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Collective modes of a charge-density wave near the lock-in transition*

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The effects of phase modulation of a charge-density wave on its collective-mode spectrum are computed. The spectrum consists of two branches, a branch of collective modes of the discommensuration lattice and a phason branch which is continuous at the lock-in phase transition.

I. INTRODUCTION

The anomalous properties of the layered transition-metal dichalcogenides have been attributed to charge-density-wave (CDW) formation.[1] In $2H$-$TaSe_2$ an incommensurate CDW forms at 122 °K and a weakly-first-order transition to the commensurate state occurs at about 90 °K. In a careful neutron-diffraction study Moncton, Axe, and DiSalvo[2] observed a nonlinear distortion of the CDW near the lock-in transition which they anticipated using a Landau-theory argument. The physics of this distortion is simple; the CDW gains bonding energy by placing the charge-density peaks between transition-metal atoms to form bonding charge. For a plane wave incommensurate CDW portions of the CDW will be in the proper phase with the lattice to produce bonding charge whereas other portions of the CDW will be out of phase and will be antibonding; for the uniform plane wave the bonding energy averages to zero. One can lower the energy by either amplitude or phase modulation of the plane-wave CDW. Increasing the amplitude in the in-phase portion and decreasing it in the out-of-phase portion will gain bonding energy at the expense of amplitude-modulation energy. Phase modulation to increase the width of the in-phase portion and decrease the width of the out-of-phase portion will gain bonding energy at the expense of phase-modulation energy. Since phase modulation is not energetically costly one expects phase modulation to be the dominant effect. The present author[3] solved the nonlinear equations exactly in a weak-coupling limit (phase modulation only) and found a continuous lock-in phase transition. Near the lock-in transition the CDW is strongly distorted and consists of wide locked-in regions separated by narrow incommensurate regions. The incommensurate regions appear to be defects, called discommensurations (DC), in an otherwise perfectly locked-in CDW. The lock-in transition is interpreted as a defect-melting transition with no DC's in the commensurate phase and a finite density of DC's in the incommensurate phase. Well into the incommensurate phase the DC's overlap; the discommensuration is a well-defined defect only near the lock-in transition. Within this phase-modulation model the interaction between DC's is repulsive and the lock-in transition is continuous (second order). Jackson *et al.*[4] have extended the calculation to include both amplitude and phase modulation and find a first-order phase transition when the amplitude modulation is strong enough. Physically, the coupling to amplitude fluctuations induces an attractive interaction between DC's which can dominate the original repulsive interaction and produce a first-order transition. Within the Landau theory the periodic lattice distortion is proportional to the CDW amplitude so that the nonlinearities in the CDW appear in the periodic lattice distortion. One actually measures the lattice distortion.

The collective modes of the CDW are amplitude and phase fluctuations of the wave. These modes are just phonons near the CDW wave vector and are the soft modes of the structural phase transition. The phase-fluctuation modes are commonly called phasons.[5] Within the uniform-plane-wave approximation for the CDW (and neglecting damping) the phasons have a linear dispersion in the incommensurate phase and a finite energy gap in the commensurate phase. This behavior is modified when one takes into account the nonlinear distortion of the CDW and the purpose of the present paper is to calculate the phase-fluctuation dispersion relation, taking into account the phase modulation of the CDW. The results are as follows: The phase-fluctuation spectrum splits into two branches. The lower branch can be interpreted as collective oscillations of the lattice of discommensurations; its dispersion relation is linear at long wavelengths. The energy of the system is independent of the position of the discommensuration lattice and the lower branch is the Goldstone mode corresponding to that translational symmetry. The upper branch exhibits an energy gap which is continuous at the lock-in transition and can be interpreted as the phason branch.

