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

L. N. Bulaevskiĭ and D. I. Khomskiĭ

P. N. Lebedev Institute, USSR Academy of Sciences

(Submitted April 13, 1977)
Zh. Eksp. Teor. Fiz. **73**, 1148–1162 (September 1977)

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.

PACS numbers: 72.15.Nj

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[1,2] (see also the reviews[3]). In all the investigated layered crystals, the appearance of a CDW superstructure is connected with change of the lattice period inside the layers. 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 $1T$ and $2H$ modification of the purely layered crystals TaS_2, $TaSe_2$, and $NbSe_2$ 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 TSeF-TCNQ below 29 K.[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 correlations of the CDW of different layers or chains has been noted. This situation takes place in KCP below 120 K[17] and in the $1T$-$Ta_{1-x}Zr_xSe_2$ alloys at $x>0.015$.[8] Finally, both possibilities are realized in $4Hb$-$TaSe_2$ 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.[9]

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 Barisich (who considered only the Coulomb interaction of the CDW) and one of us (see[3]). 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,[10] with allowance for commensurabilities for layered compounds, in our short paper,[11] and by McMillan.[12] The proposed types of three-dimensional ordering are different in these papers. We shall show that both types of solutions can be realized (and are apparently realized in experiments) in crystals, depending on the ratio of the parameters that characterize the interaction of the nearest and non-nearest neighboring layers. We investigate also the dependence of the interaction energy of CDW of different layers (chains) on the degree of disorder of the crystal and show that this energy decreases substantially with increasing disorder. The results explain qualitatively why long-range three-dimensional ordering of the CDW can exist in disordered crystals (KCP, $1T$-$Ta_{1-x}Zr_xSe_2$ at $x>0.015$).

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

0038-5646/77/4603-0608$02.40

superconductors.[13,14] 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 Fröhlich model for a system of electrons and phonons (see, e.g.,[15–17]). We consider two layers: 1 and 2. The Hamiltonian of this subsystem, without allowance for the Coulomb interaction of the electrons, is given by

$$\mathscr{H}=\mathscr{H}_1+\mathscr{H}_2+\mathscr{H}_T,\qquad \mathscr{H}_T=\sum_{\mathbf{n},s}t_\mathbf{n}a_{\mathbf{n}s}{}^+c_{\mathbf{n}s}+\text{h.c.},$$
$$\mathscr{H}_1=\sum_{\mathbf{k},s}\varepsilon_1(\mathbf{k})a_{\mathbf{k}s}{}^+a_{\mathbf{k}s}+\Omega_1[b^+(\mathrm{Q})b(\mathrm{Q})+b^+(-\mathrm{Q})b(-\mathrm{Q})]$$
$$+\frac{ig_1}{N^{1/2}}[b(\mathrm{Q})+b^+(-\mathrm{Q})]\sum_{\mathbf{k},s}a^+_{\mathbf{k}+\mathrm{Q},s}a_{\mathbf{k},s}+\text{h.c.},\tag{1}$$

and $\mathscr{H}_2$ has a similar form. $a^+_{\mathbf{n}s}$ $(c^+_{\mathbf{n}s})$ are the operators for the production of the electrons with spin s on the sites $\mathbf{n}$ of layers 1 (2), and $t_\mathbf{n}$ is the matrix element of the electron transition between the sites $\mathbf{n}$ 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 $\varepsilon_1(\mathbf{k})$; $b^+(\mathbf{Q})$ is the operator of the production of a phonon with quasimomentum $\mathbf{Q}$ and energy Ω_1, where $\mathbf{k}$ is the wave vector of the CDW. We assume that the vectors $\mathbf{Q}$ 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 $\mathbf{Q}$ phonons, which determine the instability is described by the parameters $g_{1,2}$ for layers 1 and 2; N is the density of the atoms (molecules) in the layer or chain. All the vectors $\mathbf{n}$, $\mathbf{k}$, and $\mathbf{Q}$ in (1) are two-dimensional for layered crystals and one-dimensional for the quasi-one-dimensional systems. Since the phonons with quasimomentum $\mathbf{Q}$ which condense in the CDW transition correspond to longitudinal acoustic oscillations or to fully symmetrical intramolecular oscillations,[15] there is no direct interaction of phonons with quasimomenta $\mathbf{Q}$ in different layers (chains) in the linear approximation.

We take into account the influence of the tunnel Hamiltonian $\mathscr{H}_T$ on the interaction of the CDW of layers 1 and 2 by using perturbation theory in $\mathscr{H}_T$. The limits of applicability of this approach to quasi-one-dimensional crystals 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

$$\Delta_{1,2}=|\Delta_{1,2}|\exp(i\varphi_{1,2})=2ig_{1,2}\langle b(\mathrm{Q})\rangle/N^{1/2}.$$

To describe the electron system, we use the Nambu representation

$$\hat{\psi}_\mathbf{k}{}^+=(a^+_{\mathbf{k}+\mathrm{Q}/2},\ a^+_{\mathbf{k}-\mathrm{Q}/2}),\qquad \hat{\psi}_\mathbf{k}=\begin{pmatrix}a_{\mathbf{k}+\mathrm{Q}/2}\\ a_{\mathbf{k}-\mathrm{Q}/2}\end{pmatrix},$$
$$\mathscr{H}_0=\sum_\mathbf{k}\hat{\psi}_\mathbf{k}{}^+\begin{vmatrix}\varepsilon_{\mathbf{k}+\mathrm{Q}/2} & \Delta\\ \Delta^* & \varepsilon_{\mathbf{k}-\mathrm{Q}/2}\end{vmatrix}\hat{\psi}_\mathbf{k}+\frac{\Omega N|\Delta|^2}{2g^2}.\tag{2}$$

