Theory of phase transitions from normal to modulated structures in some 1T transition-metal dichalcogenides

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Both mean-field and renormalization-group theories of the phase transitions from the normal to modulated phases in a model for 1T-$TiSe_2$ and for a related model are given. The critical properties of the $TiSe_2$ phase transition are predicted to be those of the three-component Heisenberg model.

I. INTRODUCTION

This paper describes a theoretical investigation of the phase transitions from the normal to modulated structures in some layered transition-metal dichalcogenides.[1–4] The phase transition in 1T-$TiSe_2$ is compared with that in a hypothetical material which we shall call 1T-TaX_2 (see below) from the point of view of both a mean-field analysis and a renormalization-group analysis of the appropriate Landau free energies.

The symmetry properties of the normal modes responsible for the phase transition are analyzed in detail (the case of 1T-$TiSe_2$ has been treated previously by DiSalvo *et al.*[4]) and these symmetry properties are then used in the construction of the appropriate Landau free energy. In the case of 1T-TaX_2, where the time-reversal symmetry of the basis vectors plays an important role, it is shown that a particular convention for choosing the phases of the basis vectors leads to basis vectors with simple transformation properties.

A mean-field analysis of the transitions from the normal to incommensurate phases of 1T-TaX_2 has already been given by Walker and Withers,[5] but in terms of a model in which the interlayer interaction is treated in perturbation theory; our results are compared with theirs in Sec. II below.

In 1T-$TiSe_2$, the phase transition of interest is from the normal state to a $2a\times 2a\times 2c$ superstructure and occurs at the temperature $T_c\approx 200$ K, as shown by neutron[4] and electron[6] scattering experiments. The transverse phonon mode responsible for the transition has been identified and the space-group symmetry was found to change[7] from D_{3d}^3 ($P\bar{3}m\,1$) to D_{3d}^4 ($P\bar{3}c\,1$) at the transition temperature. The temperature dependence of the satellite intensities[4] below T_c and thermal-expansion data[8,9] indicate that the transition is second order.

In the models analyzed below the order parameters are associated with wave vectors $\vec{k}=\alpha\vec{a}^*+\gamma\vec{c}^*$. For 1$T$-$TiSe_2$ α and γ have the special values $\alpha=\frac{1}{2}$ and $\gamma=\frac{1}{2}$ whereas for the hypothetical 1T-TaX_2 α and γ have arbitrary values between zero and one-half (but with $\gamma\neq\frac{1}{3}$). Although we know of no material to which the model for 1T-TaX_2 is actually applicable, it is nevertheless interesting to compare the theoretical results for the two closely related cases of 1T-TaX_2 and 1T-$TiSe_2$. It is perhaps of interest to note that the hypothetical material 1T-TaX_2 has properties approximating those of 1T-TaS_2 and 1T-$TaSe_2$.[10–12] In these latter materials, however, the basal-plane component of the wave vector is rotated approximately 1° away from the $\vec{a}^*$ direction;[10,2] unfortunately, the normal to incommensurate phase transitions which are expected to occur in these materials are not observable because the 1T structure becomes unstable first as the temperature is raised.

II. LANDAU FREE ENERGY FOR 1T-TaX_2

A Landau theory of the phase transition in this case requires a knowledge of the free energy of states of the crystal whose distortions relative to the high-temperature phase are determined by the vector

$$u=\mathrm{Re}\left[\sum_i \psi_i e_i\right],$$

where $i=1,2,3$. The transformation properties of the basis vectors e_i have been determined in the Appendix and it follows that the transformation properties of the components ψ_i of the order parameter with respect to the generators of the space group D_{3d}^3 are

$$\psi_j\rightarrow\psi_{j+1}^*$$

under S_6^+ and

$$\psi_1\rightarrow\psi_1,\psi_2\rightarrow\psi_3,\psi_3\rightarrow\psi_2$$

under σ_d.

