, 3$) turned 120° relative to one another. We introduce three parameters $\phi_{i}$ of the internal order in the layer, assuming that $\phi_{i} = \Delta_{i} \cos(\mathbf{Q}_{i} \cdot \mathbf{r})$. In the lowest order in $\Delta_{i}$ waves with identical $\mathbf{Q}_{i}$ interact between different layers, and the total free energy is given by

$$F = \sum_{\mathbf{Q}_{i}} \{F_{i}(\phi_{i}) = \sum_{\mathbf{Q}_{i}} \sum_{\mathbf{Q}_{j}} \delta_{i,j} \cos(\phi_{i} - \phi_{j}) \}$$

$$F_{i}(\phi_{i}) = \int \int \int \frac{e^{i \mathbf{Q}_{i} \cdot \mathbf{r}}}{(2\pi)^{3}} \left[ -\Delta_{i} \delta_{i,j} + \sum_{\mathbf{Q}_{j}} e^{i \mathbf{Q}_{j} \cdot \mathbf{r}} \left( \phi_{i} - \phi_{j} \right) \right] \frac{1}{S}$$

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tunnel interaction of the layers and by the first term in
the temperature interval. If in fact it is not satisfied
we still obtain
and
be observed. In the 2H modification, the neighboring
layers are the same for the next-to-neighboring
layers. In this situation, the minimization of (17) can
be carried out within the framework of perturbation the-
ory in the interaction of the layers. At
we obtain the minimum of
where
are arbitrary integers. Under this condition the minimum
of (17) is the point of the transition of the CDW phase
in the 2H modification. The term with the coefficient
is significant for 2H modifications, in which the
commensurate CDW phase is due to the strong interaction of the three
waves with a noticeable overlap of the electron wave
functions of the next-to-neighboring layers.

In the 2H modification experiment yields in the
non-cumensurate phase
and
McMillan’s solution is energywise more favored. For
this solution the phase shift of the neighboring layers is
2π/3 at
and approaches
with decreasing
Thus, the solution obtained in(19) goes over continuously
to the unique solution realized at
. The solution with
is energywise more favored than at
. If it is realized at
then as the tempera-
ture approaches
the solution is energywise more favored. For
the solution c’ = 3c goes over jumpwise into
McMillan’s solution with double the period. It is seen
from this, in particular, that our solution
in(19) can be realized only if the condition
is satisfied. Thus, at
we obtain in the 1T modification either
c’ = 2c or c’ = 3c, depending on the ratio of the parameters
and
In the 2H modification we have respec-
tively
c’ = c or c’ = 3c.

In the 1T modifications of TaSe and TaS experiment
reveals c’ = 3c(41) thus indicating a large value of
For
and a substantial role of the
term in comparison with the energy
We note that the CDW Coulomb interaction can by itself not lead to this result,
since when the estimates
and
are taken into account we obtain
For a tunnel inter-
action
that decreases with
exponentially, we ob-
tain analogously
Thus, the existence of the superstructure c’ = 3c above
in 1T-TaS and
17-TaS is due to the strong interaction of the three
waves with a noticeable overlap of the electron wave
functions of the next-to-neighboring layers.
we have $F_c \ll F_o$ or $F_o \gg F_c$, but $b_k \sim 8/10a^2$ (i.e., McMillan's solution is realized). Although in both these situations the crystal period is the same, the solution for the sequence of the CDW phases of the layers is different in these two situations. At $F_o \ll F_c$ the phase difference between neighboring layers is close to $\pi$ at all temperatures. In the second case it is close to $2\pi/3$ in modulus and alternates in sign at low temperatures, but approaches $2\pi$ as $T_o$ is approached. This difference makes it possible to explain the relative role of the commensurability effects and the three-dimensional effects in 2H crystals. If these two types of superstructure can be distinguished experimentally.

We note that the difference between the types of the NCDW superstructures in the 1T and 2H modifications ($c' = 3c$ and $c' = c$) of $\text{TaS}_2$ and $\text{TaSe}_2$ is undoubtedly due to the smaller values of $A$ and $T_2$ in the 2H crystals. In experiment, the displacements of the atoms in the 2H crystals (which are proportional to $A$) is smaller by approximately one order of magnitude than in the 1T modifications (14) and the energy $F_c$ in (2H) is correspondingly smaller. It is therefore of interest to investigate the superstructure in $1T-\text{TaS}_2$. In this compound, owing to the low value of $T_o$, one cannot exclude a solution $c' = 3c$ in the NCDW phase, at least near $T_o$.