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

For the free energy of an individual layer we have

$$F_0=-T\sum_\mathbf{k}\ln(1+e^{-\varepsilon_+/T})(1+e^{-\varepsilon_-/T})+\Omega|\Delta|^2N/2g^2,$$
$$\varepsilon_\pm(\mathbf{k})={}^1/_2(\varepsilon_{\mathbf{k}+\mathrm{Q}/2}+\varepsilon_{\mathbf{k}-\mathrm{Q}/2})\pm[{}^1/_4(\varepsilon_{\mathbf{k}+\mathrm{Q}/2}-\varepsilon_{\mathbf{k}-\mathrm{Q}/2})^2+|\Delta|^2]^{1/2},\tag{3}$$

and the gap $|\Delta|$ is determined from the equation

$$1=\frac{\sigma^2}{\Omega N}\sum_\mathbf{k}\frac{n(\varepsilon_-)-n(\varepsilon_+)}{[{}^1/_4(\varepsilon_{\mathbf{k}+\mathrm{Q}/2}-\varepsilon_{\mathbf{k}-\mathrm{Q}/2})^2+|\Delta|^2]^{1/2}},\qquad n(\varepsilon)=\frac{1}{1+e^{\varepsilon/T}},\tag{4}$$

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 $\hat{G}(\mathbf{k},\omega)$we have in the temperature technique $(i\omega-\hat{\mathscr{H}}_0)\hat{G}=\hat{I}$ and

$$\hat{G}(\mathbf{k},\omega)=\begin{vmatrix}i\omega-\varepsilon_{\mathbf{k}-\mathrm{Q}/2} & \Delta\\ \Delta^* & i\omega-\varepsilon_{\mathbf{k}+\mathrm{Q}/2}\end{vmatrix}\frac{1}{(i\omega-\varepsilon_+)(i\omega-\varepsilon_-)}=\begin{vmatrix}G_{11} & G_{12}\\ G_{21} & G_{22}\end{vmatrix}\tag{5}$$

$\omega=\pi T(2m+1)$. The components of the densities $\rho_e(\mathbf{Q})$ and $\rho_i(\mathbf{Q})$ of electrons and ions with wave vector $\mathbf{Q}$ are defined by the following expressions:

$$\rho_e(\mathrm{Q})=\sum_{\mathbf{k},s}\langle a^+_{\mathbf{k}+\mathrm{Q}/2}a_{\mathbf{k}-\mathrm{Q}/2}\rangle=2T\sum_{\mathbf{k},\omega}G_{12}(\mathbf{k},\omega)=\frac{\Delta}{\lambda}N(0),$$
$$\rho_i(\mathrm{Q})=\rho_0\,\mathrm{div}\,\mathbf{u}=\rho_0\left(\mathrm{Q}\frac{\mathbf{u}}{|\mathbf{u}|}\right)\frac{\Delta}{g}\left(\frac{\hbar}{M\Omega}\right)^{1/2},\qquad \lambda=\frac{2g^2}{\Omega}N(0),\tag{6}$$

where $N(0)$ is the state density on the Fermi surface, ρ_0 and M are the density and mass of the ions and $\mathbf{u}$ 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 φ_1 and φ_2 of the CDW of the layers, since only this part of the energy determines the three-dimensional ordering of the CDW in the crystal. For the density of the Coulomb interaction of the CDW we obtain from (6)

$$F_Q(\varphi_1,\varphi_2)=2e^2\cos(\varphi_1-\varphi_2)\rho_1(\mathrm{Q})\rho_2(\mathrm{Q})G(RQ),$$
$$\rho(\mathrm{Q})=\rho_e(\mathrm{Q})-\rho_i(\mathrm{Q}),$$
$$G(RQ)=\int_{-\infty}^{+\infty}d\mathbf{r}\frac{\cos\mathrm{Q}\mathbf{r}}{(R^2+\mathbf{r}^2)^{1/2}}=\begin{cases}K_0(RQ) & \text{for chains}\\ |\mathrm{Q}|^{-1}e^{-R|\mathrm{Q}|} & \text{for layers}\end{cases}\tag{7}$$

where R is the distance between the layers (chains) and $K_0(x)$ 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

$$F_T(\varphi_1,\varphi_2)=2T\sum_{\mathbf{k},\mathbf{k}',\omega}\mathrm{Sp}\,\hat{G}_1(\mathbf{k},\omega)\hat{G}_2(\mathbf{k}',\omega)|t_{\mathbf{k}-\mathbf{k}'}|^2=F_{T0}$$
$$+4T\sum_{\mathbf{k},\mathbf{k}',\omega}\frac{|\Delta_1\Delta_2||t_{\mathbf{k}-\mathbf{k}'}|^2\cos(\varphi_1-\varphi_2)}{[i\omega-\varepsilon_+(\mathbf{k})][i\omega-\varepsilon_-(\mathbf{k})][i\omega-\varepsilon_+(\mathbf{k}')][i\omega-\varepsilon_-(\mathbf{k}')]},\tag{8}$$
$$t_\mathbf{k}=\sum_\mathbf{n}t_\mathbf{n}e^{i\mathbf{k}\mathbf{n}},$$

where F_{T0} is that part of the interaction free energy which does not depend on the phases of the phases of the layers, and will hereafter be left out from the expressions for F_T. The total interaction of the layers is described by the sum of the contributions (7) and (8).[1)]