The free-energy functional invariant with respect to the above transformation properties is

$$F-F_N=\tfrac{1}{2}a(T)\sum_{i=1}^{3}|\psi_i|^2+u_1\sum_{i=1}^{3}|\psi_i|^4+u_3\sum_{i<j}|\psi_i|^2|\psi_j|^2,$$

where F_N is the free energy of the normal phase, $a(T)\equiv\alpha(T-T_c)$ and u_1,u_3 are real coefficients assumed to be independent of temperature. Stability of the free energy imposes the following constraints on the coefficients of fourth-order terms: $u_1>0$ and $u_1+u_3>0$. For $a(T)>0$ the solutions that minimize the free energy are $\psi_j=0$, whereas for $a(T)<0$ two types of minimum energy solutions are possible:

(i) $|\psi_1|^2=|\psi_2|^2=|\psi_3|^2=\dfrac{|a|}{4(u_1+u_3)}$

if $u_1>\dfrac{u_3}{2}$

and

(ii) $|\psi_1|^2=\dfrac{|a|}{4u_1}$, $|\psi_2|^2=|\psi_3|^2=0$, etc.

if $u_1<\dfrac{u_3}{2}$.

Let us call the former solutions $(3Q)$ states and the latter solutions $(1Q)$ states. The critical properties of these states will be discussed in Sec. IV.

It is of interest to note that free energy for a single layer[5,13] of the layered $1T$-TaS_2 structure contains a term cubic in the order parameter which would apparently cause the phase transition to be first order. However, Walker and Withers[5] have argued that when the free energy is summed over all layers, there is a destructive interference between the cubic terms in different layers which causes the total effect of the cubic term to vanish. This result is thus in agreement with our finding that there is no cubic term in our above free energy.

III. LANDAU FREE ENERGY FOR $1T$-$TiSe_2$

In this case, the states of the crystal of interest are those with distortions given by the vector

$$u=\sum_{i=1}^{3}\psi_i e_i ,$$

where both the basis vectors e_i and the components of the order parameter ψ_i are real, for $i=1,2,3$. From the transformation properties of the basis vectors e_i given in the Appendix, it follows that the transformation properties of the components of the order parameter under generators of the space group D_{3d}^3 are

$$\psi_j\rightarrow-\psi_{j+1}$$

under S_6^+ and

$$\psi_1\rightarrow-\psi_1,\quad \psi_2\rightarrow-\psi_3,\quad \psi_3\rightarrow-\psi_2$$

under σ_d.

The Landau free-energy invariant with respect to these transformations is

$$F-F_N=\tfrac{1}{2}a(T)\sum_{i=1}^{3}\psi_i^2+u_1\sum_{i=1}\psi_i^4+u_3\sum_{i<j}\psi_i^2\psi_j^2 ,$$

where, again, $a(T)\equiv\alpha(T-T_c)$ and u_1,u_3 are real coefficients assumed to be independent of temperature.

Minimization of the free energy with respect to the order parameters gives rise to the $(3Q)$ and $(1Q)$ states as before [for $a(T)<0$], but in contrast to case (a), for $1T$-$TiSe_2$ the order parameters are all real. The space group of the $(3Q)$ state is found to be D_{3d}^4 which is the space group obtained from neutron scattering experiments.[4,7] On the other hand if $0<u_1<u_3/2$, the $(1Q)$ state has minimum energy and the crystal symmetry corresponding to that state is monoclinic with space group $C_{2h}^4(P2/c)$.

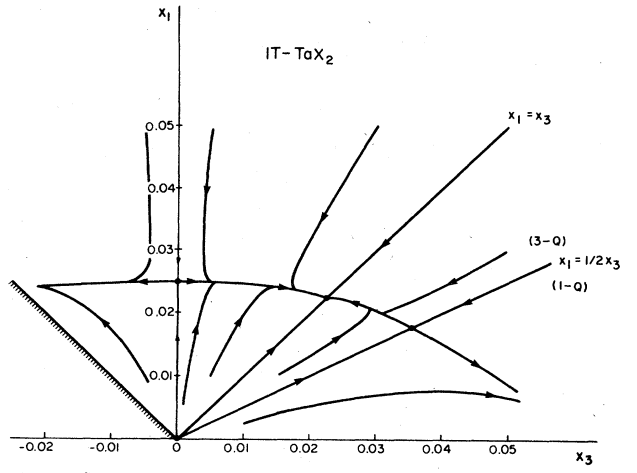

FIG. 1. Flow diagram for the free energy of Sec. II plotted in the (x_1,x_3) plane with $x_1=K_4u_1$ and $x_3=K_4u_3$ $[K_4=1/(8\pi^2)]$. The regions for mean-field triple-Q and single-Q states are indicated in the figure. See text for a discussion on the $1T$-TaX_2 structure.

