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The dynamic Peierls instability*

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A mean-field model of a one-dimensional conductor is shown in the presence of a fixed total current to exhibit a dynamic charge-density-wave (CDW) solution which can propagate without Landau damping at a temperature higher than T_c, the transition temperature for the static instability. However, the free energy of the moving CDW state becomes less than that of the undistorted state with the same current at a temperature only below T_c. The phase transition at this lower temperature is first-order. There exists a critical current above which the free energy of the CDW state is always higher than that of the undistorted state.

I. INTRODUCTION

It has been well established that, within mean-field theory, one-dimensional conductors exhibit a second-order phase transition (the Peierls instability) characterized by a lattice distortion of wave vector $2k_F$. Fröhlich[1] investigated the properties of the coupled electron-phonon system at zero temperature and showed that, in addition to the static distortion, there exist solutions to the equations of motion which represent moving waves. In these moving charge-density waves (CDW's) the motion of each ion is oscillation about its average position, but the electrons are free to move through the lattice in such a way that the average velocity of the electrons is equal to that of the CDW. Thus the moving CDW states are current carrying. Fröhlich's model was extended to finite temperature by Kuper[2] who calculated the critical temperature $T_c(0)$ of the static CDW instability and demonstrated that the transition was second order. More recently Rice and Strässler[3] showed that in a one-dimensional conductor the giant Kohn anomaly can be the precursor of the static CDW state. The phase transition to the current-carrying CDW state has been discussed by Hopfield[4] who found that the critical temperature of the moving CDW state is higher than that of the static CDW.

The purpose of this paper is to demonstrate that the temperature T^* at which the dynamical equations of motion first allow a CDW solution is higher for a moving wave than for a static wave. $T^*(\omega)$ is the temperature at which a sinusoidal lattice distortion of wave vector $2k_F$ and frequency ω can first propagate with no Landau damping. However, the free energy of the moving CDW state first becomes less than that of the undistorted state (with the same total current) at a temperature lower than $T_c(0)$. Thus the critical temperature for the CDW state with frequency ω is actually less than that for the static wave, that is, $T_c(\omega) < T_c(0)$ for $\omega \neq 0$. At $T_c(\omega)$ the CDW comes in with finite amplitude and the transition is first order. This is contrary to the result of Hopfield[4] who found that at $T^*(\omega)$ the free energy of the moving CDW becomes less than that of the undistorted state with the same current. The reason for this difference is discussed in the Appendix.

II. STATIC PEIERLS TRANSITION

As a simple model for a one-dimensional system, consider a linear chain with n atoms per unit length. Take the unperturbed electronic states to be free-particle states. The motion of the ions can be treated classically. Let the displacement of the ions from their equilibrium positions (in the undistorted phase) be given by $u = A \sin qx$ where $q = 2k_F$. The interaction of the electrons with the lattice displacements of wave vector $2k_F$ is given by the interaction Hamiltonian

$$H_{\text{int}} \equiv 2C \frac{\partial u}{\partial x} = 2G \cos qx, \tag{1}$$

where C is a constant and $G = CAq$. The interaction of electrons with phonons of other frequencies is neglected as are electron-electron interactions.

The magnitude of the CDW energy gap can be calculated self-consistently as done by Fröhlich.[1] A value is assumed for G, and the deviation from uniform electron density caused by the periodic potential H_{int} is calculated. Owing to this nonuniform electron density there is a force on the ions through H_{int}. Dynamical self-consistency is obtained by adjusting the parameter G so that the motion of the ions satisfies Newton's second law.

In order to calculate the electron probability density, the eigenfunctions and energy spectrum of the electron Schrödinger equation must be found.

Although compact solutions to this equation cannot be written down, the following artifice provides sufficient accuracy. The perturbation (1) is dealt with in two parts, one which leads to an energy gap at $k=-k_F$ and the other which leads to the gap at $k=k_F$. Each part is treated by degenerate perturbation theory because the wave functions are significantly altered near the gaps. Away from the gaps these wave functions reduce to those found using nondegenerate perturbation theory. The simplifying feature of this method is that the effects of both parts on the electron probability density are additive.

