hree-dimensional order of charge-density waves ı layered compounds

L. N. Bulaevskiĭ and D. I. Khomskiĭ

P. N. Lebedev Physics Institute, USSR Academy of Sciences
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The period of the charge-density waves in a direction perpendicular to the layers is determined for layered compounds of the 2H-$TaSe_2$ and 1T-$TaSe_2$ type on the basis of the phenomenological Landau theory. The predictions of the theory agree with the experimental data.

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Superstructures of the type of charge-density waves (CDW) were observed in ayered compounds of transition-metal dichalcogenides below the temperature $_0$.[1–3] In the 2*H* modifications of $TaSe_2$, TaS_2, and $NbSe_2$, the temperature T_0 equal to 120, 80, and 35 °K, respectively. In the 1*T* modification of $TaSe_2$ ıd TaS_2, according to indirect data,[4] $T_0 \approx 600$ °K. In all these compounds, the ɜriod of the superstructure in the layer directly below T_0 is not commensurate ith the period of the initial two-dimensional hexagonal lattice. When the temɜrature is lowered to the point T_d, in all the investigated crystals except *T*-$NbSe_2$, transition is observed from the noncommensurate two-dimensional ttice of the layer into a commensurate charge-density wave (the NCDW—CDW transition). The temperature T_d is equal to 80, 473, and 200 °K in 2*H*-aSe_2, 1*T*-$TaSe_2$, and 1*T*-TaS_2, respectively. A qualitative explanation of the ɜincipal characteristics of two-dimensional superstructures and NCDW—CDW transitions on the basis of the Landau phenomenological theory of phase ansitions is given in[2,5]. We shall show below that this theory makes it also ɔssible to determine the period of the superstructure in a direction perpendicur to the layers (along the *c* axis).

Just as in[2,5], we shall use as the CDW transition parameter the relative ıange of the electron density $\alpha_n(\mathbf{r})$, where n is the number of the layer and $= (x, y)$ is the coordinate inside the layer. The hexagonal symmetry of the ini-al lattice of the dichalcogenides causes the CDW to consist of three waves ith two-dimensional vectors $\mathbf{q}_i$, rotated 120° relative to each other, and the ansition parameter $\alpha_n(\mathbf{r})$ is given by the expression

$$\alpha_n(\mathbf{r}) = \mathrm{Re} \sum_i \psi_{in}(\mathbf{r}), \qquad \psi_{in} = u e^{i(\mathbf{q}_i \mathbf{r} + \phi_{in})}, \tag{1}$$

here ϕ_{in} is the phase of wave i in layer n, and u is the wave amplitude, which e assume the same for all i and n. In the expansion of the free energy in ɔwers of ψ_{in}, the only part of the free energy which is important to us is that hich does not contain gradient terms in r

$$\mathcal{F} = \sum_n \int d\mathbf{r} \left\{ a(\mathbf{r}) a_n^2 - b(\mathbf{r}) a_n^3 + c(\mathbf{r}) a_n^4 + d(\mathbf{r}) \left[|\psi_{1n}\psi_{2n}|^2 + |\psi_{1n}\psi_{3n}|^2 + |\psi_{2n}\psi_{3n}|^2 \right] \right\} + \sum_n \int d\mathbf{r}\, d\mathbf{r}'\, g(\mathbf{r}, \mathbf{r}') [a_n(\mathbf{r}) a_{n+1}^*(\mathbf{r}') + \text{H.c.}]. \tag{2}$$

The last term takes into account here the Coulomb interaction of the CDW of the neighboring layers, where the coefficients a, b, c, d and g are periodic functions of the coordinate $\mathbf{r}$ with the same period as the initial hexagonal lattice, for example,

$$b(\mathbf{r}) = b_0 + b_1 \sum_i e^{i\mathbf{K}_i \mathbf{r}}, \qquad (1$$

where $\mathbf{K}_i$ are the reciprocal-lattice vectors for the initial structure in the laye The gradient terms in $\mathbf{r}$ lead to a minimum of the total free energy at a definit value q_0 of the vectors q_i and at definite directions of $\mathbf{q}_i$, which coincide with the lines of the atoms of the hexagonal lattice.

