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Phase-locked charge-density waves in $NbSe_3$

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Using a simple Ginzburg-Landau theory which incorporates the crystal symmetry of $NbSe_3$, we show that the approximate relation, $2(\vec{k}_1+\vec{k}_2)\simeq(1,1,1)$, between the two charge-density-wave (CDW) wave vectors leads to a fourth-order phase locking of the CDW's. Some experimental consequences of this effect are discussed.

I. INTRODUCTION

Recently there has been considerable interest[1-8] in the properties of the transition-metal trichalcogenides, of which $NbSe_3$ is the most well-studied example. This linear chain metal undergoes two seemingly independent charge-density-wave (CDW) transitions[5-7] at[4] $T_1 = 142$ K and $T_2 = 58$ K, respectively. Below each of these temperatures, the resistivity shows rather large increases, indicating that substantial fractions of the charge carriers condense into the CDW states which accompany the destruction[4] of portions of the Fermi surface.

In addition to the peculiar non-Ohmic behavior[8] associated with the resistivity anomalies (we return to this point later) another puzzling feature of $NbSe_3$ is that the emergence of the second CDW at 58 K seems to have very little effect on the first CDW. This is evidenced by the fact that no observable change occurs at T_2 (or below) in either the position or intensity of the diffraction spots[7] associated with the first CDW. The independence of the two CDW's is further supported by the fact that the Ohmic resistivity anomalies can be fitted in a model[4] which employs *independent* CDW gap functions. Thus $NbSe_3$ may appear to be the first linear chain material in which *two* CDW's coexist independently.

However, another experimental fact seems to challenge this independence. Namely, the wave vectors characterizing the two CDW's given by[7] $\vec{k}_1 = (0, 0.243 \pm 0.005, 0)$ and $\vec{k}_2 = (0.5, 0.263 \pm 0.005, 0.5)$ [in units of the reciprocal unit-cell[9] lengths (a^*, b^*, c^*)] satisfy the approximate relation

$$2(\vec{k}_1+\vec{k}_2) \simeq (1,1,1), \tag{1.1}$$

i.e., twice their sum is approximately a reciprocal-lattice vector. *Can this relation be merely a coincidence*, or *is there in fact a connection between the two* CDW's?

Several authors[10-12] have independently noted that relation (1.1) suggests the existence of a phase coupling between the two CDW's below T_2. Simple arguments based on a Ginzburg-Landau (GL) theory[11,12] incorporate the additional invariant which appears in the free-energy expansion as a result of this wave-vector relation and this term leads to a locking of the phases[10-12] of the two CDW's below T_2.

In this paper, we give the details of our previous analysis[11] which showed that because the phase-coupling term is of fourth order in the CDW amplitudes, the phase locking of the CDW's has only a minor influence on the values of these amplitudes, in the form of a small mutual enhancement barely (if at all) observable at low temperatures. The smallness of the phase-coupling energy allows us to reconcile Eq. (1.1) with the *apparent* independence of the CDW's suggested by the diffraction and *Ohmic* transport measurements mentioned above. In addition, we consider the implications of the phase-locking effect for other properties of $NbSe_3$ with emphasis on experimental consequences.

In the absence of a detailed microscopic theory of the CDW transitions in $NbSe_3$, the discussion below is of necessity qualitative in nature. We therefore rely on general arguments and make use of experimental information at key points in the discussion. In Sec. II, we consider the nature of the CDW between T_1 and T_2 when the second CDW is absent. This will help clarify the relative magnitude of various competing energies involved in the CDW formation and the interaction with the lattice. The crystal symmetry of $NbSe_3$ is explicitly incorporated in the construction of a GL free-energy functional. Minimization of the free energy leads to discommensurations[13,14] in the CDW phase. However, the absence of a lattice lock-in transition to a commensurate CDW suggests that these discommensurations are very weak. In Sec. III we construct a GL expansion which contains a term due to the particular relation (1.1) between the CDW wave vectors. This term represents the coupling between the phases of the CDW's. The immediate consequences of the phase coupling are discussed, such as a small mutal gap enhancement. In Sec. IV we turn our attention to less obvious consequences of the phase-locking effect

which may have implications for experiments other than diffraction and dc Ohmic transport. In Sec. V we summarize our results and conclusions.