For the discussion take the part of the periodic potential which causes the unperturbed state k to be mixed with the state $k-q$ producing the gap at $k=k_F$. Treating this mixing by degenerate perturbation theory leads to the energy eigenvalues for states above and below the gap.

$$E_\pm(k)=\tfrac{1}{2}(\epsilon_k+\epsilon_{k-q})\pm\tfrac{1}{2}[(\epsilon_k-\epsilon_{k-q})^2+4G^2]^{1/2}, \tag{2}$$

where $\epsilon_k=\hbar^2k^2/2m$. The corresponding eigenfunctions are

$$\Phi_k=\cos\theta e^{ikx}-\sin\theta e^{i(k-q)x}, \tag{3}$$

$$\Psi_k=\sin\theta e^{ikx}+\cos\theta e^{i(k-q)x}, \tag{4}$$

for states below and above the gap, respectively. The coefficients obey the relation

$$\sin 2\theta=2G/(E_+-E_-)\equiv 2G/W. \tag{5}$$

Note that in this reduced zone scheme $-k_F\leqslant k\leqslant k_F$.

The linear deviation from uniform probability density for the state Φ_k is given by

$$|\Phi_k|^2-1=-(2G/W)\cos qx. \tag{6}$$

The corresponding deviation for Ψ_k is opposite in sign.

The total change in electron density $\Delta N\cos qx$ is found by summing over all states k weighted by the appropriate Fermi–Dirac occupation probability. Owing to this nonuniform electron distribution there is a force on the ions through H_{int} given by

$$F_{\text{ion-el}}=-(2G/An)\Delta N\sin qx. \tag{7}$$

Dynamical self-consistency is obtained by requiring that the ionic motion obeys Newton's second law. For ions with mass M and unperturbed $2k_F$ phonon frequency ω_0, this requirement becomes

$$M\ddot{u}=-M\omega_0^2u+F_{\text{ion-el}}. \tag{8}$$

For a static wave this reduces to

$$M\omega_0^2+(2G/A^2n)\Delta N=0. \tag{9}$$

The attractive force of the electrons on the ions exactly balances the ion-ion repulsion so that the displacements of the ions are maintained.

At zero temperature the amplitude ΔN of the nonuniform part of the electron probability density can be evaluated analytically. Only states below the gap are filled. The sum over k can be replaced by an integral,

$$\Delta N=-8G\int_{-k_F}^{k_F}\frac{1}{W}\frac{dk}{2\pi}, \tag{10}$$

where a factor of 4 has been included to account for spin degeneracy and for the contribution of both parts of the perturbation. The integral can be evaluated and with Eq. (9) gives G_0, the zero-temperature energy gap for the static CDW:

$$G_0=4\epsilon_F[\sinh(\hbar^2M\omega_0^2/8C^2m)]^{-1}, \tag{11}$$

where $\epsilon_F=\hbar^2k_F^2/2m$. This is equivalent to the result of Fröhlich.[1]

For finite temperatures the states above the gap will be occupied and ΔN will decrease with increasing temperature. The expressions (9) and (10) can be evaluated to find the critical temperature at which the force on the ions caused by the electrons cannot balance the ion-ion repulsion even for arbitrarily small values of G. To calculate ΔN it is sufficient to use the unperturbed electron energies in the Fermi–Dirac occupation probability. In the reduced zone scheme this becomes

$$\Delta N=-8G\int_{-k_F}^{k_F}\frac{1}{W}(f_-^0-f_+^0)\frac{dk}{2\pi}, \tag{12}$$

where

$$f_-^0=\{\exp[(\epsilon_k-\epsilon_F)/k_BT]+1\}^{-1}$$

and

$$f_+^0=\{\exp[(\epsilon_{k-q}-\epsilon_F)/k_BT]+1\}^{-1}.$$

This expression can be evaluated numerically with Eq. (9) and gives the critical temperature for the static CDW,

$$k_BT_c(0)\cong 4.56\epsilon_F\exp(-\hbar^2M\omega_0^2/8C^2m), \tag{13}$$

which is conveniently written

$$k_BT_c\cong 0.57G_0 \tag{14}$$

as found by Kuper.[2]