The latter structure has not been observed so far in these systems.

IV. CRITICAL PROPERTIES OF THE MODEL FREE ENERGIES

We have studied the critical properties of the model free energies of the previous sections by a renormalization-group (RG) analysis. $1T$-TaX_2 and $1T$-$TiSe_2$ show quite different critical behavior due to the fact that their order-parameter dimensionalities (n) are different; for the former $n=6$, whereas for the latter $n=3$. This difference in the order-parameter dimensionality is reflected in the RG flow diagrams plotted in Figs. 1 and 2

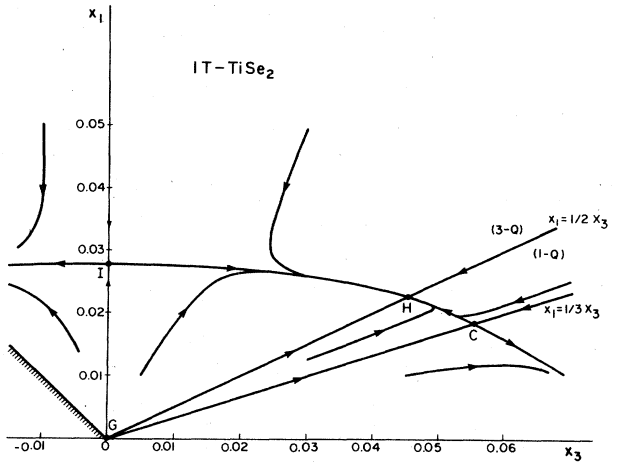

FIG. 2. Flow diagram for the free energy of Sec. III plotted in the (x_1,x_3) plane where $x_1=K_4u_1$ and $x_3=K_4u_3$ $[K_4=1/(8\pi^2)]$. The four fixed points are labeled as G (Gaussian), I (Ising), H (Heisenberg), and C (Cubic). The regions for mean-field triple-Q and single-Q states are indicated in the figure.

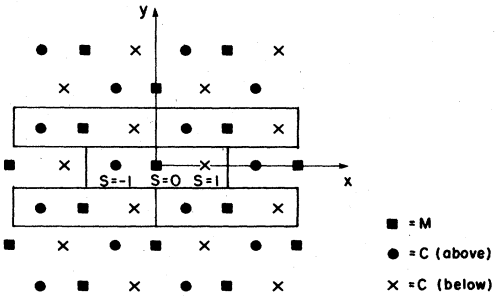

FIG. 3. Basal-plane projection of the position of atoms in $1T$-transition metal dichalcogenides with chemical formula MC_2, where M=Ta or Ti and C=Se or sulfur. The three atoms in a unit cell are labeled by $S(=\pm 1,0)$.

following Refs. 14—17. As shown by the mean-field analysis of Sec. II, the region to the left of the line $u_1=\frac{1}{2}u_3$ corresponds to $(3Q)$ states, whereas the region to the right of $u_1=\frac{1}{2}u_3$ corresponds to the $(1Q)$ states.

From Fig. 1 it is seen that a second-order transition to a $(3Q)$ state is possible if $u_1>u_3/2>0$; otherwise the transition is driven to first order by fluctuations. The RG flow diagram for $1T$-$TiSe_2$ is given in Fig. 2. A second-order phase transition is possible if $u_1>u_3/3>0$; otherwise the transition is first order. Since the observed phase transition in $1T$-$TiSe_2$ is second order, the critical properties are predicted to be those of the three-component Heisenberg model.

V. SUMMARY

Model free energies describing and contrasting phase transitions from the normal to modulated phases in $1T$-$TiSe_2$ on the one hand, and in $1T$-TaX_2 on the other hand, have been developed. A special convention for defining the phases of the normal modes was found to be useful in accounting for the effects of time-reversal symmetry in the latter case. The critical properties of the two cases were found to be different because the order parameters are real in one case and complex in the other. The free energy for the $1T$-$TiSe_2$ phase transition was found to be identical to that of the three-component Heisenberg model with cubic anisotropy, and a careful measurement of the critical exponents for $1T$-$TiSe_2$ and a comparison with those of the Heisenberg model, would thus be of interest.