II. GINZBURG-LANDAU THEORY OF THE FIRST CDW

In this section we construct a Ginzburg-Landau (GL) expansion for the free energy of $NbSe_3$ near the first CDW transition at $T_1 = 142$ K and analyze its consequences for the nature of the CDW phase. In our use of GL theory near T_1 (and also below T_2) we neglect critical fluctuations; they appear[4] to contribute to the resistivity only very near to T_1 and T_2 and the diffraction experiments do not exhibit diffuse sheets [as in[15] tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ)]. This neglect is consistent with the reasonable fit[4] of the mean-field theory to the Ohmic resistivity data, and suggests further that interchain coupling in $NbSe_3$ is substantial.[16] In addition, we note that there is no drastic difference between the six chains within the unit cell.[17] All six chains are thus regarded as equivalent except for their relative positions in the cell. The amplitudes of the CDW's are therefore taken to be the same on each chain, although the relative phases *are* allowed to adjust to minimize the Coulomb interaction energy between neighboring chains.

We define as our order parameter the modulation, $\delta\rho(\vec{r})$, of the carrier charge density. The free energy is required to be invariant under the symmetry operations in the space group, $P_2 1m$, of the crystal. The order parameter must transform under the group operations according to a linear combination of basis functions of one of the irreducible representations of the space group. The free energy is then constructed from invariant functions of $\delta\rho$ up through fourth order.

The nonsymmorphic space group contains, in addition to crystal translations, $\vec{l}$, the identity E, the inversion I, a glide-plane reflection $\sigma^* = \{\sigma|\frac{1}{2}\vec{b}\}$ (in the ac plane), and a screw-axis rotation $C_2^* = \{C_2|\frac{1}{2}\vec{b}\}$ about the chain axis ($\vec{b}$). We use oblique coordinate axes coincident with the primitive translation vectors,[5] $\vec{a}, \vec{b}, \vec{c}$, and denote the reciprocal-lattice vectors by $\vec{a}^*, \vec{b}^*, \vec{c}^*$. The wave vector $\vec{k}_1$ of the first CDW is along the chain axis with length $k_1 \cong 0.24b^*$.

The basis functions of the relevant irreducible representations[18] have the form of Bloch functions,

$$\psi(\vec{r}) = e^{\pm i\vec{k}_1\cdot\vec{r}}u(\vec{r}), \tag{2.1}$$

where $u(\vec{r}+\vec{l}) = u(\vec{r})$. The little group of $\vec{k}_1$ is $\{E, C_2^*\}$ (the star of $\vec{k}_1$ is $\{\vec{k}_1, -\vec{k}_1\}$) which has two one-dimensional irreducible ray representations, Γ^+ and Γ^-:

$$\Gamma^+(E) = 1, \quad \Gamma^+(C_2^*) = e^{-i\pi k_1}, \tag{2.2a}$$

$$\Gamma^-(E) = 1, \quad \Gamma^-(C_2^*) = -e^{-i\pi k_1}. \tag{2.2b}$$

The corresponding basis functions of Bloch form are given by

$$\phi_1^+ = e^{i\vec{k}_1\cdot\vec{r}}[u^+(\vec{r}) + u^+(C_2^{*-1}\vec{r})] \tag{2.3a}$$

and

$$\phi_1^- = e^{i\vec{k}_1\cdot\vec{r}}[u^-(\vec{r}) - u^-(C_2^{*-1}\vec{r})]. \tag{2.3b}$$

The partner functions to $\phi_1^\pm$ necessary for two-dimensional (the star of $\vec{k}_1$ has two points) irreducible representations of the space group are constructed by operating on ϕ_1^+ and ϕ_1^- with the inversion I:

$$\phi_2^\pm = e^{-i\vec{k}_1\cdot\vec{r}}[u^\pm(-\vec{r}) \pm u^\pm(-C_2^{*-1}\vec{r})]. \tag{2.4}$$