III. DYNAMIC PEIERLS TRANSITION

For the case of the moving CDW, take the ion displacements to be $u=A\sin(qx-\omega t)$ for a wave moving in the positive x direction. Consider the case where the electrons are constrained to have a net drift velocity the same as the velocity ω/q of the CDW. The effect of the perturbation on the electron density can be found in a way similar to that above except that now it is the time-dependent Schrödinger equation which must be solved. For the mixing of k and $k-q$, solutions of the form

$$e^{-i\lambda t/\hbar}(Ae^{ikx}+Be^{i\omega t}e^{i(k-q)x})$$

can be found. This results in a secular equation,

$$\det\begin{pmatrix}\epsilon_k-\lambda & G\\ G & \epsilon_{k-q}+\hbar\omega-\lambda\end{pmatrix}=0,$$

within the space defined by the basis functions k and $k-q$. The eigenvalues $\lambda_\pm$ for states above and below the gap are

$$\lambda_\pm=\tfrac{1}{2}(\epsilon_k+\epsilon_{k-q}+\hbar\omega)\pm\tfrac{1}{2}[(\epsilon_{k-q}-\epsilon_k+\hbar\omega)^2+4G^2]^{1/2}. \tag{15}$$

The stationary states corresponding to these eigenvalues are

$$\Phi_k=\cos\theta e^{ikx}-\sin\theta e^{i(k-q)x}e^{i\omega t}, \tag{16}$$

$$\Psi_k=\sin\theta e^{ikx}+\cos\theta e^{i(k-q)x}e^{i\omega t}, \tag{17}$$

for states below and above the gap, respectively. The coefficients satisfy the relation

$$\sin 2\theta=2G/(\lambda_+-\lambda_-)\equiv 2G/W. \tag{18}$$

The energies corresponding to Φ_k and Ψ_k are

$$E_-(k)=\lambda_--\hbar\omega\sin^2\theta, \tag{19}$$

$$E_+(k)=\lambda_+-\hbar\omega\cos^2\theta. \tag{20}$$

Note that the position of the gap is now $k_F+m\omega/\hbar q$.

The linear deviation from uniform electron density for Φ_k is given by

$$|\Phi_k|^2-1=-(2G/W)\cos(qx-\omega t). \tag{21}$$

For the moving wave $\ddot{u}=-\omega^2A\sin(qx-\omega t)$ so that applying Newton's second law to the motion of the ions yields

$$M(\omega_0^2-\omega^2)+(2G/A^2n)\Delta N=0. \tag{22}$$

To calculate the critical temperature $T^*(\omega)$ for dynamical self-consistency, i.e., propagation of a CDW with frequency ω with no Landau damping, it is necessary to calculate ΔN. It is sufficient to use the unperturbed electron energies in the Fermi-Dirac distribution function. However, the distribution must be shifted in k space so that the constraint on the net drift velocity is satisfied. When the resulting expression for ΔN is written as an integral, a change in the integration variable, $k\rightarrow k-m\omega/\hbar q$, is sufficient to show that ΔN for the moving wave is the same as that for the static wave for the same value of G. Then Eq. (22) gives $T^*(\omega)$,

$$k_BT^*(\omega)=4.56\epsilon_F\exp[-\hbar^2M(\omega_0^2-\omega^2)/8C^2m], \tag{23}$$

which is higher than $T_c(0)$ by a factor $\exp(\hbar^2M\omega^2/8C^2m)$ as found by Hopfield.[4] This result can be easily understood. The electron-ion force does not need to be as strong if the ions are allowed to oscillate as it must be if the ions are fixed. Thus, dynamical self-consistency can be satisfied for smaller ΔN and higher temperature in the case of the moving wave.