**Commensurate CDW phase**

For the 2H modification in the commensurate phase, an important role is played by the terms with the coefficients $b_0$ and $b_1$, the role of the terms with $b_1$ being completely analogous to the role of the term with the coefficient $b_0$. In the commensurate phase, just as in the NCDW modification, the two situations are therefore possible: $c' = c$ and $c' = 3c$. In experiment below $T_o$ in 2H-$\text{TaSe}_2$, $c' = c$ is again realized (13) for the reasons indicated above.

In the 1T modifications, the terms of significance are those with the coefficients $b_0$ and $c_1 = 0$.

Let us obtain the solution at $F_o \ll F_c$ (the solution $c' = 2c$ is realized at $F_c \gg F_o$). The minimum of $F_o$ is reached if the phases $\varphi_{c,1}$ satisfy the equations

$$\varphi_{c,1} = \varphi_{c,2} = \ldots = \varphi_{c,2n} = \varphi_{c,0} + 2\pi k_n, \quad k_n = 0, 1, 2, 3,$$

(21)

($2_n$ are integers). The solution of these equations is of the form

$$\varphi_{c,1} = 2\pi l (52n + 30n - 35), \quad \varphi_{c,2} = 2\pi l (-30n + 45 - 35),$$

(22)

and the same form is assumed by the changes of the phases on going from layer $s$ to layer $s + 1$. Minimization of $F_o$ in first order of perturbation theory yields an optimal phase shift $2\pi (2, 6, 5)/13$ between neighboring layers. When account is taken of the term $F_0$ and of the term $F_1$ in second order of perturbation theory, we obtain the solution for the phases $\varphi_{c,0}$ in this form ($2n_0$, $\varphi_{c,0} = 2\pi l (2, 6, 5) / 13$, if $b_0$ is large enough) and a doubling of the period at small $b_0$ (a solution of McMillan's type (12)).

Experiment has revealed in 1T-$\text{TaSe}_2$, below $T_c = 473 K$ a superstructure with wave numbers $(2, 6, 5) c^* / 13$. A superstructure $c' = 13c$ is also observed in 1T-$\text{TaS}_2$ below $200 K$. Thus, our solution of (21) is realized for CCDW in these compounds.

In 4Hb-$\text{TaS}_2$ crystals, octahedral layers analogous to the 1T-$\text{TaSe}_2$ layers alternate with the trigonal layers analogous to the layers in 2H-$\text{TaSe}_2$. In the octahedral layers, according to the data cited in (14), the superstructure inside the layers is similar to the 1T-$\text{TaSe}_2$ superstructure, and at $T_o = 410 K$ one observes an NCDW-CCDW transition identical with the transition in 1T-$\text{TaSe}_2$ at $T_c = 473 K$. In contrast to the 1T modification, however, below $T_o$ the period of the crystal is $c' = c$ (the unit cell of the 4Hb modification contains two octahedral and two trigonal layers which are not equivalent with respect to the arrangement of the chalcogens). In trigonal layers, CDW appear at $T_o = 75 K$, but there is no three-dimensional ordering of this superstructure down to 10 K. Inside this layer this superstructure is analogous to that observed in 2H-$\text{TaSe}_2$, except that no transition to the commensurate state is observed. The superstructures of the trigonal and octahedral layers do not interact with one another—their wave vectors $\mathbf{q}_i$ are different. Therefore the three-dimensional ordering in these subsystems is established independently. For octahedral layers, according to the results obtained above, we can have $c' = c$ (McMillan's solution) or $c' = 13c$ (see the solutions in (21)). The fact that the first possibility is realized is obviously due to the small value of the interaction of the non-nearest-neighbor octahedral layers $b_0$ (these layers are separated, besides the one octahedral layer, by two additional trigonal layers).

We now examine the influence of the disorder on the three-dimensional ordering of the CDW in layered crystals. In addition to suppressing the tunnel interaction, the disorder suppresses also the long-range order within the layers. Since the three-dimensional ordering is controlled by the small term $F_0$ or $F_c$ which decrease rapidly with increasing disorder, it is not surprising that the three-dimensional ordering is very sensitive to the degree of disorder in the crystal. According to experimental data (15) three-dimensional ordering is realized in 1T-$\text{TaS}_2$, 2H-$\text{TaSe}_2$ alloys at $x < 0.015$. When $x$ increases above 0.015, the correlation of the CDW phases of the remote layers decreases and vanishes completely at $x > 0.03$. The short-range order is determined in this case as before by the wave numbers $(2, 6, 5) c^* / 13$, a fact that manifests itself in the existence of a broad peak at the average value $c^* / 3$.

