Theory of the Splitting of Discommensurations in the Charge-Density-Wave State of $2H$-$TaSe_2$

P. B. Littlewood and T. M. Rice[a]
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 28 October 1981)

The commensurate charge-density-wave state of $2H$-$TaSe_2$ can have hexagonal (H) or orthorhombic (O) symmetry. With use of a Landau theory it is shown that near the boundary between H and O states a discommensuration splits into two H-O interfaces and thereby greatly lowers its energy. This leads to a large suppression of the incommensurate-commensurate transition temperature and a reentrant commensurate state under pressure.

PACS numbers: 64.70.Kb, 81.30.Hd

Recent experimental studies have shown that the commensurate charge-density-wave (CDW) state of $2H$-$TaSe_2$ has orthorhombic (O) rather than hexagonal (H) symmetry.[1] This symmetry occurs if the origin of the CDW, i.e., the position around which the CDW's have hexagonal point symmetry within a layer, is at a Se site (or even on the line joining Se sites) rather than at a Ta site which would give an H state.[2] The former choice is favored when there is a competition between the terms in the Landau free energy of a single layer arising from the overlap of the three CDW's and from commensurability. If the two states, H and O, have nearly equal energy, there are interesting consequences: (i) A

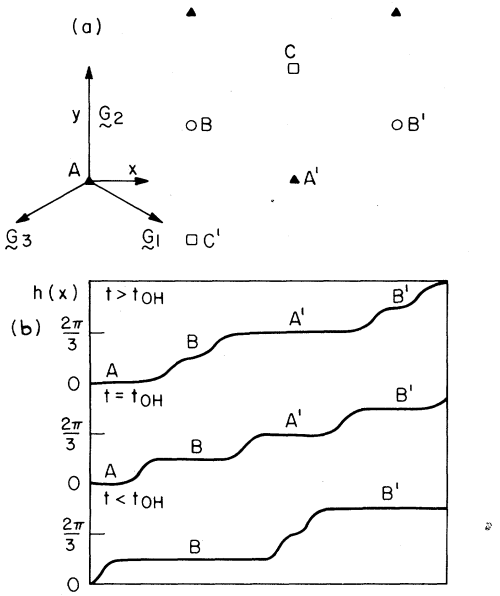
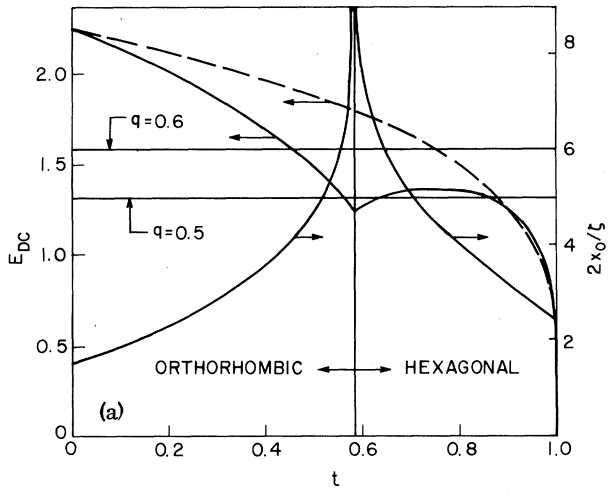


FIG. 1. (a) Geometry of a single layer of $2H$-$TaSe_2$ projected onto the $z=\frac{1}{4}$ plane. Ta atoms occupy A sites and Se atoms either B or C sites on alternate layers. (b) A plot of $h(x)$ as a function of temperature shows the splitting of a DC into two H-O interfaces close to the O-H transition.