IV. FREE ENERGY

It was shown above that the temperature T^* at which dynamical self-consistency can be satisfied is higher for a moving CDW than for a static one. It is interesting to compare the free energy of the CDW state with that of the undistorted state with the same current. The free energy of the electron-ion system can be calculated in two parts, that of the perturbed electron system and that of the ions caused by their kinetic energy and the unperturbed ion-ion interaction. Since the ionic motion is treated classically, the contribution of the lattice to the free energy is especially simple because there is no entropy associated with the lattice. The free energy of the perturbed electron system is given by $F=E-TS$ where

$$E=\sum_i E_if_i$$

and

$$S=-k_B\sum_i[f_i\ln f_i+(1-f_i)\ln(1-f_i)].$$

Here E_i is the energy and f_i is the occupation probability of state i. The problem is to find f_i. For the static CDW, of course, this is just the usual Fermi-Dirac distribution function. In the case of the moving CDW, however, there exists the additional constraint on the net electron drift velocity. If the energy of state k is given by $\hbar^2k^2/2m$, this constraint is easily incorporated by letting $k\rightarrow k-m\omega/\hbar q$ so that the distribution is centered about $m\omega/\hbar q$. When the energies of the electronic states are given by a more complicated function of k, for example Eqs. (19) and (20), how to incorporate this shift of the distribution is less obvious.

A shift of the electron distribution can be accomplished by a change in the observer's reference frame. For the case of the moving CDW, it is most convenient to change to a frame in which the drift velocity is zero, i.e., the frame moving with the velocity of the CDW. The unperturbed electron energies are easily transformed to the new frame so the problem becomes to find the way in which the perturbed energies transform. This problem has been solved by Parmenter.[5]

The Schrödinger equation for the perturbed electron system in the laboratory frame is

$$i\hbar\,\frac{\partial\Psi}{\partial t}=\left(-\frac{\hbar^2}{2m}\,\frac{\partial^2}{\partial x^2}+2G\cos(qx-\omega t)\right)\Psi. \tag{24}$$

Transforming coordinates to $x'=x-vt$, $t'=t$ and performing a canonical transformation

$$\Psi'(x',t')=\exp[-im(vx-\tfrac{1}{2}v^2t)/\hbar]\,\Psi(x,t) \tag{25}$$

results in the transformed Schrödinger equation:

$$i\hbar\,\frac{\partial\Psi'}{\partial t'}=\left(-\frac{\hbar^2}{2m}\,\frac{\partial^2}{\partial x'^2}+2G\cos qx'\right)\Psi'. \tag{26}$$

The right-hand side is $p'^2/2m+V'$ which is the sum of the kinetic and potential energy in the primed frame. To relate the energy in the two frames calculate

$$\begin{aligned}E'(k')&=\frac{\langle\Psi'|\,i\hbar\partial/\partial t\,|\Psi'\rangle}{\langle\Psi'|\Psi'\rangle}\\&=\frac{\langle\Psi|\,i\hbar\partial/\partial t\,|\Psi\rangle-\langle\Psi|-i\hbar v\partial/\partial x|\Psi\rangle}{\langle\Psi|\Psi\rangle}+\tfrac{1}{2}mv^2\\&=E(k)-vp_k+\tfrac{1}{2}mv^2,\end{aligned} \tag{27}$$

where p_k is the momentum of state k. In addition, as shown by Parmenter,[5]

$$k'=k-mv/\hbar \tag{28}$$

so that k' and k satisfy the proper transformation for momentum.