We see thus that the three-dimensional ordering of the CDW is determined by the joint action of two factors: by the three-dimensional characteristic of the band structure (and by the Coulomb interaction of the layers), and by the commensurability effects in the layer. From the type of the three-dimensional superstructure we deduce the degree of two-dimensionality of the CDW in the system. Thus, experimental data show that in 1T crystals the CDW are two-dimensional to an appreciable degree.

However, as noted above, from calculations of the band structure and from the experimental data for the
The electronic properties of 1T crystals it follows that the transitions of the electrons between layers are not very weak in these crystals. Therefore, the relative smallness of the three-dimensional effect for the CDW in 1T-TaS₂ and 1T-TaSe₂ is due primarily to the large commensurability energy. This seems to indicate unequivocally that in 1T modification we are dealing with a strong electron-phonon coupling (κ ≈ 1).

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Note added in proof (July 21, 1977). A detailed calculation shows that the influence of the Coulomb interaction on the phase fluctuations is insignificant at those parameter values which are realized in practice in quasi-one-dimensional compounds. Therefore the estimate $k_F^2 = \pi n$ remains in force also when the Coulomb interaction is taken into account.

If the chains 1 and 2 are not equivalent with respect to the positions of the atoms (molecules) and the atoms 1 and 2 are shifted relative to the atom 2 by the half-period $q/2$, so that an atom of chain 1 has two nearest neighbors in chain 2, then an additional factor $2 \cos(q\Omega/2)$ appears in the term proportional to $C_{\Omega\Omega} - C_{\Omega\Omega}$.

For crystals of the TTF-TCNQ type, the influence of the Coulomb interaction of the phase fluctuations is insignificant, since the charges produced in the course of the phase fluctuations are of opposite sign on the cation and anion chains. For such crystals we therefore have $k_F^2 = \pi n$. This estimate for TTF-TCNQ agrees with the data obtained for $I$ from quantum-mechanical calculations. ²⁻³

In systems with a fixed degree of charge transfer and corresponding with a fixed value $k_F$ the transition to a commensurate phase with a change of the superstructure period $Q$ is possible only at very small differences between $2\pi k_F$ and the rotonal fraction $q\Omega$. In fact, at $Q > 2\pi k_F$ the system is not a dielectric, some of the electrons are located above the gap (or some of the holes below the gap), and the corresponding loss of energy is $\Omega^2 - 2 \pi k_F^2 \Delta$. The energy gained from the transition to the commensurate state is $\lvert \Delta \rvert (\Delta^2/4\Omega^2) \Delta N(0)$, and should not exceed the value $\Omega^2 - 2 \pi k_F^2 \Delta$, in order that the transition to the commensurate state be energywise favorable. In compounds with chains made up of donor and acceptor molecules (of the TTF-TCNQ type), a change of $Q$ can result from a change in the degree of charge transfer, and in this case the energy loss is proportional to $Q^2 - 2 \pi k_F^2 \Delta$. The same situation obtains in layered compounds, which are metals or semimetals in the CDW phase. In these compounds the change of $Q$ is accompanied by a redistribution of the charge over the Fermi surface, and the energy loss in the transition to the commensurate state is proportional to $Q^2 - Q_0^2$, where $Q_0$ is the wave vector of the noncommensurate CDW.

McMillan has shown that the NCDW-CDW transition can be of second order. ⁴⁻⁵ The continuity of the order parameter $\psi(0)$ is ensured in this case by the appearance of noncommensurability embryos in the commensurate phase. A solution of this type is valid if the characteristic length of variation of the phase of the CDW in the embryo is large in comparison with the correlation length $\xi^2$.

In the presently known layered compounds, this solution is not satisfied and the NCDW-CDW transition is of first order.

In 1T-TaS₂ and 1T-TaSe₂ at low temperatures, the opposite inequality is satisfied (see below), so that the condition $F > 2k_F^2$ could be observed only near $T_c$. Indirect estimates yield for these compounds $T_c \sim 600 K$, and the 1T modification is destroyed $\leq 500 K$, so that the region of $T_c$ cannot be reached.

Translated by J. G. Adashko