Order-parameter vibrations in the $NbTe_4$ charge-density-wave system

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A Landau theory is used to determine the order-parameter vibrational modes in the high-temperature incommensurate charge-density-wave phase of $NbTe_4$. The dispersion relation is found to exhibit a soft mode consistent with the occurrence of a continuous incommensurate-to-incommensurate phase transition. The single-column case, which is mapped into the amenable form of a two-component Schrödinger equation with a periodic potential, is used to construct a three-dimensional model in terms of a lattice of coupled one-dimensional columns.

I. INTRODUCTION

Materials exhibiting charge-density waves (CDW's) provide a rich environment with which to study modulated phases both theoretically and experimentally. Among the structurally simplest of these materials is the metallic, tetragonal compound niobium tetratelluride. Its relatively strong intracolumn interactions effect a quasi-one-dimensional system where translational symmetry is broken by the formation of CDW's along columns of ions. It is believed[1] that the interplay between the columnar charge-density waves is responsible for the observed variety of phases, ranging from a high-temperature normal structure, through two incommensurate phases, down to a low-temperature commensurate structure.[2-7]

The behavior of $NbTe_4$ offers, in particular, the relatively unusual opportunity to study an incommensurate-to-incommensurate phase transition. Initial theoretical work indicates that the transition is continuous: As the temperature is lowered, the effective coupling between columns becomes weaker and weaker until the high-temperature incommensurate phase becomes unstable with respect to a modulation characterized by a particular wave vector, bringing about the second incommensurate phase.[8] From a dynamical viewpoint, such a transition suggests the possibility of a soft mode. In this article, we study the possibility of such a soft mode at the incommensurate-to-incommensurate transition in $NbTe_4$, and, more generally, study order-parameter vibrational modes in an incommensurate charge-density-wave system.

Our approach uses a phenomenological free energy having the symmetries of $NbTe_4$ (Ref. 1) and is based on an order parameter that characterizes the displacement modulation as measured from the normal-state displacements. In its one-dimensional form, applicable here to a charge-density wave on an isolated column of ions, the model has been well studied in other contexts, particularly that of the layered transition-metal dichalcogenides.[9-13] Through the Landau model, the incorporation of higher harmonics—in addition to the sinusoidal modulation first used to describe the incommensurate state—led to a better understanding of the incommensurate state and the nature of incommensurate-to-commensurate, or lock-in, transitions: As the transition is approached, the higher harmonics deform a sinusoidal structure into one of commensurate domains separated by localized objects, termed discommensurations.[10] This picture will prove useful in our study of the collective modes (by which we mean, as is common in the literature, order-parameter vibrations) in $NbTe_4$.

Collective modes have been discussed in charge-density-wave systems before, most particularly for the dichalcogenides,[13] for one-dimensional models, and in the theoretically appealing limit of only considering phase modulations of the order parameter (where the model is exactly soluble).[14,15] This work presents a different technique for calculating the modes, and specifically considers $NbTe_4$, its three-dimensional properties, and the soft mode. Our approach is entirely mean field and so fluctuation effects are not accounted for. The one-dimensional study serves to introduce a method akin to a Schrödinger equation for a two-component particle in a periodic potential, which is then amenable to Bloch-state analysis. A major consequence of the method, not present in other approaches, is the manifest way in which the band-gap structure arises as a function of the periodicity of the commensurate domains rather than the periodicity of the order parameter. The two-component formalism has been used before in charge-density-wave systems, but this is the first that we know of within the context of analyzing the vibrational degrees of freedom. The method is not limited to the specific Landau energy considered here for $NbTe_4$ and can be applied to certain other systems with incommensurate phases as well. Also, our one-dimensional results, obtained in a certain incommensurate region of the phase diagram, allows an analytic foothold with which to understand earlier numerical results.[13]

In three dimensions, we model $NbTe_4$ by introducing interactions between neighboring columns. The approach introduced for the one-dimensional (1D) columnar case is easily extended to this 3D system. The high-temperature incommensurate phase has a phason mode whose velocity tends towards zero as the temperature is lowered.

In addition, the frequencies of certain modes in the reciprocal space basal plane tend towards zero. A consideration of possible alternative transitions is made in terms of the coupling constants of near-neighbor interactions. One possibility in particular in which a certain soft mode drives a transition into a low-temperature incommensurate phase compares favorably with observations. We find that our model is consistent with the incommensurate-to-incommensurate transition and that we expect to see a soft mode as the transition is approached.