In the primed frame the electron distribution is centered about $k'=0$ so that difference in electron energy between the CDW state and the undistorted state in the primed frame is given by

$$\begin{aligned}E'_{\text{CDW}}-E'_0=&\frac{2}{2\pi}\int_{-\infty}^{\infty}dk'\,\frac{E'(k')}{\exp\{[E'(k')-\mu_G]/k_BT\}+1}\\&-\frac{2}{2\pi}\int_{-\infty}^{\infty}dk'\,\frac{\epsilon'_{k'}}{\exp[(\epsilon'_{k'}-\epsilon_F)/k_BT]+1}\,,\end{aligned} \tag{29}$$

where $\epsilon'_{k'}=\hbar^2k'^2/2m$ and $E'(k')$ is the energy eigenvalue of Eq. (26). Note that μ_G indicates that the Fermi energy must be a function of the size of the energy gap to keep the number of electrons constant. Using Eqs. (27) and (28) gives the energy difference in terms of unprimed variables,

$$\begin{aligned}E'_{\text{CDW}}-E'_0=&\frac{2}{2\pi}\int_{-\infty}^{\infty}dk\,\frac{E(k)-vp_k+\frac{1}{2}mv^2}{\exp\{[E(k)-vp_k+\frac{1}{2}mv^2-\mu_G]/k_BT\}+1}\\&-\frac{2}{2\pi}\int_{-\infty}^{\infty}dk\,\frac{\epsilon_k-\hbar kv+\frac{1}{2}mv^2}{\exp[(\epsilon_k-\hbar kv+\frac{1}{2}mv^2-\epsilon_F)/k_BT]+1}\,.\end{aligned} \tag{30}$$

The argument of the exponential in the second term is the usual result obtained for a system of free fermions with drift velocity v, i.e., the Fermi distribution is shifted to center at $mv/\hbar$ in k space. The first integrand shows how the constraint of a net drift velocity is included for the case when $E(k)$ is a more complicated function of k. The expression (3) can be written

$$\begin{aligned}E'_{\text{CDW}}-E'_0=&n[\langle E(k)\rangle-v\langle p_k\rangle+\tfrac{1}{2}mv^2]\\&-n(\langle\epsilon_k\rangle-v\langle\hbar k\rangle+\tfrac{1}{2}mv^2),\end{aligned} \tag{31}$$

where $\langle\ \rangle$ denotes the average value. Since both the CDW state and the undistorted state have the same total momentum and number of particles, this becomes

$$E'_{\text{CDW}}-E'_0=E_{\text{CDW}}-E_0, \tag{32}$$

so that the difference in electronic energy between the CDW state and the undistorted state with the same current is the same in both reference frames.

Similarly, the difference in entropy can be shown to be the same in both reference frames. Thus, the free energy can be calculated in either frame with the same result. It then suffices to calculate the difference for the static case.

The effect of the change of reference frame on the ion motion is to give a uniform drift to the average positions of the ions. This does not change the oscillatory motion of the ions about their equilibrium positions and thus, cannot change the difference in kinetic energy and ion-ion potential energy between the CDW state and the undistorted state with the same current. Therefore, the total change in free energy of the electron-phonon system is the same in both reference frames.

The expression (2) for the energy of the electronic state k gives the effect of one part of the perturbing potential. It is necessary to include the effect caused by the other part. This is adequately given by the first-order correction to the plane-wave energy so that

$$E^T_\pm=E_\pm+G^2(\epsilon_k-\epsilon_{k-q})^{-1}. \tag{33}$$

Using Eq. (33) the difference in electron free energy between the CDW state and the undistorted state can be calculated. This difference is given (in reduced zone notation) by

$$E_{\mathrm{CDW}} - E_0 = 4\int_0^{k_F} (E_-^T f_-^T + E_+^T f_+^T)\frac{dk}{2\pi} - 4\int_0^{k_F} (\epsilon_k f_-^0 + \epsilon_{k-q} f_+^0)\frac{dk}{2\pi}, \qquad (34)$$

where $f_\pm^T$ and $f_\pm^0$ denote the Fermi occupation factors for the upper and lower bands using Eq. (33) and the unperturbed energies, respectively. One factor of 2 is included to account for spin degeneracy and another since the contribution from the interval $-k_F \leq k \leq 0$ is equal to that from $0 \leq k \leq k_F$.

