Theory of phonon dynamics near a charge-density-wave instability*

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A dynamical Landau theory is proposed to describe the coupled motion of phonons and charge-density waves (CDW) near the CDW instability in transition-metal dichalcogenides. The dynamic structure factor is shown to exhibit a Kohn anomaly and a diverging central mode.

I. INTRODUCTION

The anomalous properties of transition-metal dichalcogenides, attributed to the formation of charge-density waves (CDW), have been of great interest in recent months.[1-3] The CDWs have been studied on a microscopic basis by Overhauser[4] and by Chan and Heine.[5] The Chan-Heine theory predicts soft-mode behavior of the lowest longitudinal-phonon branch; however, neutron-scattering studies[6] on the superlattice formation in $2H$-$NbSe_2$ and $2H$-$TaSe_2$ showed a Kohn anomaly in the longitudinal-phonon branch but no soft-mode behavior.

Static[7] and dynamic[8] Landau theories have been developed by McMillan to describe the CDWs, and predict both the sequence of normal-incommensurate-commensurate phases separated by first-order transitions and the existence of overdamped excitations of the CDW. The order parameter in the theory is a linear combination of charge-density-wave and phonon-displacement amplitudes. Moncton *et al.*[6] have independently proposed a simple form for the Landau theory.

In order to study phonon dynamics, we formulate a dynamical Landau theory treating the charge-density-wave amplitude and the phonon displacement as independent dynamical variables. The dynamical equations in the normal phase are then solved and the dynamic structure factor is computed. The theory predicts some softening of the longitudinal-phonon mode (the Kohn anomaly) and shows that there are two distinct regions where the spectral function exhibits different behavior; in one of the regions the theory shows the growth of a central ($\omega = 0$) component in the dynamic structure factor.

II. FORMULATION

The CDW order parameter ζ is a complex scalar with the d-band conduction electron density given by

$$\rho(\vec{r}) = \rho_0(\vec{r})\left[1 + \mathrm{Re}\left(\sum_q \zeta_q\, e^{i\vec{q}\cdot\vec{r}}\right)\right]. \tag{1}$$

Throughout this paper we consider a single layer of the metal; all quantities referred to are, therefore, two dimensional. The phonons are described by the normal-mode coordinates Q_q, where the transition-metal atomic coordinates are given by

$$\vec{X}_n = \vec{X}_n^0 + \mathrm{Re}\left(\sum_q Q_q \hat{q}\, e^{i\vec{q}\cdot\vec{X}_n^0}\right). \tag{2}$$

We consider only one longitudinal-phonon mode for simplicity. The free energy may then be written as

$$F = \sum_q \left[\tilde{\epsilon}_q \zeta_q^* \zeta_q + v_q(\zeta_q^* Q_q + \zeta_q Q_q^*) + \tilde{\kappa}_q Q_q^* Q_q\right], \tag{3}$$

where the first term is just the unrenormalized form of the expression for the free energy given in Refs. 7 and 8 and can be written in an analogous manner,

$$\tilde{\epsilon}_q = \tfrac{1}{2}\tilde{a} + \tilde{e}(\vec{q}_1\cdot\vec{q} - q_1^2)^2 + \tilde{f}\,(\vec{q}_1\times\vec{q})^2. \tag{4}$$

The tilde is used to denote unrenormalized parameters. The second and third terms represent the electron-phonon coupling and the lattice elastic energy, respectively. Terms of higher order than quadratic in Q and ζ are unimportant in the normal phase and have been neglected. $\tilde{a}$ is taken to be of the usual form,

$$\tilde{a} = \tilde{a}'(T - \tilde{T}^*) \tag{5}$$

(where $\tilde{T}^*$ is the unrenormalized transition temperature and $\tilde{a}'$ is a constant), while $\tilde{e}$ and $\tilde{f}$ are taken to be constant. $\vec{q}_1$ is the wave vector of the CDW in the incommensurate state. The three CDWs act independently in the normal state and we treat only one. The kinetic energy of ionic motion is

$$K = \sum M_q \dot{Q}_q^* \dot{Q}_q, \tag{6}$$

where the dot denotes partial differentiation with respect to time. The zeroth-order phonon frequency is given by

$$\omega_q^0 = (\tilde{\kappa}_q/M_q)^{1/2}. \tag{7}$$

In the normal state the coupling to the long-wavelength components of the electron-charge density, which may be treated as an incompressible fluid[8] and described by a velocity field, is unimportant and therefore we omit the electron-fluid velocity as a dynamical variable. The dissipative nature of the CDW motion is described in terms of

the dissipation function,

$$D=\gamma\sum_q \dot{\xi}_q^*\dot{\xi}_q. \tag{8}$$

From Ref. 8 an order of magnitude of γ may be obtained from the equation

$$\gamma\sim\rho_0^4/2q_1^2\sigma, \tag{9}$$

where σ is the electrical conductivity of the metal.