The theory that we use for the CDW of an individual layer describes a case when the period of the CDW is not commensurate with the period of the main structure. In the case of commensurability, it is necessary to add to the free energy (3) of the layer 1 the commensurability energy $F_c(\varphi_1)$. This energy contains an additional small parameter of the type $(|\Delta|/\varepsilon_F)^p$, $p \geq 1$, compared with the energy (3).[17] When three-dimensional ordering is considered, however, $F_c(\varphi_1)$ must be taken into account, since this is the only part of the energy that depends on the absolute value of the phase of the CDW of layer 1. In the expressions for F_T and F_Q, 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, the disorder of the crystal lowers the transition temperature T_0 (or else suppresses the transition completely) (see[3,18]). To an even greater degree, the disorder lowers the commensurability energy and the temperature T_d of the transition to the commensurate state.[18] However, the effect of the disorder of the crystal on the values of the matrix elements $t_{\mathbf{n}}$ and correspondingly on the three-dimensional ordering of the CDW should apparently be even stronger, since the overlap of the electron wave functions of neighboring layers (chains) is small, and in this situation the phases of the matrix elements $t_{\mathbf{n}}$ are sensitive to the introduction of impurities or defects into the crystals. We shall therefore consider henceforth crystals in which the disorder is so small that its influence on the commensurability effects (and all the more on the CDW transition itself) inside the layers can be neglected, but the influence of the disorder on the values of $t_{\mathbf{n}}$ is not small. This assumption agrees with the experimental situation in KCP and $1T$-$\mathrm{Ta}_{1-x}\mathrm{Zr}_x\mathrm{Se}_2$ (at $x > 0.015$), at which the correlation length of the superstructure inside the chain (inside the layer) is large, and there is no three-dimensional order. In the situation considered by us, it is necessary to average expression (8) for F_T over the parameters that describe the randomness of $t_{\mathbf{n}}$, while all the remaining expressions, including that for F_Q must be left unchanged. Introducing the correlation function $P(\mathbf{n})$ of the matrix elements, we obtain

$$F_T = 2T \sum_{\omega,\mathbf{k},\mathbf{k}'} \mathrm{Sp}\, \hat{G}_1(\mathbf{k},\omega)\hat{G}_2(\mathbf{k}',\omega)P(\mathbf{k}-\mathbf{k}')\langle|t_{\mathbf{n}}|^2\rangle,$$
$$P(\mathbf{n}) = \langle t_{\mathbf{m}} t^{*}_{\mathbf{m}+\mathbf{n}}\rangle/\langle|t_{\mathbf{n}}|^2\rangle, \qquad P(\mathbf{q}) = \sum_{\mathbf{n}} P(\mathbf{n})e^{i\mathbf{q}\mathbf{n}}, \tag{9}$$

where ⟨ ⟩ denotes averaging. We assume henceforth that the function $P(\mathbf{n})$ is given by

$$P(\mathbf{n}) = e^{-|\mathbf{n}|/l}, \tag{10}$$

where l is the correlation length of the matrix elements, $t_{\mathbf{n}}$. On the basis of the obtained expressions, we consider in Sec. 3 the ordering of CDW in quasi-one-dimensional crystals, and in Sec. 4 the ordering in layered crystals.

3. QUASI-ONE-DIMENSIONAL CRYSTALS

We assume that the appearance of CDW in quasi-one-dimensional crystals is due to the congruence of the Fermi-surface sections k_F and $-k_F$, such that $Q = 2k_F$, where k_F is the Fermi momentum of the electrons inside the chains. The Fermi surface for the chains is a point, and the crystals become dielectric after the appearance of the CDW, since the entire Fermi "surface" is submerged by the gap. We obtain first the free energy of the interaction of the chains within the framework of the method of the tunnel Hamiltonian [Eqs. (8) and (9)], after which we discuss the conditions for the applicability of this method to real quasi-one-dimensional crystals.

In the one-dimensional electron systems, at electron momenta $k \ll k_F$, the condition $\varepsilon_{\mathbf{k}+\mathbf{Q}/2} = -\varepsilon_{\mathbf{k}-\mathbf{Q}/2}$ is satisfied, and by taking this condition into account together with the estimate $\rho_i(Q) \approx \rho_e(Q)$ we obtain from (7)–(9) the expressions

$$F_Q(\varphi_1-\varphi_2) \approx 2e^2 \frac{|\Delta_1\Delta_2|}{\lambda_1\lambda_2} K_0(2k_F R) N^2(0)\cos(\varphi_1-\varphi_2), \tag{11}$$

$$F_T(\varphi_1-\varphi_2) = \frac{2\langle|t_{\mathbf{n}}|^2\rangle}{(v_{F1}v_{F2})^{1/2}} T \sum_{\omega} \frac{|\Delta_1\Delta_2|\cos(\varphi_1-\varphi_2)}{w_1 w_2(\hbar/\tau + w_1 + w_2)}; \tag{12}$$
$$\hbar/\tau = \hbar(v_{F1}v_{F2})^{1/2}/l, \qquad w_{1,2} = (\omega^2 + |\Delta_{1,2}|^2)^{1/2}.$$

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

$$F_T(\varphi_1-\varphi_2) = \frac{2\langle|t_{\mathbf{n}}|^2\rangle\cos(\varphi_1-\varphi_2)}{v_F} \times \begin{cases} f(\hbar/2\tau|\Delta|), & T \ll |\Delta| \\ \dfrac{2|\Delta|^2}{\pi^3T^2}\displaystyle\sum_{n=0}^{\infty} \frac{1}{(2n+1)^2(\hbar/2\tau T + 2n + 1)}, & |\Delta| \ll T \end{cases},$$
$$f(x) = \frac{1}{\pi x} \begin{cases} \dfrac{\pi}{2} - \dfrac{2}{(1-x^2)^{1/2}} \operatorname{arctg}\left(\dfrac{1-x}{1+x}\right)^{1/2}, & x \leq 1 \\ \dfrac{\pi}{2} - \dfrac{1}{(x^2-1)^{1/2}} \ln \dfrac{1+x+(x^2-1)^{1/2}}{1+x-(x^2-1)^{1/2}}, & x > 1 \end{cases}. \tag{13}$$

In the limit of a system without impurities, $l \to \infty$, the tunnel interaction can be reduced to the form

$$F_T(\varphi_1-\varphi_2) = \frac{2|t_n|^2\cos(\varphi_1-\varphi_2)}{v_F} g\left(\frac{\Delta}{2T}\right),$$
$$g(x) = \int_0^{\infty} dy \left[\frac{1}{\mathrm{ch}^2 y} - \frac{1}{\mathrm{ch}^2[(x^2+y^2)^{1/2}]}\right] = \begin{cases} \pi^{-1}, & T \ll |\Delta| \\ |\Delta|^2 \cdot 7\zeta(3)/4\pi^3 T^2, & T \gg |\Delta| \end{cases} \tag{14}$$

where $\zeta(x)$ is the Riemann function.