The electronic contribution to the difference in entropy is given by

$$S_{\mathrm{CDW}} - S_0 = -4k_B \int_0^{k_F} \frac{dk}{2\pi}[f_-^T \ln f_-^T + (1-f_-^T)\ln(1-f_-^T) + f_+^T \ln f_+^T + (1-f_+^T)\ln(1-f_+^T) - f_-^0 \ln f_-^0 - (1-f_-^0)\ln(1-f_-^0) - f_+^0 \ln f_+^0 - (1-f_+^0)\ln(1-f_+^0)]. \qquad (35)$$

The lattice contribution to the change in free energy is the number of ions times the average kinetic energy plus the average value of the ion-ion potential energy

$$\Delta F_{\mathrm{lat}} = \tfrac{1}{2} nM\omega_0^2\langle u^2\rangle + \tfrac{1}{2} nM\langle \dot{u}^2\rangle = \tfrac{1}{4} nMA^2(\omega_0^2 + \omega^2). \qquad (36)$$

Since a determination of G gives the amplitude of the ion displacements, Eq. (36) is readily evaluated once G is found.

At zero temperature the difference in entropy ΔS is zero. Equation (34) can be evaluated analytically to obtain the electronic contribution to the change in free energy

$$\Delta F_e(T=0) = n\epsilon_F\{1 - (1+g^2)^{1/2} - g^2 \ln[1 + (1+g^2)^{1/2}] - g^2 \ln(2/g)\}, \qquad (37)$$

where $g \equiv G_0/2\epsilon_F$. The total change in free energy for a static CDW at zero temperature is

$$\Delta F_0 = \Delta F_e(T=0) + n\epsilon_F g^2 \sinh^{-1}(2/g), \qquad (38)$$

where Eq. (11) was used for G_0.

Equations (12) and (22) can be solved numerically using the energies (33) in the Fermi occupation factor to give the dynamically self-consistent energy gap $G(T, \omega)$ as a function of temperature T and frequency ω of the CDW. Using this value for $G(T, \omega)$, Eqs. (34)–(36) can be evaluated numerically to give the difference in free energy between the CDW state and the undistorted state with the same current.

Typical results for ΔF, the difference in free energy between the CDW state and the undistorted state, are shown in Fig. 1 as a function of temperature, for several values of the ratio of the CDW frequency ω to the unperturbed $2k_F$ phonon frequency ω_0. These curves use a value $G_0/2\epsilon_F = 0.01$. The curve for $\omega/\omega_0 = 0$ is characteristic of a second-order phase transition. The curves for $\omega/\omega_0 \neq 0$ demonstrate that the free energy of the moving CDW state is higher than that of the undistorted state until the temperature reaches $T_c(\omega)$ which is lower than $T_c(0)$. At $T_c(\omega)$ the moving CDW has a finite amplitude and the transition is first order. At $T^*(\omega)$, the temperature at which the CDW with frequency ω becomes dynamically self-consistent, the curve of ΔF intersects the abscissa at finite slope.

A plot of T_c vs ω/ω_0 is shown in Fig. 2. Note that there is a cutoff value $\omega_c \cong 0.205\omega_0$ beyond which the free energy of the CDW state can never be less than that of the normal state with the same current. Near ω_c the critical temperature T_c goes as $(1 - \omega/\omega_c)^{1/2}$.

With $T_c(\omega)$ and the size of the energy gap G known, Eq. (34) can be evaluated numerically to find the latent heat of transition L. A plot of

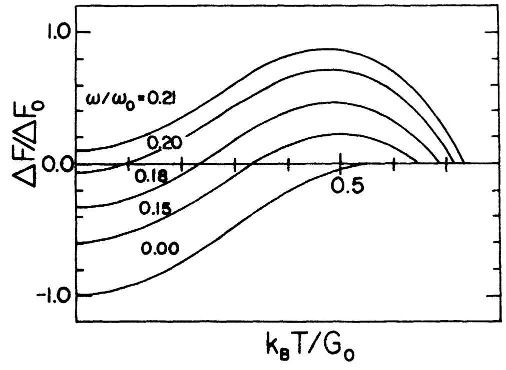

FIG. 1. Free-energy difference between CDW state and undistorted state with same current vs temperature for various CDW frequencies ω. ΔF_0 is the difference for $\omega = 0$, $T = 0°$K. G_0 is the magnitude of the static CDW energy gap at $T = 0$°K. ω_0 is the unperturbed $2k_F$ phonon frequency.