We first write down the Landau free-energy functional for one CDW in one layer. Since the collective modes are lattice vibrations we choose as the order parameter the amplitude of the periodic lattice distortion. The position of the ith Ta atom is then

$$\vec{R}_i = \vec{R}_i^0 + \hat{x}\,\mathrm{Re}[\Psi(\vec{r},t)], \tag{1}$$

where Ψ is the complex order parameter, and the CDW wave vector lies in $\hat{x}$ direction. The free-energy density (per unit cell area) is then

$$F = a|\Psi|^2 + c|\Psi|^4 - b\,\mathrm{Re}[e^{-iGx}\Psi^3] + e|\Psi_x - iq_1\Psi|^2 + f|\Psi_y|^2, \tag{2}$$

where G is the closest reciprocal lattice vector in the $\hat{x}$ direction and $\Psi_x \equiv \partial\Psi/\partial x$. The notation is slightly different from Ref. 3. The kinetic-energy density is

$$K = M^*|\Psi_t|^2, \tag{3}$$

where $M^* = 206$ a.u. is the effective mass assuming that the Se atoms adiabatically follow the Ta atoms. We include a Rayleigh dissipation density[6] due to electrical resistance or other mechanisms.

$$D = \gamma|\Psi_t|^2. \tag{4}$$

We could now write down a Lagrangian density $K - F$ and find the equations of motion for the order parameter. Let us first neglect amplitude variations of the order parameter and write

$$\Psi(\vec{x},t) = \Psi_0 e^{iGx/3} e^{i\theta(\vec{r},t)}, \tag{5}$$

where $\Psi_0^2 \approx -a/2c$. Then the Lagrangian density is

$$L = M^*\Psi_0^2\theta_t^2 - e\Psi_0^2(\theta_x - \Delta q)^2 - f\Psi_0^2\theta_y^2 + b\Psi_0^3\cos(3\theta), \tag{6}$$

where $\Delta q \equiv q_1 - \frac{1}{3}G$. The Lagrange equation of motion is

$$\frac{\partial}{\partial t}\frac{dL}{d\theta_t} + \frac{\partial}{\partial x}\frac{dL}{d\theta_x} + \frac{\partial}{\partial y}\frac{dL}{d\theta_y} - \frac{dL}{d\theta} = -\frac{dD}{d\theta_t}. \tag{7}$$

One often includes a random thermal force in (7) to drive the thermal fluctuations of the order parameter but that is not required here. The equation of motion for θ is

$$M^*\theta_{tt} - e\theta_{xx} - f\theta_{yy} + \tfrac{3}{2}b\Psi_0\sin(3\theta) = -\gamma\theta_t. \tag{8}$$

We assume a static solution plus a small dynamic fluctuation

$$\theta(\vec{r},t) = \theta^0(x) + \alpha(\vec{r},t). \tag{9}$$

The static solution then satisfies

$$-e\frac{d^2\theta^0}{dx^2} + 3b\Psi_0\sin(3\theta^0) = 0, \tag{10}$$

which is the sine-Gordon equation. The solution found in (3) is periodic and can be written

$$\theta^0(x) = \delta\Delta qx + \sum_{n=1}^{N} A_x \sin(3n\delta\Delta qx). \tag{11}$$

The A_n and δ were actually found by minimizing the free energy. The period of the solution is $2\pi/3\delta\Delta q$, which is the distance between discommensurations. We now linearize the equation of motion in the small fluctuation α and find

$$M^*\alpha_{tt} - e\alpha_{xx} - f\alpha_{yy} + \tfrac{1}{2}9b\Psi_0\cos(3\theta^0)\alpha = -\gamma\alpha_t. \tag{12}$$

This differential equation is separable in x, y, and t; writing

$$\alpha(x,y,t) = \eta(t)\beta(x)e^{ik_y y}, \tag{13}$$

we find

$$-e\beta_{xx} + \tfrac{1}{2}9b\Psi_0\cos(3\theta^0)\beta = E_{nk_x}^2\beta, \tag{14}$$

which is the Schrödinger equation for a particle moving in a periodic potential. We take advantage of the Bloch theorem[7] to write

$$\beta(x) = e^{ik_x x}u(x), \tag{15}$$

where $u(x)$ is periodic with period $2\pi/3\delta\Delta q$ and k_x is a quasimomentum confined to the first "Brilloin zone," $-1.5\delta\Delta q < k_x < 1.5\delta\Delta q$. The solutions of (14) are characterized by the quasimomentum k_x and the band index n. The differential equation for $\eta(t)$ is

$$M^*\eta_{tt} + \gamma\eta_t + (E_{nk_x}^2 + fk_y^2)\eta = 0, \tag{16}$$

with a solution

$$\eta(t) = \eta(0)e^{i\omega t} \tag{17}$$

and a complex frequency

$$\omega = \{i\gamma \pm [(i\gamma)^2 + 4M^*(E_{nk_x}^2 + fk_y^2)]^{1/2}\}/2M^*. \tag{18}$$