Only two-dimensional structures were considered in[2,5], that is, the dependence of the phases ϕ_i on n was not taken into consideration. In this situation, the following conclusions that agree with the experimental data were obtained: a) The interaction of the waves $b_0(\psi_1\psi_2\psi_3 + \text{H. c.})$ leads to an additional lowering of the free energy in a state with three waves, and it gives a first-order transition from the normal metallic state to the CDW state in the $2H$ and $1T$ modifications.[5] b) In $2H$ modifications, the terms $b_1(\psi_i^3 + \text{H. c.})$ in the NCDW state lead to the appearance of additional harmonics in ψ_i, of the type $v\exp[i(\mathbf{q}_i'\mathbf{r} + \lambda_i)]$ and $\mathbf{q}_i' = \mathbf{K}_i - 2\mathbf{q}_i$, since in $2H$ crystals q_0 is close to $K/3$, and q' as well as q turns out to be close to q_0. Owing to the appearance of these harmonics, q and q' come closer to $K/3$ when the temperature drops below T_0 in $2H$-$TaSe_2$ and $2H$-$NbSe_2$. At 80 °K, a first-order transition to the CCDW wit $q = K/3$ takes place in $2H$-$TaSe_2$ on account of the same term in the free energy.[2] c) In the $1T$ modifications we have $q = 0.285$ K, which is far from $K/3$ and $K/4$. In this case the transition to the commensurate structure is attained by rotating the vectors q_i of the noncommensurate superstructure through 13°54′, so that after the rotation the new vectors $\mathbf{q}_i$ satisfy the relations $3\mathbf{q}_i - q_{i+1} = \mathbf{K}_i$, where $i = 1, 2, 3$ and $\mathbf{q}_4 \equiv \mathbf{q}_1$. A gain in the free energy is provided in this time by the terms $c_1(\psi_i^3\psi_{i+1}^* + \text{H. c.})$.[5]

We shall show now that all these effects can be observed only at definite cor relations between the phases ϕ_{in} in different layers. We assume a dependence $\phi_{in} = p_i n$ and determine those admissible values of p_i at which effects (a)—(c) can be observed.

In the noncommensurate phase, the interaction that leads to the effect (a) is possible only in the case when

$$p_1 + p_2 + p_3 = 2\pi s, \quad s\text{- are integers;} \qquad (4$$

otherwise the corresponding terms in (2) fall out after the summation over n. In the $1T$ modification, all the layers are equivalent and the Coulomb interaction of the neighboring layers is $Q \sim g\sum_i \cos p_i$. Under condition (4), Q reaches a minimum if $p_i = 2\pi/3$. Thus, the period c'' along the c axis in the NCDW of th $1T$ modifications must be tripled. Experiment indeed yielded $c' = 3c$ in $1T$-TaS and $1T$-TaS_2 above T_d.[1]

In the $2H$ modifications, a condition on p_i' in the NCDW and CCDW results also from terms that determine the effects (b). The contribution of these term after summation over n differs from zero if $p_i = 0$ or $2\pi/3$, i. e., superstructures with $c' = c$ or $c' = 3c$ are possible. The unit cell of a $2H$ crystal contains

o nonequivalent layers, but this circumstance, as can be readily seen, does t change our conclusion. At the same time, the nonequivalence of the neighring layers does not allow us to make an unequivocal choice between these o possibilities from considerations of the minimum of the Coulomb energy. :periment seems to yield at $c'=c$ for $2H$-$TaSe_2$ [1] and apparently also $2H$-$)Se_2$.[3]

In the commensurate phase of the $1T$ modifications, effects (a) and (c) can be served only under condition (5) and the conditions

$$3p_i - p_{i+1} = 2\pi s_i . \tag{5}$$

ıe solutions of (4) and (5) are

$$p_1 = \frac{s_1 + 4s_2 + s_3}{13} 2\pi, \quad p_2 = \frac{3s_1 - s_2 + 3s_3}{13} 2\pi, \quad p_3 = \frac{9s_1 - 3s_2 - 4s_3}{13} 2\pi, \tag{6}$$

ıere s_i are integers, and as a result we obtain of necessity $c'=c$ or $c'=13c$. ıe Coulomb interaction Q is smaller for the superstructure with $c'=13c$, and ; minimum of Q is reached under condition (4) and (5) for (p_1, p_2, p_3) 2, 6, 5) $2\pi/13$. Experiment[1] has yielded $c'=13c$ for the commensurate phases $1T$-$TaSe_2$ and $1T$-TaS_2.

We note that the Coulomb interaction in the $1T$ modifications reaches an abılute minimum when the period is doubled along the c axis. The realization of riods $c'=c$, $3c$, or $13c$ is connected with the existence of three $\mathbf{q}_i$ waves and :h the strong influence of the commensuration in comparison with the ulomb interaction of the CDW of different layers.[1)] In the quasi-one-dimenmal crystals $K_2Pt(CN)_4Br_{0.3}\cdot 3H_2O$, the chains are equivalent, and only one ıcommensurate wave exists in them. Experiment[6] has revealed in this comınd a doubling of the period in a direction perpendicular to the chains.

phase with $c'=2c$ could be realized near T_0 at small CDW amplitudes, so ıat in principle, with decreasing temperature, it is possible to have the ansition sequence: metal—second order transition to NCDW with $c'=2c$—rst-order transition NCDW with $c'=3c$—first-order transition to CCDW.

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