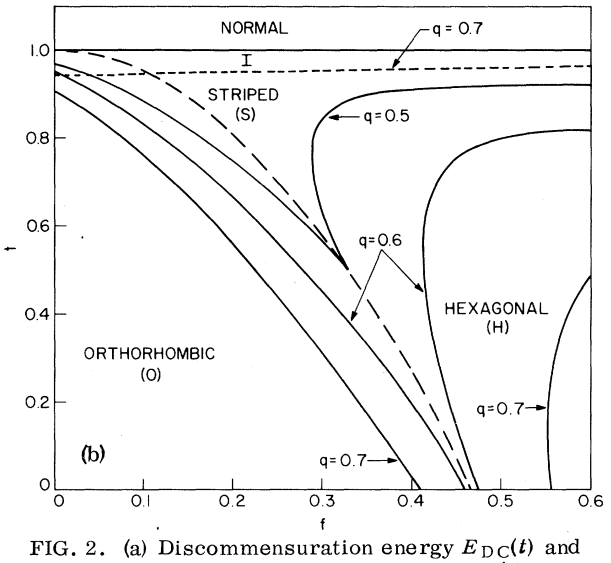


FIG. 2. (a) Discommensuration energy $E_{DC}(t)$ and spacing $2x_0/\xi$ of H-O interfaces within a DC ($f = 0.3$, $e=1.0$, $d \gg e$, $\eta=\pi$, $\beta=\pi/3+0.2$). The dashed line is a scaled $\psi^{1/2}$ dependence of a DC far from the H-O boundary. (b) Phase diagram t vs f (pressure) from the Landau free-energy expansion ($\beta=\pi/3+0.2$, $d \gg e$, $e=1.0$, $\eta=\pi$) for several values of q. The O-H boundary is marked by the dashed line and the S-I boundary by the dotted line for the value of $q=0.7$ only.

discommensuration (DC) splits into two H-O interfaces, greatly reducing its energy, (ii) this energy reduction of a DC can drive the transition to an incommensurate state, (iii) a small increase in interlayer coupling can favor H over O, and (iv) the incommensurate stripe state (S) is favored over the hexagonal incommensurate state (I) in a larger temperature interval. In this Letter we show that a choice of parameters in the Landau theory favoring O but with H nearby in energy at zero pressure gives rise to the consequences (i)–(iv), in agreement with experimental observations at zero pressure,[1,3,4] and to the reentrant pressure dependence of the commensurate state.[5,6]

The Landau free energy of the CDW state in $2H$-$TaSe_2$ was written in its general form by Jacobs and Walker.[6,7] In reduced units and with amplitude variation ignored, it is, to third order in the phase-dependent terms,

$$F=\int d^2r\{\tfrac{1}{3}q^2+\tfrac{2}{3}[(\tfrac{1}{2}\sqrt{3})h'-q]^2+\tfrac{1}{6}h'^2+2g'^2-d\psi\cos(3\theta+\gamma)$$
$$-e\psi[2\cos(3\theta-3g+\chi)\cos 3h+\cos(3\theta+6g+\chi)]+f[2\cos(2\theta-2g+\alpha)+\cos(2\theta+4g+\alpha)]\}, \quad (1)$$

where the phases of individual CDW order parameters with wave vectors $\frac{1}{3}\vec{G}_i$ (see Fig. 1) in the layers ($\pm$) are

$$\theta_1^{\pm}=\pm\theta\mp g(x)+h(x); \quad \theta_2^{\pm}=\pm(\theta+2g); \quad \theta_3^{\pm}=\pm\theta\mp g-h. \quad (2)$$

This choice is the most general which preserves inversion symmetry between layers.[2] The coefficients d, e, and f are real and positive and γ, χ, and α are the arguments of the complex interlayer, commensurability, and interlayer terms in the Jacobs-Walker free energy.[7] In simplifying the gradient terms we consider only spatial variation in the x direction (see Fig. 1) and assume equal elastic coefficients $\parallel$ and $\perp$ to a $\vec{Q}$ vector. Furthermore we neglect the spatial dependence of θ which is valid when $d \gg e$—the form of our results is generally insensitive to the value of d. The amplitude of the order parameter ψ is taken to be $(1-t)^{1/2}$ where $t=T/T_0$ is the reduced temperature.