To calculate the dynamic structure factor, we need to consider the system in thermal equilibrium with a reservoir. This is achieved by adding on a random thermal force which pumps power into the system to counteract the power given up to the reservoir, represented by D. The thermal force term is

$$R=\tfrac{1}{2}\gamma\sum_q (g_q^*\dot{\xi}_q+g_q\dot{\xi}_q^*), \tag{10}$$

where $g_q(t)$ is a Gaussian-distributed random variable. It can be represented by an ensemble of functions $g_q^n(t)$ with the ensemble averaged correlation function

$$\langle g_q^*(t)g_{q'}(t')\rangle=(4kT/\gamma)\,\delta_{\vec{q},\vec{q}'}\,\delta(t-t'). \tag{11}$$

The equations of motion obeyed by Q_q and ξ_q are then

$$\frac{\partial}{\partial t}\frac{\partial K}{\partial\dot{Q}_q}=-\frac{\partial F}{\partial Q_q} \tag{12a}$$

and

$$0=-\frac{\partial F}{\partial\xi_q}-\frac{1}{2}\frac{\partial D}{\partial\dot{\xi}_q}+\frac{\partial R}{\partial\dot{\xi}_q}, \tag{12b}$$

where the inertial forces are on the left, and the elastic, dissipative, and thermal-force terms are on the right.

III. STATIC BEHAVIOR: RENORMALIZATION OF TRANSITION TEMPERATURE

Before we go on with the dynamical problem, we consider the normal modes of the system in the static case. The free energy of Eq. (3) is easily put into a diagonal form by introducing new field variables ϕ_q and δ_q which are linear combinations of ξ_q and Q_q,

$$\phi_q=(\xi_q-z_qQ_q)/(1+z_q^2), \tag{13a}$$

$$\delta_q=(Q_q+z_q\xi_q)/(1+z_q^2), \tag{13b}$$

where

$$z_q=\frac{2v_q/(\tilde{\kappa}_q-\tilde{\epsilon}_q)}{1+[1+4v_q^2/(\tilde{\kappa}_q-\tilde{\epsilon}_q)^2]^{1/2}}. \tag{14}$$

The free energy in terms of ϕ_q and δ_q is

$$F=\sum_q(\tilde{\epsilon}_q+z_q^2\tilde{\kappa}_q-2z_qv_q)\phi_q^*\phi_q$$
$$+(\tilde{\kappa}_q+z_q^2\tilde{\epsilon}_q+2z_qv_q)\delta_q^*\delta_q\equiv\sum_q(\epsilon_q\phi_q^*\phi_q+\kappa_q\delta_q^*\delta_q), \tag{15}$$

where ϵ_q and κ_q are renormalized parameters.

Near the (renormalized) transition temperature T^*, we can solve for the renormalized parameters by linearizing Eqs. (14) and (15) in $(T-T^*)$. We obtain, after some straightforward algebra, the result

$$\epsilon_q=\tfrac{1}{2}a'(T-T^*)+e(\vec{q}_1\cdot\vec{q}-q_1^2)^2+f(\vec{q}_1\times\vec{q})^2, \tag{16a}$$

$$\kappa_q=\tilde{\kappa}_q[1+(v_q^2/\tilde{\kappa}_q^2)]^2+O(T-T^*), \tag{16b}$$

where T^*, the renormalized transition temperature is given by

$$T^*=\tilde{T}^*+2v_{q_1}^2/\tilde{\kappa}_{q_1}a', \tag{17}$$

and for the particular normalization chosen for ϕ_q and δ_q in Eqs. (13), a', e, and f are equal to their unrenormalized values used in Eq. (4). Thus we drop the tilde from these parameters hereafter.

As a result of coupling of the CDW and the ion motion, the normal modes of the system are linear combinations of the two; the order parameter used in previous papers[7,8] is to be identified with ϕ_q, whose eigenvalue goes to zero at the transition temperature. The other mode is a high-frequency mode at these temperatures, as can be seen from Eq. (16b), and does not take part in the critical behavior.