There are consequently only two possible forms for the order parameter $\delta\rho(\vec{r})$:

$$\delta\rho^\pm(\vec{r}) = c_1^\pm\phi_1^\pm + c_2^\pm\phi_2^\pm, \tag{2.5}$$

where $c_{1,2}^\pm$ are constants. We have exhausted the symmetry properties in arriving at Eq. (2.5); from the group-theoretic point of view, $\delta\rho^+$ and $\delta\rho^-$ are equally valid forms for the order parameter. We choose between $\delta\rho^+$ and $\delta\rho^-$ by selecting the form which appears to minimize the interchain Coulomb energy, namely, $\delta\rho^-$ with u^- chosen as the simplest possible periodic function:

$$u^-(\vec{r}) = \cos(2\pi z/c)\sin(2\pi x/a). \tag{2.6}$$

The relative phase ordering between chains is shown schematically in Fig. 1(a). The assumed form for the charge modulation associated with the first CDW is thus

$$\delta\rho_1(\vec{r}) = \Delta_1 \sin\frac{2\pi x}{a}\cos\frac{2\pi z}{c}\sin[\vec{k}_1\cdot\vec{r} + \theta_1(y)], \tag{2.7}$$

where the subscript 1 denotes the quantities appropriate to the first CDW. The amplitude Δ_1 is taken to be independent of position[19] and the phase $\theta_1(y)$ depends only on position (y) along the chain direction.

The free energy per unit length is then written in GL form as[13]

$$F_1 = A_1\Delta_1^2 + B_1\Delta_1^4 + \frac{D_1\Delta_1^4}{L}\int_0^L dy\cos[4(\theta_1 + \delta k_1 y)] + \frac{\gamma_1\Delta_1^2}{L}\int_0^L dy\left(\frac{d\theta_1}{dy}\right)^2, \tag{2.8}$$

where L is the length of the sample and $\delta k_1 = k_{1y} - \frac{1}{4}b^* \simeq -0.01b^*$. The first two terms in (2.8) are the usual GL terms with $B_1 > 0$ and $A_1 \gtrless 0$ ($T \gtrless T_1$). The third term represents the commensurability (or "lock-in") energy and by itself would be minimized if $\theta_1(y) = \frac{1}{4}\pi - \delta k_1 y$, i.e., if the effective

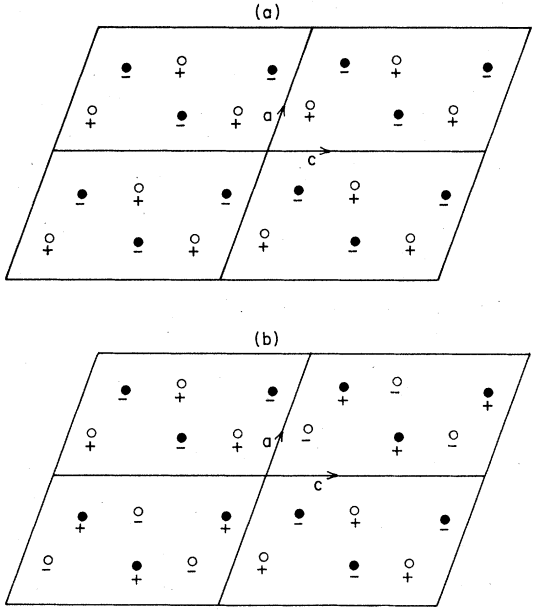

FIG. 1. Relative signs (in the *ac* plane) of the CDW's on the niobium chains for (a) $\delta\rho_1^{\rightarrow}$ and (b) $\delta\rho_2^{\rightarrow}$. The origin is an inversion center above T_1. The filled circles represent chains which are shifted by $\frac{1}{2}b$ from the chains represented by open circles. Note the doubling of the unit cell in case (b) appropriate to the second CDW wave vector $k_2 \cong (0.5, 0.26, 0.5)$.

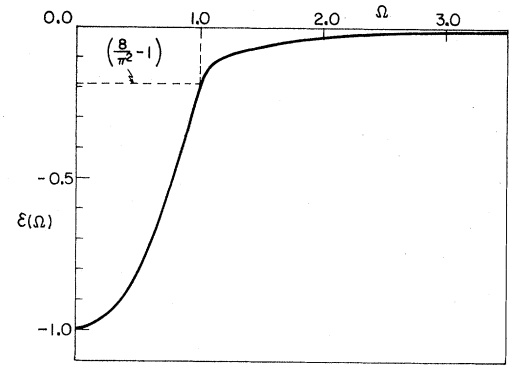

FIG. 2. Plot of the dimensionless quantity $\mathcal{E}(\Omega)$ vs Ω which enters the discommensuration free-energy density [Eq. (2.10)]. If $\Omega[=(\pi/2\sqrt{2})(|\delta k_1|/|\sqrt{\kappa})]$ becomes less than unity, a lock-in transition occurs where the discommensurations disappear. For $NbSe_3$, however, Ω appears to be much larger than unity so that $\mathcal{E}(\Omega)$ is always very small and no lattice lock-in occurs.