First we consider the commensurate states with $g'=h'=0$ and, for the moment, $f=0$. Minimizing the energy gives

$$F=-\psi[d^2+9e^2+6ed\cos(\chi-\gamma+2m\pi/3)]^{1/2} \quad (3)$$

with the phases $g=m\pi/9$, $h=n\pi/3$ (m, n integer and $m+n$ even). The solutions $m=0,3,6$ are H states with origins at Ta sites (A in Fig. 1). Those with $m=2,5,8$ or $1,4,7$ are O states with origins at Se sites (B) or Se "holes" (C), respectively. Although all three solutions have hexagonal symmetry about the origin in a single layer, only in the $m=0$ case does the three-dimensional crystal have H symmetry ($P6_3/mmc$) with an inversion center of the crystal midway between Ta atoms in adjacent layers. For $m=1$ or 2 the crystal symmetry is orthorhombic with space group $Cmcm$ (Ref. 2) and in (2) we have chosen the orthorhombic axes in the layers to be $\parallel$ and $\perp$ to $\frac{1}{3}\vec{G}_2$. This space group is one of two possible space groups deduced by Fung *et al.* from electron microscopy.

To obtain the form of a DC we take the functional derivatives of (1) leading to

$$h''-\tfrac{9}{2}e\psi\cos(\beta-3g)\sin 3h=0, \quad (4)$$

$$g''-\tfrac{3}{2}e\psi[\sin(\beta+6g+\chi)-\sin(\beta-3g+\chi)\cos 3h]+2f\cos(\eta+g)\sin 3g=0, \quad (5)$$

where $\beta=3\theta+\chi$ and $\eta=2\theta+\alpha$. Again with the neglect of interlayer coupling ($f=0$), a solution to (4) and (5) is $h(x)=3g(x)$ which corresponds to displacing the origin along the line AC (Fig. 1). Integrating with the boundary condition $\lim_{x\to\infty}h(x)=0$ gives

$$h'^2=\tfrac{9}{8}e\psi[3\cos\beta-2\cos(\beta+2h)-\cos(\beta-4h)]. \quad (6)$$

This can be solved exactly when $\beta=\pi/3$, which is at the boundary where the $H(m=0)$ and $O(m=2)$ states have equal energy, to give

$$|\sin(h_I)/\sin(h_I+\pi/3)|=\exp(x/\xi) \quad (7)$$

with $\xi=\frac{2}{3}(3e\psi)^{-1/2}$. This solution describes an interface between an H state ($h=g=0$) at $x\to-\infty$ and an O state ($h=-\pi/3$, $g=-\pi/9$) as $x\to+\infty$. In this interface the origin is displaced continuously from A to B.

There is a similar solution to (4) and (5) with $h_I(x) = -2\pi/3 + 3g_I(x)$, which describes an interface between an O state at B and the H state with origin at A' ($h = -2\pi/3$, $g = 0$), of the form

$$|\sin(h_I + \pi/3)/\sin(h_I + 2\pi/3)| = \exp(x/\xi). \tag{8}$$

Combining one each of (7) and (8) produces a single DC in the H state (ABA') or the O state ($BA'B'$). Near the H-O boundary ($\beta \simeq \pi/3$) a single DC consists of two well-separated H-O interfaces and has a small energy $[1.83(e\psi)^{1/2}]$.

We now consider the effect of the interlayer coupling (f) term. This term is independent of ψ in (1) and therefore more important at high temperatures. Further, we expect that f will increase rapidly with pressure as the layers are pressed together. The lowest-energy commensurate states still have H or O symmetry.[2] The H solutions have the same form discussed above but the O states are modified to $h = \pm\pi/3$, $g = \pm g_0$ with $\lim_{f\to 0} g_0 = \pi/9$. An increase of the interlayer term f can stabilize the H state relative to the O state. For example, in the limit $d \gg 3e$ and $\beta \approx \pi/3$ the energy difference is

$$F_H - F_O \simeq 3\sqrt{3}e\psi(\beta - \pi/3) + f[3\cos\eta - \sqrt{3}\cos(\eta + \pi/18)]. \tag{9}$$

Since θ is fixed only modulo $2\pi/3$ by the d term, η can be chosen in the range $2\pi/3 < \eta < 4\pi/3$. Thus for $\beta - \pi/3$ small and positive the phase boundary between H and O states is $f \simeq 4e\psi(t_{OH})(\beta - \pi/3)/|\cos\eta|$.