An analysis of expressions (12) and (13) for F_T shows that the disorder leads to a considerable decrease of the CDW tunnel interaction. At $l \ll \hbar(v_{F1}v_{F2})^{1/2}|\Delta|$ the values of F_T decreases in proportion to l with decreasing l. If $\langle|t_n|^2\rangle$ remains unchanged, F_T decreases by an approximate factor ε_F/T_0 when l decreases from ∞ to distances on the order of interatomic. However, a comparison of F_T and F_Q even in the most disordered system (when F_T is minimal) shows that F_Q is smaller than F_T by at least a factor of ε_F/T_0 if $|t_n|^2$ decreases with increasing R not faster than $\varepsilon_F^2\exp(-2k_F R)$.

Before we proceed to an interpretation of the experimental data, let us discuss the conditions of the applicability of perturbation theory for the tunnel Hamiltonian in the case of quasi-one-dimensional compounds. We consider a system of identical chains and start from a three-dimensional band structure with a spectrum $\varepsilon(\mathbf{k}) = \varepsilon(k_z) - 2t(\cos k_x + \cos k_y)$, where k_z is the momentum along the chain and (k_x, k_y) 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 $\Delta(T)$. We consider only strongly anisotropic systems with $t \ll \varepsilon_F$. The vector $\mathbf{Q}$, which determines the three-dimensional period of the superstructure, has a component $Q_z = 2k_F$, and its transverse component $\mathbf{Q}_\perp = (Q_x, Q_y)$ should be determined from the condition that the free energy be a minimum. In real systems in which $\varepsilon(k_z)$ is not linear, the transition of the CDW takes place if $t^2/\varepsilon_F \lesssim T_0$ (see[19]), and we shall consider below separately systems for which $t \leqslant T_0$ or $t^2/\varepsilon_F \lesssim T_0 \lesssim t$.

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

$$F = \frac{\Omega|\Delta|^2 N}{2g^2} - 2T \sum_{\mathbf{k}} \left[\ln\left(2 \operatorname{ch} \frac{\varepsilon_+}{2T}\right) + \ln\left(2 \operatorname{ch} \frac{\varepsilon_-}{2T}\right) \right],$$

$$\varepsilon_\pm = \frac{1}{2}\left[\varepsilon\left(\mathbf{p} + \frac{\mathbf{Q}}{2}\right) + \varepsilon\left(\mathbf{p} - \frac{\mathbf{Q}}{2}\right)\right] \pm \left\{\frac{1}{4}\left[\varepsilon\left(\mathbf{p} + \frac{\mathbf{Q}}{2}\right) - \varepsilon\left(\mathbf{p} - \frac{\mathbf{Q}}{2}\right)\right]^2 + |\Delta|^2\right\}^{1/2}. \tag{15}$$

and the first nonvanishing term of the expansion of F in t yields expression (14), the expansion parameter being t/ε_F at $T=0$ or t/T_0 near T_0.

Similar results are valid also at $T_0 < t < (\varepsilon_F T_0)^{1/2}$, except that in the weak-coupling limit $\lambda \ll 1$ a solution with $\Delta \neq 0$ exists only when the phase difference $\varphi_1 - \varphi_2$ satisfies the condition $t\cos[(\varphi_1 - \varphi_2)/2] \lesssim |\Delta(T)|$. This inequality determines the limits within which deviations of $\varphi_1 - \varphi_2$ from π as a result of the commensurability effects are permissible.

Adding now to the chain interaction energy the commensurability energy (which is significant if $2k_F b$ is close to a rational fraction, where b is the period of the chain) and minimizing the total free energy with respect to the phases, we obtain the solution of the problem of three-dimensional ordering of CDW in a quasi-one-dimensional crystal within the framework of the self-consistent-field (SCF) approximation. However, the question of the applicability of the SCF approximation to quasi-one-dimensional crystals calls for an additional investigation. It is clear that at very small values of t this approximation is certainly not applicable, and a critical value t_c exists below which (at $t < t_c$) the fluctuations are large in the entire temperature region $T < T_0$. At $t \gg t_c$, the fluctuations are small and the SCF approximation is valid everywhere except the immediate vicinity of T_0. For a Peierls transition, it is the phase fluctuations that are mainly significant (allowance for only the fluctuations of the modulus of the order parameter yields $t_c \approx T_0^2/\varepsilon_F$).[3] An estimate of the region of the strong phase fluctuations without allowance for the long-range Coulomb forces which arise under these fluctuations yields $t_c \approx T_0$.[19] No consistent calculation of the phase fluctuations with allowance for the Coulomb interaction has been performed so far, and all that can be stated is that t_c lies in the region between T_0^2/ε_F and T_0 (see the note added in proof).

At $T_0 \lesssim t \lesssim (\varepsilon_F T_0)^{1/2}$ the SCF is certainly applicable. In fact we are dealing here with an ordinary three-dimensional transition, in which the CDW wave vector $\mathbf{Q}$ is determined from the condition that the Fermi-surface sections be maximimally congruent, and $\mathbf{Q}$ in the weak-coupling approximation is of necessity close to the vector $(\pi, \pi, 2k_F)$ in the entire temperature region below T_0, owing to the conditions $t\cos[(\varphi_1 - \varphi_2)/2] \lesssim |\Delta(T)|$.

In the region $t_c \lesssim t \lesssim T_0$ (if $t_c \ll T_0$) we can again use the SCF approximation, a solution with $\Delta \neq 0$ exists at any phase difference $\varphi_1 - \varphi_2$, 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 phases.

At $t \lesssim t_c$ 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. Within the framework of this analysis, the long-range three-dimensional order, which corresponds to the maximum value of the free energy of the chain interaction [(11) and (12)], appears at a temperature $T_3 \lesssim T_0/4$ and the value of T_3 can be obtained in the self-consistent-field approximation from the chain interaction.[20,3] In the region $T_3 < T$ there is no correlation of the Peierls distortions between the chains. A three-dimensional superstructure appears below T_3, but the fluctuations remain strong also at temperatures $T \lesssim T_3$, i.e., $\langle\Delta\rangle^2 \ll \langle\Delta^2\rangle$ (at low temperatures it is necessary to take the quantum fluctuations into account[20]).