CDW wave vector would be $\vec{k}_1 - \delta\vec{k}_1\, y = \vec{q}_1 \equiv (0, \frac{1}{2}b^*, 0)$. However, the fourth term, representing the "strain" energy associated with deformation of θ_1, competes with the commensurability energy. Minimization of F_1 with respect to θ_1 (for fixed Δ_1) leads to the static sine-Gordon equation[20,21] for $\phi_1 \equiv \theta_1 + \delta k_1 y$. The relevant solution is

$$\sin 2\phi_1 = -\mathrm{sn}\left(2(\epsilon+\kappa)^{1/2} y \left| \frac{2\kappa}{\epsilon+\kappa}\right.\right), \qquad (2.9)$$

where $\kappa \equiv D_1\Delta_1^2/\gamma_1$, sn is a Jacobi elliptic function,[22] and ϵ is an integration constant which is determined by minimizing F_1, yielding a transcendental equation for ϵ: $E(m) = (\pi/2\sqrt{2})|\delta k_1|\sqrt{m/\kappa}$, where $m \equiv 2\kappa/(\epsilon+\kappa)$ and E is the complete elliptic integral of the second kind.[22] For $\Omega \equiv (\pi/2\sqrt{2})|\delta k_1|\sqrt{\kappa} > 1$, the solution for θ_1 represents a "lattice" of discommensurations[13,14] with spacing $\lambda = (m/2\kappa)^{1/2} K(m)$, where K is the complete elliptical integral of the first kind.[22] However, if $\Omega < 1$, then $\phi_1 = \frac{1}{4}\pi$, corresponding to a commensurate phase with $\theta_1 = \frac{1}{4}\pi - \delta k_1 y$ and no discommensurations. This lattice lock-in would occur at a temperature such that $\Omega = 1$. However, it appears that for $NbSe_3$, $\Omega \gg 1$, so that there is no lock-in transition and as a consequence, λ (and hence the effective CDW wave vector) is essentially temperature independent down to the lowest temperatures obtained in the diffraction experiments.[6,7] This situation is quite consistent with the expectation that $D_1 \ll B_1$ due[23] to the high order (fourth) of the commensurability term, i.e., the tendency toward lock-in is very weak. The dependence of F_1 on Δ_1 is given explicitly as

$$F_1 = A_1\Delta_1^2 + B_1\Delta_1^4 + D_1\Delta_1^4 \mathcal{E}\left(\frac{\pi|\delta k_1|}{2(2D_1/\gamma_1)^{1/2}}\,\frac{1}{|\Delta_1|}\right), \qquad (2.10)$$

where $\mathcal{E}(\Omega)$ is shown in Fig. 2. Note that as long as $D_1 \ll B_1$ (and $\Omega \gg 1$), $\mathcal{E}(\Omega)$ is only weakly dependent on Δ_1 and hence the free energy (2.10) is minimized by the Landau result $\Delta \cong (|A_1|/B_1)^{1/2}$ just below T_1. In this situation κ is small and the discommensurations provide only slight deviations of θ_1 from zero. The spacing λ is approximately equal to $25b$ and $(\epsilon+\kappa)^{1/2} \simeq \pi/2\lambda$ so that $\phi_1 \simeq -\frac{1}{2}\pi$, $y/\lambda \simeq \delta k_1 y$, and $\theta_1 \simeq 0$. The discommensurations should, in principle, give rise to closely spaced satellite spots in a diffraction experiment at scattering vectors $\vec{q}_n = \vec{k}_1 + (2n\pi/\lambda)$ (n integer). However, since $\sqrt{\kappa}$ is likely less than $\sim\lambda^{-1}$, we estimate that the intensity of the satellite spots is $\lesssim 10^{-3}$–10^{-4} of the intensity of the main spot ($n=0$), and hence the satellites would be unobservable in present-day experiments[6,7]; in fact, no satellites are seen.