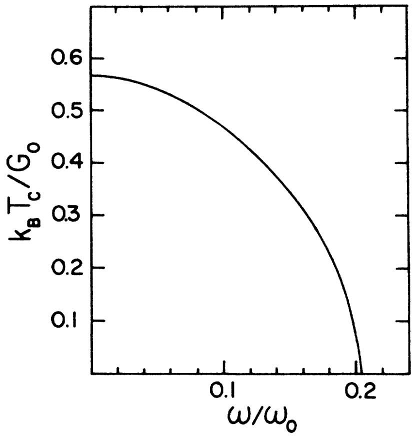

FIG. 2. Critical temperature vs CDW frequency.

the magnitude of L vs. ω/ω_0 is shown in Fig. 3. L goes to zero at ω_c since the entropy of both the CDW and the undistorted states goes to zero at $T = 0$ °K.

V. CONCLUSION

It was shown that in a simple mean-field model of a one-dimensional conductor the temperature at which a moving CDW can propagate without Landau damping is higher than $T_c(0)$, the Peierls transition temperature for the static wave. However, the free energy of the moving CDW state does not become less than that of the undistorted state with the same current until a temperature below $T_c(0)$. At this temperature the phase transition is first order. There exists a cutoff value for the CDW frequency (and the current) at which the CDW free energy is never less than that of the undistorted state with the same current.

APPENDIX

Expression (23) for the increase of T^* (the temperature at which the CDW solution is dynamically self-consistent) with the velocity of the CDW agrees with that calculated by Hopfield[4] (except for a numerical factor which results from the use of different expressions for the unperturbed electron energy). However, this result was derived by Hopfield by comparing the free energy of the CDW state to that of the normal state. He found that at T^* the moving CDW has a lower free energy than does the undistorted state with the same current. This result contradicts the findings in Sec. IV.

Hopfield treats the problem of the moving CDW from the reference frame in which the net electron drift velocity is zero. The Hamiltonian for the electron-phonon system is given in this reference frame by

$$H = \sum_k \epsilon_k c_k^\dagger c_k + \hbar\omega_0 (a_q^\dagger a_q + a_{-q}^\dagger a_{-q}) + g \sum_k [(a_q^\dagger + a_{-q}) c_{k-q}^\dagger c_k e^{i\omega_d t} + \text{H.c.}], \tag{A1}$$

where $c_k^\dagger$, c_k, $a_q^\dagger$, and a_q are the electron and phonon creation and annihilation operators, g is a coupling constant, and ω_d/q is the net electron drift velocity in the lab frame. The Hamiltonian (A1) can be obtained from that in the lab frame by the transformation discussed in Sec. IV and is the total energy of the electron-phonon system.

To remove the explicit time dependence Hopfield makes a canonical transformation in which

$$\Psi' = e^{-iAt}\Psi, \quad A = (-a_q^\dagger a_q + a_{-q}^\dagger a_{-q})\omega_d . \tag{A2}$$

Ψ' is found to satisfy a Schrödinger equation

$$i\hbar \frac{\partial \Psi'}{\partial t} = H_{\text{eff}} \Psi' , \tag{A3}$$

where

$$H_{\text{eff}} = e^{-iAt} H e^{iAt} + \hbar A, \quad a'_{-q} = e^{-iAt} a_{-q} e^{iAt} = a_{-q} e^{i\omega_d t} . \tag{A4}$$

The effective Hamiltonian (in terms of the primed variables) is given by

$$H_{\text{eff}} = \sum_k \epsilon_k c_k^\dagger c_k + \hbar(\omega_0 + \omega_d) a'^\dagger_{-q} a'_{-q} + \hbar(\omega_0 - \omega_d) a'^\dagger_q a'_q + g \sum_k [(a'^\dagger_q + a'_{-q}) c_{k-q}^\dagger c_k + \text{H.c.}] . \tag{A5}$$