It appears that the situation $t \gg T_0$ 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 incomplete charge transfer, the hybridization gap at $t \gg T_0$ is large in comparison with the Peierls gap, so that the CDW transition cannot be energy favored. In addition, at $t \gg T_0$ 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.[5,21] 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 $t \ll t_c$ situation. As a most probable situation in TCNQ salts is therefore $t_c \lesssim t \lesssim T_0$, to which the SCF approximation is applicable[2)] (the case $t \ll t_c$ is not excluded for KCP).

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

$$F=\sum_{\mathbf{n},\mathbf{m}} h_{\mathbf{nm}}\cos(\varphi_{\mathbf{n}}-\varphi_{\mathbf{m}}),\quad \mathbf{n}=(n_1,n_2),\quad \mathbf{m}=(m_1,m_2), \tag{16}$$

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 data the CDW is not commensurate with the period of the host lattice.$^{3)}$ 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.[20,23] 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 ($l \approx b$), 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 $b'=6.70$ is observed already at 300 K.

In TSeF-TCNQ the superstructure $b'=3.15b$ appears below 238 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[6] the superstructure has a doubled period along the a direction ($a'=2a$) below 29 K. According to (11) and (12), this period of the superstructure, within the framework of the SCF approximation ($t \gtrsim t_c$) can be observed in the case when the Peierls displacements are present only on chains of one type ($|\Delta|_2<|\Delta|_1$) in the region where the transverse period is doubled. Since most of the scattering by the superstructure is due to Se atoms,[6] it follows that in TSeF-TCNQ the Peierls instability should be due principally to the TSeF chains, if the experimental data of[6] are correct.

In TTF-TCNQ, as shown in[5], the superstructure $b'=3.4b$ has a period $a'=2a$ 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.[24] 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 $b'=1.7b$ observed in[25].

4. LAYERED DICHALCOGENIDE CRYSTALS

The total interaction of the CDW of different layers is determined by the form of their Coulomb interaction F_Q, defined by formula (7), and the tunnel interaction T_{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 Mattheis[26] yield information on the spectrum, and $F_{\mathrm{T}}(\Delta)$ 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_Q suggests that $F_Q \ll F_{\mathrm{T}}$, just as in quasi-one-dimensional crystals. Actually, F_Q must contain an additional small factor of the type (T_0/ε_F) in comparison with F_{T}, and we have $F_Q \ll F_{\mathrm{T}}$ even if $|t_{\mathbf{n}}|^2$ decreases with decreasing distance R between layers, in analogy with the Coulomb interaction of the CDW, i.e., $|t_{\mathbf{n}}|^2 \approx \varepsilon_F^2 e^{-QR}$. In fact, however, the matrix elements $t_{\mathbf{n}}$, at least for the nearest neighbors ($t_{\mathbf{n}1}$), turn out to be larger than $\varepsilon_F e^{-QR/2}$. The estimate $|t_{\mathbf{n}1}| \approx \varepsilon_F e^{-QR/2}$ would yield $|t_{\mathbf{n}1}| \approx 0.02$ eV and an effective-mass anisotropy of the order of 100 (at $\varepsilon_F \approx 2$ eV). According to Mattheis' calculations, $|t_{\mathbf{n}1}|$ is larger by approximately one order of magnitude, and the experimental anisotropy of layered crystals does not exceed 10.[1,3]

2. We shall be interested below in the interaction of the first and second neighboring layers $F_{\mathrm{T}1}$ and $F_{\mathrm{T}2}$. Undoubtedly, $F_{\mathrm{T}2} \ll F_{\mathrm{T}1}$, but in principle there are no grounds for assuming that $F_{\mathrm{T}n}$ decreases exponentially with increasing n.

3. Just as in the one-dimensional case, the disorder weakens the tunnel interaction between the layers $F_{\mathrm{T}1}$, and all the more $F_{\mathrm{T}2}$.

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 $\mathbf{Q}_k$ ($k=1,2,3$) turned 120° relative to one another. We introduce three parameters ψ_k of the internal order in the layer, assuming that $\psi_k=|\Delta|\cos(\mathbf{Q}_k\mathbf{r}+\varphi_k)$. In the lowest order in Δ, waves with identical $\mathbf{Q}_k$ interact between different layers, and the total free energy is given by

$$F=\sum_n\left\{F_c(\varphi_{nk})+\sum_{m=1}^{2}\sum_{k=1}^{3}h_m\cos(\varphi_{nk}-\varphi_{n+m,k})\right\},$$

$$F_c(\varphi_{nk})=4\int d^2r\left\{-b_0\psi_1\psi_2\psi_3-\sum_{\mathbf{K}}\sum_{k=1}e^{i\mathbf{K}\mathbf{r}}[b_1\psi_{nk}{}^3-2c_1\psi_{nk}{}^3\psi_{n,k+1}]\right\}\frac{1}{S}=$$

$$=-b_0\Delta^3\cos(\varphi_{n1}+\varphi_{n2}+\varphi_{n3})-\sum_{k=1}^{3}[b_1\Delta^3\cos 3\varphi_{nk}$$

$$+c_1\Delta^4\cos(3\varphi_{nk}-\varphi_{n,k+1})],\qquad S=\int d^2r, \tag{17}$$

where $F_c(\varphi_{nk})$ is the free-energy density of the layer n (see[10]), **K** is the reciprocal-lattice vector of the layer, and $\varphi_{n4}\equiv\varphi_{n1}$.