The Landau result, $\Delta_1 = (|A_1|/B_1)^{1/2}$, cannot, of course, be used well below T_1, since quasiparticle fluctuations give the actual Δ_1 a more BCS-type shape[4] (see Sec. III below). As the temperature is reduced below T_1, experiment[4,7] shows that Δ_1 has essentially saturated before T_2 is reached. Thus, in the next section we replace F_1 by an ef-

fective free energy $\tilde{F}_1(\Delta_1)$ which is only weakly dependent on Δ_1 below T_2.

III. GINZBURG-LANDAU THEORY OF THE SECOND CDW AND ITS PHASE COUPLING TO THE FIRST CDW

In constructing a GL free-energy functional appropriate to the second CDW transition at $T_2 = 58$ K, we use an analysis similar to that employed above for the first CDW. The appropriate order parameter is $\delta\rho(\vec{r}) = \delta\rho_1(\vec{r}) + \delta\rho_2(\vec{r})$, where $\delta\rho_2$ refers to the modulation associated with the second CDW. If we ignore the slight symmetry breaking due to $\delta\rho_1 \neq 0$, then the possible basis functions for $\delta\rho_2$ have the form

$$\phi_1^{\pm}(\vec{r}) = e^{i\vec{k}_2\cdot\vec{r}}[u^{\pm}(\vec{r}) \pm e^{-i(\vec{a}^*+\vec{c}^*)\cdot\vec{r}}u^{\pm}(C_2^{*-1}\vec{r})], \quad (3.1a)$$

$$\phi_2^{\pm}(\vec{r}) = e^{-i\vec{k}_2\cdot\vec{r}}[u^{\pm}(-\vec{r}) \pm e^{i(\vec{a}^*+\vec{c}^*)\cdot\vec{r}}u^{\pm}(-C_2^{*-1}\vec{r})]. \quad (3.1b)$$

As before, we have two choices (+ or −) for $\delta\rho_2$ and we make the choice which appears to minimize the interchain Coulomb energy, namely, the u^- function given by Eq. (2.6). Since the two CDW's have different periods along the chain direction ($\vec{b}$), we can ignore their Coulomb interaction with each other to lowest order. Thus we take $\delta\rho_2$ to have the form

$$\delta\rho_2(\vec{r}) = \Delta_2 \sin\frac{2\pi x}{a}\cos\frac{2\pi z}{c}\cos\left[\pi\left(\frac{x}{a}+\frac{z}{c}\right)\right] \times \sin\left[\vec{k}_2\cdot\vec{r} - \pi\left(\frac{x}{a}+\frac{z}{c}\right) + \theta_2(y)\right]. \quad (3.2)$$

The GL free energy per unit length is now

$$F_2 = \tilde{F}_1(\Delta_1) + A_2\Delta_2^2 + B_2\Delta_2^4 + \frac{D_2\Delta_2^4}{L}\int_0^L dy\cos[4(\theta_2+\delta k_2 y)] + \frac{\gamma_2\Delta_2^2}{L}\int_0^L dy\left(\frac{d\theta_2}{dy}\right)^2 + \frac{\Delta_1^2\Delta_2^2}{L}\int_0^L dy\,(B_+\cos\{2[\theta_1+\theta_2+(\delta k_1+\delta k_2)y]\} + B_-\cos\{2[\theta_1-\theta_2+(\delta k_1-\delta k_2)y]\}), \quad (3.3)$$

where $\delta k_2 = k_{2y} - \frac{1}{4}b^* \simeq 0.01b^* \simeq -\delta k_1$. The last term (involving B_+ and B_-) in this GL expansion represents the coupling between the two CDW's. From the discussion above, we know that θ_1 is essentially constant except for the weak discommensurations. Similar considerations show that θ_2 will also be essentially constant since $\vec{k}_2$ is also independent of temperature.[7] The terms involving D_2, γ_2, and B_- in Eq. (3.3) then give negligible contribution to F_2, which can now be approximated by

$$F_2 \simeq \tilde{F}_1(\Delta_1) + A_2\Delta_2^2 + B_2\Delta_2^4 + B_+\Delta_1^2\Delta_2^2\cos 2(\theta_1+\theta_2), \quad (3.4)$$

where the B_+ term survives the integration over y only because $\delta k_2 \simeq -\delta k_1$. Clearly, this term is minimized by $\theta_2 = -\theta_1 + \frac{1}{2}\pi$ (if $B_+ > 0$) or $\theta_2 = -\theta_1$ (if $B_+ < 0$) so that

$$F_2 \simeq \tilde{F}_1(\Delta_1) + (A_2 - |B_+|\Delta_1^2)\Delta_2^2 + B_2\Delta_2^4. \quad (3.5)$$

The weak discommensurations associated with the spatial variation of θ_1 will be accompanied by sympathetic discommensurations in θ_2, giving rise to a *composite* "soliton" lattice.[13,14,21] However, the intensity of satellite spots due to these is, of course, also expected to be very small.