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APPENDIX: BASIS VECTORS FOR 1T-TaX_2 AND 1T-$TiSe_2$

In this appendix, we introduce a convention for determining the phase of the basis vectors in terms of which the lattice displacements can be written.

An irreducible representation of a space group can be induced in the following way (e.g., see Lyubarskii[18]). Let e_1 be a basis vector for a one-dimensional (we require only such one-dimensional representations below) representation of the group of wave vector $\vec{k}_1$. Then, if the star of $\vec{k}_1$ is the set of inequivalent wave vectors $\vec{k}_j=g_j\vec{k}_1$ where $j=1,2,\ldots$ and g_j is an appropriate element of the space group, a basis for an irreducible representation of the full space group is the set of vectors $e_j=g_je_1$. Now suppose that the wave vector $-k_1=g_{\bar{1}}\vec{k}_1$ is in the star of $\vec{k}_1$. Then the basis vector $e_{\bar{1}}=g_{\bar{1}}e_1$ is a Bloch function corresponding to wave vector $-\vec{k}_1$. The complex conjugate of e_1, namely, e_1^*, is also a Bloch function with wave vector $-\vec{k}_1$. If (as will be the case below) the complex conjugation operation has no effect on the degeneracy of the eigenvalues, it will be possible to choose e_1 so that $e_{\bar{1}}$ and e_1^* are the same to within a phase factor (recall that e_1 gave a one-dimensional representation of the little group). The phase factor can be chosen so that $e_{\bar{1}}=e_1^*$ and this is the convention we will adopt.

An arbitrary displacement of the ions in a crystal can be given in terms of the column vector

$$u=\sum_{l,s,\alpha} u_\alpha(_s^l)e_\alpha(_s^l)\ , \tag{A1}$$

where $u_\alpha(_s^l)$ is the αth component $(\alpha=x,y,z)$ of the displacement of the sth basis atom in the lth unit cell. The column vector $e_\alpha(_s^l)$ has unity in the row $ls\alpha$ and zero in all other rows. In the $1T$ structure the basis atom can be labeled by $s=1,0,-1$, as shown in Fig. 3 and the effect of the inversion operator C_i on the basis vectors $e_\alpha(_s^l)$ is

$$C_ie_\alpha(_s^l)=-e_\alpha(_{-s}^{-l})\ . \tag{A2}$$

The wave vector of interest for a discussion of the transition from the normal state to the charge-density-wave state of $1T$-TaX_2 is

$$k_1=\alpha\vec{a}^*+\gamma\vec{c}^*\ , \tag{A3}$$

where $0<\alpha,\gamma<1$ and $\vec{a}^*$ and $\vec{c}^*$ are basal-plane and c axis reciprocal-lattice vectors. The star of $\vec{k}_1$ contains six wave vectors, including $-\vec{k}_1=C_i\vec{k}_1$. The little group of wave vector $\vec{k}_1$ contains two elements, the identity and the reflection σ_d in the plane containing a^* and c^*, and has two one-dimensional irreducible representations A' and A'' for which the basis vectors transform as

$$\sigma_de_{A'}=e_{A'}$$
and
$$\sigma_de_{A''}=-e_{A''}\ , \tag{A4}$$

respectively. The application of a standard character test (e.g., see Lyubarskii[18] or Maradudin and Vosko[19]) shows that both of these representations are real, so that the inclusion of the complex conjugation operation in the symmetry group of the problem does not affect the degeneracy of the eigenvalues.