For small E_{n,k_x} and k_y the modes are overdamped with a decay time

$$\tau_{nk_xk_y} = \gamma/(E_{nk_x}^2 + fk_y^2). \tag{19}$$

For small γ and large E_{nk_x} or k_y the modes are oscillatory with real frequency

$$\omega \approx [(E_{nk_x}^2 + fk_y^2)/M^*]^{1/2}. \tag{20}$$

It remains to solve the Schrödinger equation to find E_{nk_x}. We first transform to a dimensionless variable $z = 3\delta\Delta qx$ so that $\theta^0(z)$ is periodic with period 2π. The Schrödinger equation is

$$-(\partial^2\beta/\partial z^2) + (Y/2\delta^2)\cos[3\theta^0(z)]\beta = \epsilon_{nk_x}^2\beta, \tag{21}$$

where $Y = b\Psi_0/e(\Delta q)^2$ is the dimensionless (temperature-dependent) coupling constant and

$$E_{nk_x}^2 = e(3\delta\Delta q)^2\epsilon_{nk_x}^2. \tag{22}$$

We fix ϵ_{nk_x} and integrate the differential equation on the interval $-\pi < z < \pi$ using the Runge-Kutta method to find the even solution $g(z)$ and the odd solution $h(z)$. Applying the boundary conditions implied by (15) the quasimomentum is determined from the logarithmic derivatives

$$\tan^2\left(\frac{2\pi k_x}{3\delta\Delta q}\right)=\frac{g_z/g}{h_z/h}\bigg|_{z=\pi}. \tag{23}$$

Numerical results for ϵ_{nk_x} are shown in Fig. 1 in the extended zone scheme for several values of coupling constant Y. For $0<Y<1.2337$ the system is in the incommensurate phase and at $Y_c=1.2337$ a second-order transition occurs to the commensurate state. Y normally increases with decreasing temperature due to the temperature variation of Ψ_0 and q_1. The parameter δ, which is proportional to the difference between the mean CDW wavelength and the locked-in wavelength, is unity far from the lock-in transition and goes to zero continuously at the lock-in transition. The distance between discommensurations increases as one approaches lock-in and the "Brillouin-zone" boundary at $k_x=1.5\delta\Delta q$ moves toward the origin. There are two striking features of the dispersion curves. The first is the large energy gap at the first Brillouin-zone boundary which splits the spectrum into two branches. We will see below that the lower branch can be interpreted physically as collective oscillations of the DC lattice. The second striking feature is the absence of energy gaps at the higher zone boundaries. As one approaches the lock-in transition the upper branch approaches the dispersion curve for phasons in the commensurate state in a continuous way. We therefore name the upper branch the phason branch. The absence of energy gaps at higher zone boundaries implies that the phason is not backscattered by the discommensuration; it is only forward scattered.

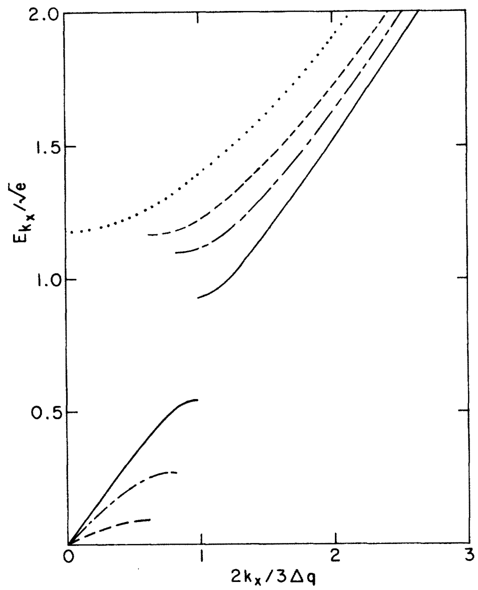

FIG. 1. Energy of the collective modes $E_{k_x}/\sqrt{e}$ vs momentum $2k_x/3\Delta q$ for (a) $Y=0.5$, $\delta=0.9667$ (solid line); (b) $Y=1.0$, $\delta=0.8246$ (broken line); (c) $Y=1.2$, $\delta=0.6224$ (short dashed line); and (d) $Y=1.2337$, $\delta=0$, commensurate phase (dotted line).