We note from Eq. (3.5) that the presence of the phase-locking term (B_+) in Eq. (3.4) has the consequence that the occurrence of the second CDW is aided by the presence of the first CDW, i.e., if A_2 changes sign at T_2^* then the actual second transition occurs at a slightly higher (observed) temperature $T_2 > T_2^*$. One possible consequence of this enhancement is the tendency for k_{2y} to be shifted to the observed value from a slightly different value k_{2y}^* that might have been preferred in the absence of the first CDW. This is not likely to be a large effect, however, since B_+ is most certainly small.

Another consequence of the phase-locking effect is that $\Delta_1(T)$ undergoes a small change in slope at T_2 and reaches a $T=0$ value which is slightly larger than what would occur in the absence of B_+. While a small change in slope would be very difficult to measure, we do note that if the diffraction data[7] for $\Delta_1(T)$ are fitted by a BCS curve (for example) between T_1 and T_2, and this curve is extrapolated below T_2, then the data points for $\Delta_1(T)$ below T_2 seem to lie systematically above the extrapolated curve, indicating a small enhancement of Δ_1 (see Fig. 3). Unfortunately, the error bars are too large for the enhancement to be estimated accurately (and of course there is no reason to assume that a BCS curve for Δ_1 would be exact in the absence of B_+).

The smallness of these enhancement effects is the reason for the apparent independence of the two CDW's in the diffraction[7] and Ohmic transport[4] measurements. In order to determine experimentally whether the phase locking actually occurs, it is necessary to consider other consequences of

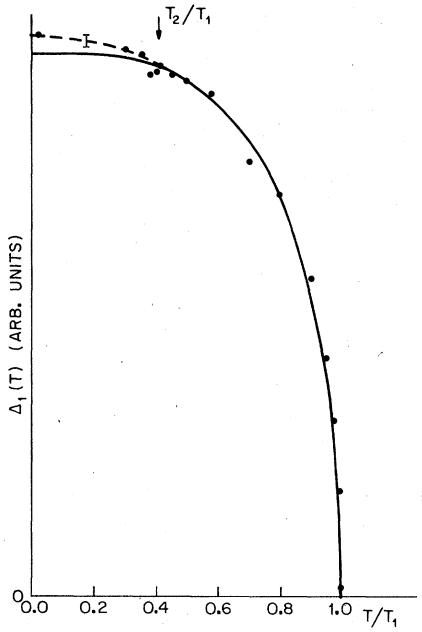

FIG. 3. Possible enhancement of the first CDW amplitude (Δ_1) due to phase-locking to the second CDW. The solid curve is a BCS fit (between T_1 and T_2) to the diffraction intensity data of Ref. 7. The dashed line is an aid to the eye. The size of the possible error precludes a definite estimate of the enhancement. (In performing the fit, we noticed that the arrow indicating T_2 in Fig. 2 of Ref. 7 was incorrectly placed according to the temperature scale of the resistivity plot, rather than the reduced temperature scale T/T_1. This has been corrected in the present figure.)

this effect. We consider some of these in the next section.

IV. OTHER CONSEQUENCES OF PHASE LOCKING

It should be clear from the above discussion that the phase locking of the two CDW's in $NbSe_3$ has only a minor effect on the equilibrium properties such as free energy, etc., and on the steady-state properties *near* equilibrium, such as dc conductivity in small fields (Ohmic behavior). In order to observe the effects of phase locking it is therefore necessary as a practical matter to try to *move* one CDW with respect to the other. If the phase locking exists, it will inhibit such attempts since the CDW's are "commensurability-pinned" to each other. If the degree of inhibition can be measured, one would have a handle on the effect.