The first term in F_c is in fact not connected with commensurability effects, takes the wave interaction into account, and leads to a first-order transition from the normal metallic phase into the CDW phase at the point T_0 (if b_0 is small, then the transition can be very close to second-order). The second term in F_c takes into account effects of commensurability of the CDW and of the hexagonal host lattice. The term with the coefficient b_1 is significant for $2H$ modifications, in which $|\mathbf{Q}|$ is close to $|\mathbf{K}/3|$. This term leads to a transition from a noncommensurate CDW phase (NCDW) to a commensurate phase (CCDW) in $2H$-TaSe$_2$ at $T_d=90$ K.[4)] The term with the coefficient c_1 leads to a first order NCDW–CCDW transition in $1T$-TaSe$_2$ at $T_d=473$ K and in $1T$-TaSe$_2$ at $T_d=200$ K. This transition is attained by rotating the vectors $\mathbf{Q}_k$ through 13°54′, after which the conditions $3\mathbf{Q}_k-\mathbf{Q}_{k+1}=\mathbf{K}$ are satisfied in the commensurate phase. Minimizing (17) with respect to the phase φ_{nk}, we can now determine the possible types of three-dimensional CDW ordering in the layers.

Noncommensurate CDW phase

An important role in the NCDW phase is played by the tunnel interaction of the layers and by the first term in F_c. In the general case, minimization of (17) yields a system of nonlinear finite-difference equations. The situation can be analyzed to conclusion in two limiting cases $F_T\ll F_c$ and $F_T\gg F_c$.

We consider first the solution for $F_c\ll F_T$. An inequality of this type can be satisfied in $1T$-VSe$_2$[27] and in $2H$ modifications of TaSe$_2$, TaS$_2$, and NbSe$_2$ in the entire temperature interval. If in fact it is not satisfied at low temperatures, as a result of the relations $F_c\sim\Delta^3$ and $F_T\sim\Delta^m$, $m\leq 2$ for second-order transitions (or of first-order transitions close to those of second order) we still obtain $F_c\ll F_T$ near T_0.[5)] It follows from (17) that at $F_c\ll F_T$ and $h_1\gg h_2$ there exists a unique solution for which the CDW of neighboring layers should be approximately in antiphase. In $1T$ modifications, all the layers are equivalent and a superstructure $c'=2c$ should be observed. In the $2H$ modification, the neighboring layers are not equivalent with respect to the chalcogen atom positions, and in this case $c'=c$.

Let us investigate now the solution (17) at $F_c\gg F_T$, assuming that the interaction F_{T1} of the nearest layers greatly exceed the interaction F_{T2} of the next-nearest layers. In this situation, the minimization of (17) can be carried out within the framework of perturbation theory in the interaction of the layers. At $b_0>0$ we obtain the minimum of F_c at $\varphi_{n1}+\varphi_{n2}+\varphi_{n3}=2\pi s$, where s are arbitrary integers. Under this condition the minimum of F_{T1} in first order in F_{T1} is reached if the phase differences of all three waves are the same for the neighboring layers and $|\varphi_{n+1,k}-\varphi_{nk}|=|2\pi/3+2\pi s|$. Thus, the minimum of F_c+F_{T1} is realized in first order in F_{T1} for the phase-shift sequence $\pm 2\pi/3$, $\pm 2\pi/3,\ldots$ (accurate to insignificant terms that are multiples of 2π). The choice of the signs in this sequence can be arbitrary, and the energy F_c+F_{T1} does not determine the three-dimensional ordering in first order of perturbation theory in F_{T1}. The degeneracy with respect to the signs of the phase shifts is lifted if one takes into account the term F_{T2} or the interaction F_{T1} in second order of perturbation theory in F_{T1}.

The energy F_{T2} is minimal if the phase shifts are of the same sign, i.e., $\varphi_{nk}=\varphi_{0k}\pm 2\pi n/3$. In this case $c'=3c$, and the free energy of the CDW (per layer) is

$$F=-3(b_0\Delta^3+{}^1/_2h_1+{}^1/_2h_2). \tag{18}$$

A solution of this type was obtained by us earlier.[11] A sequence with alternating signs of the phase shift leads to McMillan's solution.[12] Taking the phase sequence in the form ε, $2\pi/3-\varepsilon$, $\varepsilon,\ldots$, we obtain

$$F(\varepsilon)=-3(b_0\Delta^3\cos 3\varepsilon-h_1\cos 2\varepsilon-h_2). \tag{19}$$

Minimizing (19) with respect to ε, we obtain at $h_1\ll b_0\Delta^3$

$$F=-3\left(b_0\Delta^3+\frac{1}{2}h_1+\frac{1}{6}\frac{h_1^2}{b_0\Delta^3}-h_2\right). \tag{20}$$

Comparing (18) and (20) we verify that at $h_2<h_1^2/9b_0\Delta^3$ McMillan's solution is energywise more favored. For this solution the phase shift of the neighboring layers is $2\pi/3$ at $h_1\ll b_0\Delta^3$ and approaches π with decreasing Δ.

Thus, the solution obtained in[8] goes over continuously to the unique solution realized at $F_c\ll F_T$. The solution with $c'=3c$ is energywise more favored than at $h_2>h_1^2/9b_0\Delta^3$. If it is realized at $T\ll T_0$, then as the temperature approaches T_0 (if T_0 is the point of the transition of second order or of first order but close to second) the value of Δ decreases, and at the point where $h_2=h_1^2/9b_0\Delta^3$, 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[11] can be realized only if the condition $F_T\ll F_c$ is satisfied. Thus, at $F_T\ll F_c$ we obtain in the $1T$ modification either $c'=2c$ or $c'=3c$, depending on the ratio of the parameters h_2 and $h_1^2/9b_0\Delta^3$. In the $2H$ modification we have respectively $c'=c$ or $c'=3c$.