II. COLLECTIVE MODES OF THE DISCOMMENSURATION LATTICE

Near the lock-in transition the discommensurations are well separated and equally spaced. The solution of the sine-Gordon equation for an isolated discommensuration is

$$\theta(x)=\tfrac{2}{3}\cos^{-1}\{\tanh[\delta\Delta q(x-x_i)]\}, \tag{24}$$

where x_i is the position of the center of the discommensuration and $\alpha=(\tfrac{1}{2}9Y)^{1/2}$. For uniform motion, $x_i=v_it$, the kinetic energy per unit length of the discommensuration is

$$M^*\Psi_0^2\int dx\,\theta_t^2=\tfrac{8}{9}\alpha M^*\Psi_0^2\Delta q^2v_i^2. \tag{25}$$

From Ref. (3) the interaction energy of two discommensurations at x_i and x_j is

$$e\Psi_0^2\Delta q^2 16.8\exp(-\alpha\Delta q\,|x_i-x_j|). \tag{26}$$

A standard calculation of lattice vibration frequencies yields

$$\omega_{k_x}^2=\frac{e\Delta q^2}{M^*}9.45\exp\left(-\frac{2\pi\alpha}{3\delta}\right)\sin^2\left(\frac{\pi k_x}{3\delta\Delta q}\right). \tag{27}$$

This expression yields quantitative agreement with both the shape and magnitude of the lower branch of Fig. 1 for $Y=1.2$. This justifies calling the lower branch the collective mode of the discommensuration lattice when one is near the lock-in transition. For $Y=1$ the dispersion curve deviates from $\sin(\pi q/3\delta\Delta q)$ by 7% and the velocity of the mode at long wavelength is 16% less then predicted by (27), indicating that the potential is softer than the exponential (26) for short distances. This also indicates that the simple picture of well-defined discommensurations is valid only near the lock-in transition. As one moves away from the lock-in transition the discommensurations overlap and are no longer well-defined defects. The numerical calculation of the collective mode energies presented in the last section is still valid, of course.

III. THERMAL FLUCTUATION EFFECTS

It is interesting to consider the effect of thermally excited collective modes on the lock-in phase transition.[8] These effects were omitted in Ref. 3. The free-energy difference between the incommensurate and commensurate phases due to the collective modes is

$$\Delta F_c = \tfrac{1}{2} kT \sum_k \left[\ln(E_{k_x}^2 + fk_y^2) - \ln(\tfrac{1}{2} 9e\,\Delta q^2 Y + ek_x^2 + fk_y^2)\right]. \qquad (28)$$

Since the phason branch is continuous at the phase transition it is not expected to affect the transition and we restrict the sum in (28) to include only the lower branch, $-1.5\delta\Delta q < k < 1.5\delta\Delta q$. In a strictly one-dimensional system the entropy of (28) is overwhelming and the lock-in transition temperature is reduced to zero. We consider here the two-dimensional case and find

$$\Delta F_c = CN_d + N_d \Delta q \tfrac{1}{16}\pi (9.45e/f)^{1/2} e^{-\alpha\pi/36}, \qquad (29)$$

where N_d is the density of discommensurations and C is a constant. The first term is the change in free energy of the phasons due to the presence of individual DC's; it leads to a renormalization of the transition temperature. The second term is an effective interaction of DC's due to thermally excited phasons. This interaction is repulsive and of longer range than the mean field interaction term (26). Since the interaction is repulsive it does not qualitatively modify the phase transition; the only effect is to reduce somewhat the number of DC's present at a given reduced temperature. For the three-dimensional case, which is applicable to $2H$-$TaSe_2$, the phason contribution is unimportant.

IV. CONCLUSIONS

We have calculated the collective mode spectrum of a single charge-density wave near the lock-in phase transition, including the effects of phase modulation but neglecting amplitude modulation of the CDW. The spectrum consists of two branches, a branch of collective modes of the discommensuration lattice and a phason branch which is continuous at the phase transition.

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