Now define

$$e_{\alpha;\lambda}(\vec{k}_1)=\exp(i\phi_\lambda)N^{-1/2}\sum_l \exp[i\vec{k}_1\cdot\vec{R}(l)]e_{\alpha;\lambda}(l)\ , \tag{A5}$$

where l is a sum over all N unit cells in the crystal; $\lambda=1,0,-1$; $\phi_\lambda=0$ for $\lambda=-1$, and $\phi_\lambda=\pi/2$ for $\lambda=1,0$;

$$e_{\alpha;\pm1}(l)=2^{-1/2}[e_\alpha(^l_1)\pm e_\alpha(^l_{-1})]$$

and (A6)

$$e_{\alpha;0}(l)=e_\alpha(^l_0)\ .$$

There are nine distinct vectors $e_{\alpha;\lambda}(\vec{k}_1)$ for a given $\vec{k}_1$. The three vectors corresponding to $\alpha=y$ give A'' representations of the group of wave vector $\vec{k}_1$, whereas the six vectors corresponding to $\alpha=x$ and z give A' representations. As a result of our particular choice of phase factors ϕ_λ, and linear combinations (A6), the basis vectors (A5) satisfy the convention $C_i e_{\alpha;\lambda}(\vec{k})=e^*_{\alpha;\lambda}(\vec{k})$ which we had chosen to adopt above.

The mode responsible for the normal to charge-density-wave phase transition in $1T$-TaX_2 is an A' mode and can therefore be written as a linear combination of the six A' basis vectors; the vector describing this mode is

$$e_1(A')=\sum{}'_{\alpha,\lambda} c_{\alpha\lambda}e_{\alpha;\lambda}(\vec{k}_1)\ ,$$

where the prime indicates a summation over $\alpha=x$ and z, and $\lambda=-1,0,1$. Because we shall require e_1 to satisfy the convention $C_i e_1=e_1^*$, the coefficients $c_{\alpha\lambda}$ are real.

A basis for an irreducible corepresentation of the space group D^3_{3d} is therefore the set of three vectors,

$$\{e_1,\ e_2(=C_3e_1),\ e_3\ (=C_3^{-1}e_1)\}\ ,$$

together with their complex conjugates. The transformation properties of these basis vectors with respect to the generators S_6^+ and σ_d of the space group D^3_{3d} are

$$S_6^+e_j=e^*_{j-1}\ ,$$

where $e_{j+3}=e_j$, and (A7)

$$\sigma_d e_1=e_1,\ \sigma_d e_2=e_3,\ \sigma_d e_3=e_2\ .$$

In constructing a Landau theory of the phase transitions in $1T$-TaX_2, one is interested in states of the system for which the displacement vector has the form

$$u=\mathrm{Re}\left[\sum_i \psi_i e_i\right]\ ,$$

where $i=1,2,3$ and the three components ψ_i of the order parameter are arbitrary complex numbers.

In the case of $1T$-$TiSe_2$ to which we now turn, the order parameter is associated with the wave vector $\vec{k}$, given by (A3) but with $\alpha=\gamma=\frac{1}{2}$. The star of $\vec{k}_1$ contains only three wave vectors (instead of six as for $1T$-TaX_2) because $-\vec{k}_1$ and $\vec{k}_1$ differ by a reciprocal-lattice vector. Neutron scattering experiments[4] show that the mode responsible for the phase transition in $1T$-$TiSe_2$ is a transverse A_u mode. Arguments similar to those above give as a basis vector for this mode the result

$$e_1(A_u)=\sum_{\lambda=0}^{1} c_{y\lambda}e_{y\lambda}(\vec{k}_1)\ ,$$

where $e_{y\lambda}$ is given by (A5) and (A6). The phase factors ϕ_λ are chosen zero and the $c_{y\lambda}$ are chosen real which makes the basis vector real and eliminates the problem (which occurs for $1T$-TaX_2) of relating the complex conjugate of a basis vector with wave vector $\vec{k}_1$. The transformation properties of the set of basis vectors, $\{e_1,e_2\ (=C_3e_1),\ e_3\ (=C_3^{-1}e_1)\}$, under the generators S_6^+ and σ_d of the space group D^3_{3d} are

$$S_6^+e_j=-e_{j-1}\ ,$$

$$\sigma_d e_1=-e_1,\ \sigma_d e_2=-e_3,\ \text{and}\ \sigma_d e_3=-e_2\ .$$

The states of interest for a Landau theory of the phase transition are those described by the displacement vector

$$u=\sum_{i=1}^{3}\psi_i e_i\ ,$$

where the three components of the order parameter ψ_i are real numbers.

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