We begin with a review of the phenomenological theory of the one-dimensional model (Sec. II), then map the problem into the two-component Schrödinger form, employ conventional Bloch-state analysis (Sec. III), and discuss the vibrational modes at the zone center and boundaries as measured from the static incommensurate wave vector (Sec. IV). We step up to three dimensions (Sec. V) by including in the free energy an intercolumn interaction, which is considered weak and treated perturbatively. Since the effective coupling strength between nearest-neighbor columns goes soft as the commensurate structure is approached, further-neighbor terms are introduced (Sec. VI) and these lead to a discussion as to whether a soft-mode drives the transition to a second incommensurate phase or whether the crystal becomes unstable under homogeneous phason strain. We conclude with a phenomenological inclusion of dissipative effects and describe where in reciprocal space one expects to see such soft modes.

II. $NbTe_4$ AND THE PHENOMENOLOGICAL THEORY

The crystal structure of $NbTe_4$ in its normal $a \times a \times c$ state above 790 K is shown in Fig. 1. When the temperature is lowered, the presence of charge-density waves alters the c-axis periodicity and the size of the basal-plane unit cell. A high-temperature incommensurate phase above 150 has a $\sqrt{2}a \times \sqrt{2}a$ basal-plane unit cell and a low-temperature incommensurate phase between 150 and 50 K has a $2a \times 2a$ basal-plane unit cell. Below 50 K, a commensurate state with a trimerized distortion along the c axis and a $2a \times 2a$ basal-plane unit cell is stable.

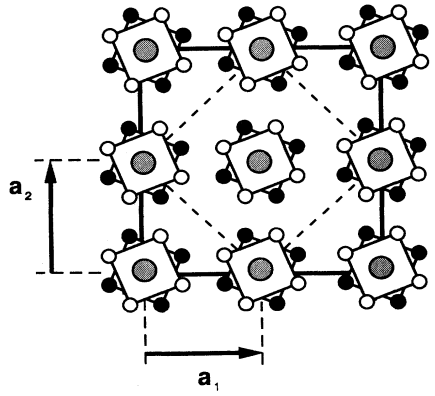

FIG. 1. A basal-plane projection of $NbTe_4$ in the average structure with unit cell $a \times a \times c$ ($|\mathbf{a}_1| = |\mathbf{a}_2| = a$). The shaded circles represent the Nb ions at $\frac{1}{4}c$ and $\frac{3}{4}c$; the smaller solid and open circles represent Te ion at $z = 0$ and $c/2$, respectively. The $\sqrt{2}a \times \sqrt{2}a$ (dashed line) and $2a \times 2a$ (solid line) unit cells are outlined.

For structural purposes, niobium tetratelluride acts as a two-dimensional grid of loosely coupled columns.[2,5] We will focus on the low-frequency longitudinal distortion modes in which the tellurium atoms follow the motion of the niobium ions. It is then sufficient to chronicle only the position of the niobium atoms. We treat a column as a one-dimensional lattice of niobium ions and will first study the phase diagram and distortion modes for that system. In the trimerized commensurate state for a single column, the displacements of the niobium ion at a point z may be written $u(z) = a\sin(Qz)$, where $Q \equiv 2c^*/3$ and $c^* = 2\pi/c$. Variations from this may be incorporated by introducing a complex time- and space-dependent order parameter $\psi(z,t)$ that spatially varies slowly with respect to the commensurate modulation,

$$u(z,t) = \mathrm{Im}[e^{iQz}\psi(z,t)]. \tag{2.1}$$

As the temperature is lowered from the normal to the incommensurate phase, a modulation characterized by the wave vector $q = Q + \delta_I$ appears. For this continuous transition, the magnitude of ψ is small, and its spatial dependence is approximately $\exp(i\delta_I z)$, where δ_I is observed to be on the order of 3% of Q.[2,7] From the space-group symmetry of the column in the normal phase, the Landau free energy for an isolated $NbTe_4$ column is[1]

$$F[\psi] = \int dz[\gamma|(i\nabla + \delta_I)\psi|^2 + v|\psi|^2 - \mathrm{Re}\,\psi^3 + \tfrac{1}{2}|\psi|^4]. \tag{2.2}$$

This one-dimensional prototypical model has also arisen previously in a different context.[10,12,13] The coefficients depend on the material and on experimental conditions, and we assume that $\gamma \geq 0$ and $v \propto T - T_0$, where T_0 is the normal-to-incommensurate phase transition temperature. Although length can be scaled so that the constant $\delta_I = 1$, we will frequently use δ_I for clarity. The temperature and quartic terms are responsible for symmetry breaking, $|\psi| \neq 0$, and the gradient term favors incommensurate modulation. The cubic term encourages the phase to lock in to a fixed value, thus breaking global phase (gauge) invariance.