IV. DYNAMICS: THE DYNAMICAL STRUCTURE FACTOR

The Eqs. (12) are linear in ξ_q and Q_q and are easily solved by Fourier transforming all variables in time, e.g.,

$$\xi_q(t)=(1/2\pi)\int d\omega\,\xi_q(\omega)\,e^{i\omega t}.$$

For $Q_q(\omega)$, we obtain

$$[-(i\omega+2\epsilon_q/\gamma)(\tilde{\kappa}_q-M_q\omega^2)+2v_q^2/\gamma]\,Q_q(\omega)=v_qg_q(\omega). \tag{18}$$

The normal modes are just the roots of the polynomial on the left of Eq. (18). Far away from the transition where effects of the coupling are not drastic, this yields an overdamped CDW mode, and damped phonon modes with frequencies $\pm\omega_q$, with ω_q slightly smaller than the zeroth-order frequency ω_q^0. To look at the details of the behavior of the frequency and width of the phonon mode, we look at the dynamic structure factor $S(q,\omega)$, which is just the Fourier transform of the correlation function $\langle Q_q(t)Q_q(t')\rangle$.

We may calculate the correlation function for a given random force g_q^n using Eq. (18) and then perform an average over the ensemble of functions

g_q^n according to Eq. (11) to get

$$S(q,\omega)=\frac{2\beta k T/\omega_q^0\tilde{\kappa}_q}{[\beta-(1/\omega_q^0\tau_q+\beta)(1-x^2)]^2+x^2(1-x^2)^2}\,, \tag{19}$$

where $x=\omega/\omega_q^0$ is the reduced frequency,

$$\tau_q=\gamma/[a'(T-T^*)+2e(\vec{q}\cdot\vec{q}_1-q_1^2)^2+2f|\vec{q}\times\vec{q}_1|^2] \tag{20a}$$

is a relaxation time characteristic of the dissipation process, which diverges at the actual (renormalized) transition temperature T^* as $(T-T^*)^{-1}$, and

$$\beta=2v_q^2/\gamma\tilde{\kappa}_q\omega_q^0 \tag{20b}$$

is a dimensionless coupling constant (approximately independent of q).

V. DISCUSSION OF RESULTS

Equation (19) is the result of an exact solution of the dynamical equations of motion. In order to discuss its consequences, we consider the two frequency regimes $\omega_q^0\tau_q \ll 1$ and $\omega_q^0\tau_q \gg 1$ separately. Far from T^*, $\omega_q^0\tau_q \ll 1$, and in this fast relaxation case, the CDW adiabatically follows the ion motion. $S(q,\omega)$ has the usual two-peaked behavior with poles (phonons) at the frequencies given by

$$\omega_q^2 \simeq \omega_q^{02}(1-\beta\omega_q^0\tau_q),$$

which gives a Kohn anomaly which progressively deepens as the temperature is lowered. This is the behavior predicted by microscopic mean-field models[5] which use the Born-Oppenheimer adiabatic approximation. On the other hand, when one gets close enough to T^* that $\omega_q^0\tau_q$ is greater than unity, the CDW can no longer follow the ion motion, and Eq. (19) predicts a broadening of the phonon peak with no further softening, and the appearance of a zero-frequency peak in $S(q,\omega)$. At $\omega=0$, $S(q,\omega)$ diverges as $(T-T^*)^{-2}$ and the integrated intensity diverges as $(T-T^*)^{-1}$. Thus the arrest of the soft phonon and the appearance of the zero-frequency mode result from the breakdown of the adabatic approximation, and the measurements to date are not in conflict with the Chan-Heine theory. This theory, with its emphasis on Fermi-surface nesting and a strong electron-phonon interaction, seems to be a viable microscopic model for CDW formation in the dichalcogenides. High-resolution neutron measurements should provide an important test of the theory.

Moncton *et al.*[6] report the observation of quasielastic critical scattering in the normal phase of $2H$-$TaSe_2$. In order to distinguish scattering from thermal fluctuations treated here (which is dynamical) and scattering from impurity driven fluctuations treated earlier[7] (which is static), it is necessary to measure the width of the central mode; this measurement is not yet available.

Dynamical central peaks are observed in many structural transitions. Yamada[9,10] and co-workers have studied a model of the structural transition in ND_4Br where the orientational motion of the ND_4 couples to the phonon coordinates. They obtain an expression similar to Eq. (19) for the dynamic structure factor. It appears that any model with an internal relaxing order parameter coupled to the phonon coordinates will produce a similar soft-phonon–central-peak behavior. The present model should be applicable to the Peierls transition[11] model of tetrathiofulvalene-tetracyanoquinodimethane[12] (TTF-TCNQ) and the platinum salts[13] (except for one-dimensional fluctuation effects), and with modifications to the Gorkov model[14] of the structural transition of V_3Si and Nb_3Sn.[15]

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