To study the transition to the incommensurate state we consider the energy E_{DC} of a single DC including the f term. We have made a variational calculation using a trial function which is a superposition of two interface solutions (7) separated by $2x_0$. For a DC in the H state we take

$$h(x) = -2\pi/3 + h_I(x + x_0) + h_I(x - x_0), \quad g(x) = (3g_0/\pi)[h_I(x + x_0) - h_I(x - x_0)] \tag{10}$$

and for a DC in the O state

$$h(x) = -\pi/3 + h_I(x + x_0) + h_I(x - x_0), \quad g(x) = g_0 - (3g_0/\pi)[h_I(x + x_0) - h_I(x - x_0)]. \tag{11}$$

We determine x_0 by minimizing the energy and find that x_0 diverges as $t \to t_{OH}$—the O-H transition temperature. E_{DC} goes through a minimum at this point [see Fig. 2(a)]. Away from the O-H boundary E_{DC} varies as $\psi^{1/2}$ shown as the dashed line in Fig. 2(a).

This minimum has important consequences for the transition from the commensurate to the incommensurate state. This phase boundary is determined[8] by equating E_{DC} to the driving term linear in q in (1). This gives

$$E_{DC}(t, f) = (4\pi/3\sqrt{3})q. \tag{12}$$

The solutions of (12) are shown in Fig. 2(b) for several values of q. As the boundary from O to S is crossed the stripe state initially is a series of O-to-O discommensurations (BAB' in Fig. 1). As t increases these O-to-O DC split into O-H interfaces [see Fig. 1(b)] and at a higher t, crossing the dashed line in Fig. 2(b), recombine to give H-to-H DC (ABA'). We believe that this behavior has been observed.[1,4] Because the OS boundary in Fig. 2(b) is steep the region of O-to-O DC is narrow and considerable hysteresis can be expected.

At higher temperatures, outside the DC regime, we can estimate the energies of the incommensurate states from a perturbation expansion in the e term. The simple I state with hexagonal symmetry of the CDW has phases $\theta_i^{\pm} = \vec{q}_i \cdot \vec{r} \pm \theta$ and energy

$$F_I = -d\psi + 3f\cos(2\theta + \alpha) - 1.5e\psi_2, \tag{13}$$

where $\theta = -(\gamma + 2n\pi)/3$ and the last term results from the second harmonic which is small at high temperatures.[9] The S state has one commensurate and two incommensurate $\vec{Q}$ vectors with separate phases which allows one to minimize the energy of the d and e terms to give

$$F_S = \tfrac{1}{2}q^2 - d\psi - e(\psi + \psi_2) + f[\cos(2\varphi_1 + \alpha) + 2\cos(2\varphi_2 + \alpha)], \tag{14}$$

where $\varphi_1 + 2\varphi_2 = -(\gamma + 2n\pi)$ and $3\varphi_1 + \chi = 2m\pi$. The relative stability of the S and I states depends on a competition between elastic and commensurability energies, similar to that at the commensurate-incommensurate transition. However, it is relatively insensitive to the f term and to the choice of χ and γ unlike the boundary to the commensurate state which has a large dip near the OH phase boundary as shown in Fig. 2(b).