The only known way to induce motion of essentially rigid CDW's is by application of an electrical field. If $NbSe_3$ samples were free of impurities and other defects, the electric field would not cause *relative* motion of the CDW's (unless the "damping" constants were different for the two). Fortunately, the presence of impurities leads to pinning of the CDW's in real samples.[23,24] It is found experimentally[8] that below T_2 the pinning of the first CDW is quite effective relative to that of the second CDW (although both pinning strengths are quite weak[8] on an absolute scale). Recently, Fleming and Grimes[25] have observed a non-Ohmic conductivity below T_2 of the form $\sigma \sim \exp[E_0/(E_T - E)]$ for applied fields E above a very small "threshold" field $E_T \simeq 10$ mV/cm. Their measurements were performed at a temperature below T_2 where the Ohmic resistivity is peaked and Δ_2 has essentially saturated. The characteristic field E_0 has previously been associated[24] with impurity pinning because of its dependence[24,10] on impurity concentration. If E_T is interpreted as a breakaway field,[10] then it should be due to a barrier formed by *both* impurity pinning *and* phase locking, whereas above T_2 the barrier is due to impurities only. A test of the existence of phase locking could thus be made by detailed measurements of the impurity dependence of E_T below T_2. If E_T approaches a constant in the pure limit, this would be indicative of intrinsic pinning of the second CDW to the first.

Another observation by Fleming and Grimes[25] deserves comment in connection with the phase-locking effect. They found that when the threshold field is exceeded, a dramatic change takes place in the frequency spectrum of the noise voltage, namely, a well-defined peak appears (along with several harmonics) at very low frequency. The fundamental frequency increases with increasing field and eventually *another* frequency appears with *its* harmonics. While the origin of this fascinating effect is unclear at present, Fleming and Grimes pointed out the analogy of this behavior to that encountered in the transition to turbulence in a variety of fluid systems where intermediate quasiperiodic regimes exist. Indeed, Huberman and Crutchfield[26] have noted that a periodic driving force on the first (pinned) CDW as the second CDW slides past (for $E > E_T$) might induce a quasiperiodic response of the first CDW. Clearly, the phase coupling discussed above could provide the source for such an oscillating driving force. More work, both theoretical and experimental, is needed to test this intriguing hypothesis. In particular, the dependence of the fundamental noise frequency on impurity concentration would be quite valuable information since this frequency presumably depends on the relative strength of impurity pinning of the first CDW and its coupling (B_+) to the second CDW. A corresponding calculation of the type performed by Huberman and Crutchfield[26] would be most desirable. This, in turn, requires a reasonable model for the dynamics of the second CDW for $E > E_T$.

Finally, we note that if an oscillating (microwave) field is applied at or near the pinning frequency of the first CDW, the simultaneous measurement of E_T below T_2 may show a reduction of E_T due to the "averaging out" of the phase-coupling term. On the other hand, if the CDW's are truly independent, little or no affect on E_T should be observed.

V. SUMMARY AND CONCLUSIONS

In this paper we have presented a detailed discussion of our previously reported[11] Ginzburg-Landau theory of the change-density-wave transitions in $NbSe_3$. We explicitly incorporated the crystal symmetry in constructing free-energy functionals for the two transitions and found that the intimate connection [Eq. (1.1)] between the CDW wave vectors leads to an additional fourth-order invariant responsible for phase locking of the CDW's below T_2. We argued that the independence of the wave vectors upon temperature suggests only a weak tendency toward lock-in of either CDW to the lattice; rather the CDW's become locked to each other.

The importance of the phase-locking effect for equilibrium and near-equilibrium properties was argued to be minimal; for example, the mutual gap enhancement below T_2 is small and barely observable, if at all, thus reconciling the apparent *independence* of the CDW's suggested by diffraction[7] and Ohmic transport[4] measurements with the *connection* implied by the wave-vector relation. Nevertheless, in Sec. IV we explored some other more interesting consequences for the properties of $NbSe_3$, noting that the phase-locking effect should be more evident in the non-Ohmic conductivity. We urge the performance of detailed measurements of the impurity-concentration dependence of (i) the threshold field E_T below T_2 and (ii) the low-frequency peaks in the noise voltage above E_T, both of which have been observed by Fleming and Grimes.[25]

Further progress in theoretical understanding of the phase behavior of the CDW's in $NbSe_3$ is most desirable. In particular, a microscopic theory of the CDW transitions themselves would be beneficial in developing even a phenomenological theory of the non-Ohmic transport properties; simple pictures[10] involving CDW "dislocation" generation and motion could then be developed further.

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