In the $1T$ modifications of TaS$_2$ and TaSe$_2$ experiment reveals $c'=3c$,[1] thus indicating a large value of F_c ($F_c\gg F_T$) and a substantial role of the F_{T2} term in comparison with the energy F_{T1}^2/F_c. We note that the CDW Coulomb interaction can by itself not lead to this result, since when the estimates $b_0\sim\varepsilon_F^{-2}$ and $\Delta\ll\varepsilon_F$ are taken into account we obtain $F_{Q2}\ll F_{Q1}^2/9b_0\Delta^3$. For a tunnel interaction F_{Tm} that decreases with m exponentially, we obtain analogously $F_{T2}\ll F_{T1}^2/9b_0\Delta^3$. Thus, the existence of the superstructure $c'=3c$ above T_d in $1T$-TaS$_2$ and $1T$-TaSe$_2$ 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 noncommensurate phase $c'=c$,[28] and in these modifications we have $F_c \ll F_T$ or $F_c \gg F_T$, but $h_2 < h_1^2/9b_0\Delta^3$ (i.e., McMillan's solution is realized). Although in both these cases 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 $F_c \ll F_T$ the phase difference between neighboring layers is close to π 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 as T_0 is approached. This difference makes it possible to explain the relative role of the commensurability effects and the three-dimensional effects in 2*H* 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 1*T* and 2*H* modifications ($c' = 3c$ and $c' = c$) of TaS_2 and $TaSe_2$ is undoubtedly due to the smaller values of Δ (and T_0) in the 2*H* crystals. In experiment, the displacements of the atoms in the 2*H* crystals (which are proportional to Δ) is smaller by approximately one order of magnitude than in the 1*T* modifications,[1,3] and the energy F_c in (17) is correspondingly smaller. It is therefore of interest to investigate the superstructure in 1*T*-VSe_2. In this compound, owing to the low value of T_0, one cannot exclude a solution $c' = 2c$ in the NCDW phase, at least near T_0.

Commensurate CDW phase

For the 2*H* 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 noncommensurate one, two situations are therefore possible: $c' = c$ and $c' = 3c$. In experiment below T_d, in 2*H*-$TaSe_2$ $c' = c$ is again realized[1] for the reasons indicated above.

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

Let us obtain the solution at $F_T \ll F_c$ (the solution $c' = 2c$ is realized at $F_T \gtrsim F_c$). The minimum of F_c is reached if the phases φ_{nk} satisfy the equations

$$\begin{gathered}\varphi_{n1}+\varphi_{n2}+\varphi_{n3}=2\pi S_{n0}, \quad \varphi_{n4}\equiv\varphi_{n1},\\ 3\varphi_{nk}-\varphi_{n,k+1}=2\pi S_{nk}, \quad k=1,\ 2,\ 3.\end{gathered} \tag{21}$$

(S_n are integers). The solution of these equations is of the form

$$\begin{gathered}\varphi_{n1}={}^2/_{13}\pi(3S_{n1}+3S_{n0}-S_{n3}), \quad \varphi_{n2}={}^2/_{13}\pi(-4S_{n1}-4S_{n0}-3S_{n3}),\\ \varphi_{n3}={}^2/_{13}\pi(S_{n1}+S_{n0}+4S_{n3})\end{gathered} \tag{22}$$

and the same form is assumed by the changes of the phases on going from layer n to layer $n+1$. Minimization of F_{T1} in first order of perturbation theory yields an optimal phase shift $\pm 2\pi(2, 6, 5)/13$ between neighboring layers. When account is taken of the term F_{T2} and of the term F_{T1} in second order of perturbation theory, we obtain the solution for the phases in the forms $(\varphi_{n1}, \varphi_{n2}, \varphi_{n3}) = 2\pi(2, 6, 5)n/13$, if h_2 is large enough,[11] and a doubling of the period at small h_2 (a solution of McMillan's type[12]).

Experiment has revealed in 1*T*-$TaSe_2$ below $T_d = 473$ K a superstructure with wave numbers $(2, 6, 5)c^*/13$.[8] A superstructure $c' = 13c$ is also observed in 1*T*-TaS_2 below 200 K.[1] Thus, our solution of[11] is realized for CCDW in these compounds.

In 4*Hb*-$TaSe_2$ crystals, octahedral layers analogous to the 1*T*-$TaSe_2$ layers alternate with the trigonal layers analogous to the layers in 2*H*-$TaSe_2$. In the octahedral layers, according to the data cited in[9], the superstructure inside the layers is similar to the 1*T*-$TaSe_2$ superstructure, and at $T_{d1} = 410$ K one observes an NCDW–CCDW transition identical with the transition in 1*T*-$TaSe_2$ at $T_d = 473$ K. In contrast to the 1*T* modification, however, below T_{d1} the period of the crystal is $c' = c$ (the unit cell of the 4*Hb* 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 $T_{02} = 75$ 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 2*H*-$TaSe_2$, 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 $\mathbf{Q}_k$ 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[11]). 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 h_2 (these layers are separated, besides the one octahedral layers, by two additional trigonal layers).

We now examine the influence of the disorder of the lattice on the three-dimensional ordering of the CDW of layered crystals. In addition to suppressing the tunnel interaction, the disorder suppresses also the long-range order within the layers.[23] Since the three-dimensional ordering is controlled by the small terms F_{T2} or F_{T1}^2/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[8] three-dimensional ordering is realized in 1*T*-$Ta_{1-x}Zr_xSe_2$ 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 $x \geqslant 0.03$. 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 $c^*/3$.[8]

We see thus that the three-dimensional ordering of the CDW is determined by the joint action of two factors: by the three-dimensional character 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 1*T* 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 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 $1T$-TaSe$_2$ and $1T$-TaS$_2$ is due primarily to the large commensurability energy. This seems to indicate unequivocally that in the $1T$ modification we are dealing with a strong electron-phonon coupling ($\lambda \approx 1$).

The authors thank the participants of V. L. Ginzburg's seminar, and particularly Yu. V. Kopaev, for a useful discussion of the work and for critical remarks.

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

---

[1] If the chains 1 and 2 are not equivalent with respect to the positions of the atoms (molecules) and the atoms 1 are shifted relative to the atoms 2 by the half-period $b/2$, so that an atom of chain 1 has two nearest neighbors in chain 2, then an adidtional factor $2|\cos(Qb/2)|$ appears in the term proportional to $\cos(\varphi_1 - \varphi_2)$.