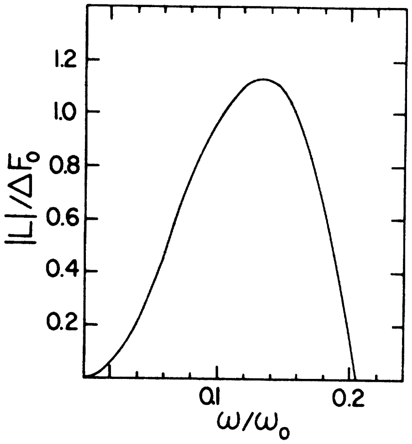

FIG. 3. Magnitude of latent heat of transition vs CDW frequency.

This effective Hamiltonian is then used to calculate the free energy of the CDW state.

However, because of the explicit time dependence of the canonical transformation, H_{eff} does not represent the total energy of the system. H_{eff} is a conserved quantity and generates the dynamical evolution of the system in terms of the primed variables, but the "extra" part $\hbar A$ makes H_{eff} unequal to the sum of the kinetic and potential energies of the system. That this is true is seen by starting with H, which is the sum of the kinetic and potential energy. The energy is given by

$$\begin{aligned} E = \langle \Psi | H | \Psi \rangle &= \langle e^{iAt} \Psi' | H | e^{iAt} \Psi' \rangle \\ &= \langle \Psi' | e^{-iAt} H e^{iAt} | \Psi' \rangle \\ &= \langle \Psi' | H_{\text{eff}} | \Psi' \rangle - \langle \Psi' | \hbar A | \Psi' \rangle . \end{aligned} \tag{A6}$$

Thus the expectation value of H_{eff} differs from the energy by $\langle \Psi' | \hbar A | \Psi' \rangle$. It is precisely this difference which leads to Hopfield's result.

Hopfield interpreted the terms

$$\hbar(\omega_0 + \omega_d) a^\dagger_{-q} a_{-q} \quad \text{and} \quad \hbar(\omega_0 - \omega_d) a^\dagger_q a_q$$

as the unperturbed phonon energies in which the frequency is replaced by the Doppler-shifted frequencies $\omega_0 \pm \omega_d$. Thus the $2k_F$ mode is softened. However, since the unperturbed phonon mode involves the displacements of the ions from their equilibrium positions and the time rate of change of these displacements, a uniform translation of the equilibrium positions will not change the frequency or energy of the mode aside from the additional kinetic energy per ion $\frac{1}{2}Mv_d^2$ associated with the translation velocity v_d of the equilibrium positions. The envelope of the wave is Doppler shifted, but the ionic oscillation frequency is the same in both reference frames. An illustration of this point is the application of the canonical tranformation (A2) to the unperturbed phonon Hamiltonian in an insulator,

$$H = \hbar\omega_0 (a^\dagger_q a_q + a^\dagger_{-q} a_{-q}),$$

with the choice $\omega_d = \omega_0$. This leads to the effective Hamiltonian

$$H_{\text{eff}} = \hbar(\omega_0 + \omega_0) a^\dagger_{-q} a_{-q} + \hbar(\omega_0 - \omega_0) a^\dagger_q a_q ,$$

so that the energy of the mode q is identically equal to zero. This result is clearly impossible.

Thus, a softening of the unperturbed $2k_F$ mode does not occur. The "softening" which does occur for a moving CDW is in the electron-ion force which can satisfy the requirements of dynamical self-consistency with a smaller value in the case of the moving CDW.

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[1] H. Fröhlich, Proc. R. Soc. A 223, 296 (1954).

[2] C. G. Kuper, Proc. R. Soc. A 227, 214 (1955).

[3] M. J. Rice and S. Strässler, Solid State Commun. 13, 125 (1973).

[4] J. J. Hopfield, Solid State Commun. 14, 727 (1974).

[5] R. H. Parmenter, Phys. Rev. 89, 990 (1953).