In conclusion, our model, based on a splitting of a DC into two H-O interfaces, leads to a large suppression of the incommensurate-commensurate transition temperature and a reentrant commensurate state under pressure. An independent study of the Landau free energy[1] by Walker and Jacobs[10] has recently given the same explanation of the orthorhombic commensurate (O) state. However, these authors neglected interlayer coupling and did not consider the commensurate-to-incommensurate transition. The phase diagram we obtain is qualitatively similar to the experimental results of McWhan *et al.*[5]

We are grateful to J. W. Steeds, J. A. Wilson, C. H. Chen, and J. M. Gibson for sending us details of their work prior to publication. We have also benefitted from discussions with R. M. Fleming, D. B. McWhan, D. E. Moncton, L. Pfeiffer, and R. E. Walstedt.

[a]Present address: Institut für Theoretische Physik, Eidgenössische Technische Hochschule Hönggerberg, CH-8093, Zurich, Switzerland.

[1]K. K. Fung, S. McKernan, J. W. Steeds, and J. A. Wilson, to be published.

[2]P. B. Littlewood and T. M. Rice, to be published.

[3]R. M. Fleming, D. E. Moncton, D. B. McWhan, and F. J. DiSalvo, Phys. Rev. Lett. 45, 576 (1980).

[4]C. H. Chen, J. M. Gibson, and R. M. Fleming, Phys. Rev. Lett. 47, 733 (1981), and to be published.

[5]D. B. McWhan, R. M. Fleming, D. E. Moncton, and F. J. DiSalvo, Phys. Rev. Lett. 45, 269 (1980).

[6]An earlier theory by one of us [T. M. Rice, Phys. Rev. B 23, 2413 (1981)] was restricted to H states and to DC which were not composed of two H-O interfaces.

[7]A. E. Jacobs and M. B. Walker, Phys. Rev. B 21, 4132 (1980).

[8]W. L. McMillan, Phys. Rev. B 14, 1496 (1976).

[9]C. H. Chen and J. M. Gibson, private communication.

[10]M. B. Walker and A. E. Jacobs, Phys. Rev. B 24, 6770 (1981).

Electronic Attenuation of Longitudinal Acoustic Phonons in Tungsten

M. J. G. Lee, J. M. Perz, and J. Plotnick
Department of Physics, University of Toronto, Toronto, Canada M5S 1A7
(Received 5 October 1981)

The conduction-electron–limited mean free path of long-wavelength longitudinal phonons in tungsten is calculated on the basis of an empirical deformation-potential description of the electron-phonon interaction. Good agreement with acoustic attenuation data of Jones and Rayne demonstrates the importance of the inclusion of renormalization effects when the deformation potential is constructed from the strain response of the Fermi surface. Lifetime broadening of the phonon spectrum is discussed.

PACS numbers: 63.20.Kr, 63.20.Dj

The mean free path of long-wavelength phonons in normal-metal single crystals of high purity at low temperature is limited by scattering by the conduction electrons. The phonon mean free path Λ can be studied experimentally either by measuring the ultrasonic attenuation coefficient $\alpha = \Lambda^{-1}$, or by measuring the lifetime broadening of the phonon dispersion curve, $2\Gamma^{ep} = \Lambda^{-1} v_s$, where v_s is the speed of sound. Ultrasonic experiments show that, for longitudinal phonons of wave vector q, the product $q\Lambda$ approaches a constant value in the limit of very long electron mean free path l, i.e., when $ql \gg 1$.

In this limit, the phonon mean free path can be readily calculated from the golden rule of time-dependent perturbation theory. The mean free path Λ of a longitudinal phonon, whose wave vector $\vec{q}$ is sufficiently small that transitions between different sheets of the Fermi surface can be neglected, is given by

$$\Lambda^{-1} = (V/2\pi^2) \oint \rho_\perp (\mathfrak{M}_{\vec{k},\vec{k}+\vec{q}}/\hbar v_{\vec{k}})^2 ds , \qquad (1)$$

where $\mathfrak{M}_{\vec{k},\vec{k}'}$ is the matrix element of the electron-phonon interaction between Bloch states of wave vectors $\vec{k}$ and $\vec{k}'$, V is the volume of the crystal, and $\vec{v}_{\vec{k}}$ is the Fermi velocity renormal-