[2] 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 $t_c \approx T_0$ and $t \gtrsim T_0$. This estimate for TTF–TCNQ agrees with the data obtained for t from quantum-mechanical calculations.[22]

[3] In systems with a fixed degree of charge transfer and correspondingly 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 $2k_F b$ and the rotional fraction q/p. In fact, at $Q \neq 2k_F$ 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 $|Q - 2k_F||\Delta|$. The energy gained from the transition to the commensurate state is $(|\Delta|/\varepsilon_F)^{p-1}|\Delta|N(0)$, and should not exceed the value $|Q - 2k_F||\Delta|$, 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 $(Q - 2k_F)^2$. 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 electrons over the Fermi surface, and the energy loss in the transition to the commensurate state is proportional to $|Q - Q_0|^2$, where Q_0 is the wave vector of the noncommensurate CDW.

[4] McMillan has shown that the NCDW–CDDW transition can be of second order.[12] The continuity of the order parameter $\psi(r)$ is ensured in this case by the appearance of non-commensurability 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 $\hbar v_F/\Delta$. In the presently known layered compounds, this solution is not satisfied and the NCDW–CCDW transition is of first order.

[5] In $1T$-TaS$_2$ and $1T$-TaSe$_2$ at low temperatures, the opposite inequality is satisfied (see below), so that the condition $F_c \ll F_T$ could be observed only near T_0. Indirect estimates yield for these compounds $T_0 \approx 600$ K, and the $1T$ modification is destroyed at $T \approx 500$ K, so that the region of T_0 cannot be reached.

[1] J. A. Wilson, F. J. Di Salvo, and S. Mahajan, Adv. Phys. **24**, 117 (1975).
[2] R. Comes, M. Lambert, H. Launois, and H. R. Zeller, Phys. Rev. B **8**, 571 (1973); Phys. Status Solidi B **58**, 587 (1973).
[3] L. N. Bulaevskiĭ, Usp. Fiz. Nauk **115**, 263 (1975); **120**, 259 (1976) [Sov. Phys. Usp. **18**, 131 (1975); **19**, 836 (1976)].
[4] D. E. Moncton, J. D. Axe, and F. J. Di Salvo, Phys. Rev. Lett. **34**, 734 (1975).
[5] R. Comes, S. M. Shapiro, G. Shirane, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. **35**, 1518 (1975).
[6] C. Weyl, E. M. Engler, K. Bechgaard, G. Jehanno, and S. Etemad, Solid State Commun. **19**, 925 (1976).
[7] R. Renker, L. Pitschovius, W. Gläser, H. Rietschel, R. Comes, L. Liebert, and W. Drexel, Phys. Rev. Lett. **38**, 836 (1974).
[8] D. E. Moncton, F. J. Di Salvo, J. D. Axe, L. J. Sham, and B. R. Patton, Phys. Rev. B **14**, 3432 (1976).
[9] F. J. Di Salvo, D. E. Moncton, J. A. Wilson, and S. Mahajan, Phys. Rev. B **14**, 1543 (1976).
[10] W. L. McMillan, Phys. Rev. B **12**, 2042 (1975).
[11] L. N. Bulaevskiĭ and D. I. Khomskiĭ, Pis'ma Zh. Eksp. Teor. Fiz. **23**, 581 (1976) [JETP Lett. **23**, 532 (1976)].
[12] W. L. McMillan, Phys. Rev. B **14**, 1486 (1976).
[13] W. Lawrence and S. Doniach, Proc. Twelfth Intern. Conf. on Low Temp. Physics, Kyoto, 1971, p. 361.
[14] L. N. Bulaevskiĭ, Usp. Fiz. Nauk **116**, 449 (1975) [Sov. Phys. Usp. **18**, 514 (1975)].
[15] M. J. Rice, C. B. Duke, and N. O. Lipari, Solid State Commun. **17**, 1089 (1975).
[16] H. G. Schuster, Phys. Rev. B **11**, 613 (1975).
[17] P. A. Lee, T. M. Rice, and P. W. Anderson, Solid State Commun. **14**, 703 (1974).
[18] F. J. Di Salvo, J. A. Wilson, B. G. Bagley, and J. V. Waszczak, Phys. Rev. B **12**, 2220 (1975).
[19] B. Horovitz, H. Gutfreund, and M. Weger, Phys. Rev. B **12**, 3174 (1975).
[20] K. B. Efetov and A. I. Larkin, Zh. Eksp. Teor. Fiz. **66**, 2290 (1974) [Sov. Phys. JETP **39**, 1129 (1974)].
[21] Y. Tomkiewicz, B. A. Scott, L. J. Tao, and R. S. Title, Phys. Rev. Lett. **32**, 1362 (1974).
[22] J. Berlinsky, J. Carolan, and L. Weiler, Solid State Commun. **15**, 795 (1974).
[23] K. B. Efetov and A. I. Larkin, Zh. Eksp. Teor. Fiz. **72**, 2350 (1977) [Sov. Phys. JETP **45**, 1236 (1977)]; L. J. Sham and B. R. Patton, Phys. Rev. B **13**, 3151 (1976); D. J. Bergman, T. M. Rice, and P. A. Lee, Phys. Rev. B **15**, 1706 (1977).
[24] P. Bak and V. J. Emery, Phys. Rev. Lett. **36**, 978 (1976).
[25] J. P. Puget, S. K. Khanna, F. Denoyer, R. Comes, A. F. Garito, and A. J. Heeger, Phys. Rev. Lett. **37**, 437 (1976).
[26] L. F. Mattheis, Phys. Rev. B **8**, 3719 (1973).
[27] F. J. Di Salvo and J. V. Waszczak, J. Phys. (Paris) **37**, C4-157 (1976).
[28] P. M. Williams, G. S. Parry, and C. B. Scruby, Philos. Mag. **29**, 695 (1974); C. B. Scruby, P. M. Williams, and G. S. Parry, Philos. Mag. **31**, 225 (1975).

Translated by J. G. Adashko