By varying the free energy, the minimizing solution ψ_0 is found to obey the equation

$$\gamma(i\nabla + \delta_I)^2\psi_0 + v\psi_0 - \tfrac{3}{2}\psi_0^{*2} + |\psi_0|^2\psi_0 = 0. \tag{2.3}$$

The phase diagram as a function of γ and v is given in Fig. 2.[12,16] The three phases are (N) normal: $\psi_0 = 0$; (C) commensurate: $\psi_0 = A_c e^{i\frac{2\pi}{3}n}$ with A_c a γ, v dependent constant, and $n = 0, 1, 2$; and (I) incommensurate:

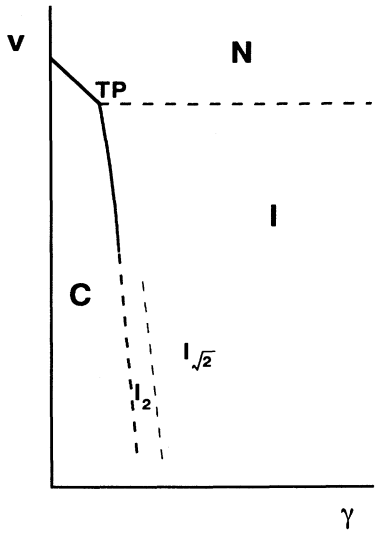

FIG. 2. Phase diagram for the one-dimensional charge-density-wave system [Eq. (2.2)]. Solid lines represent first-order transitions, and dashed lines represent second-order transitions. The triple point (TP) lies at $v = 0$, $\gamma = \frac{1}{2}$. In three dimensions, an incommensurate-to-incommensurate phase boundary (thin dashed line) arises separating a $\sqrt{2}a \times \sqrt{2}a$ basal-plane phase ($I_{\sqrt{2}}$) with $2a \times 2a$ basal-plane phase (I_2).

$$\psi_0(z) = e^{i\delta z} \sum_n e^{3i\delta n z} \phi_n, \tag{2.4}$$

where $\delta = \delta(\gamma, v)$ is chosen to minimize $F[\psi]$ and the ϕ_n are real.

The incommensurate phase parameter δ, which can be thought of as the wave vector describing the periodic array of discommensurations, changes as a function of temperature from δ_I at the normal-commensurate phase boundary to zero at the incommensurate-commensurate phase boundary, or lock-in temperature, if the latter transition is continuous. The higher harmonics help lower the free energy as the commensurate phase is approached, and they play an important role in the theoretical determination of the order of the transition.

Our approach for calculating the vibrational modes in $NbTe_4$ can be applied to other systems described by a complex order parameter and a free energy favoring an incommensurate state. The cubic term in Eq. (2.2), arising here because of the space group of $NbTe_4$, also arises in the study of the layered dichalcogenides. Other free energies,[17] for example those describing ferroelectrics,[18] replace the cubic and quartic term in (2.2) with $\gamma_n \mathrm{Re}\psi^{2n} + |\phi|^{2n}$, and can also be analyzed with the formalism that we present in the next section.

The three-dimensional properties of $NbTe_4$ are modeled by the introduction of intercolumn interactions. The lowest-order term consistent with the symmetries describing the interaction between two columns i and j is[1]

$$F_{ij} = g \int dz\, \mathrm{Re}\,[\psi_i^*(z)\psi_j(z)], \tag{2.5}$$

where g is g_1 for nearest neighbors, g_2 for next-nearest neighbors, etc.

In the following sections, we will look at the distortional modes in both the one- and three-dimensional models.

III. FORMALISM FOR THE DYNAMICS IN ONE DIMENSION

We consider the vibrations $\zeta(z,t)$ about the static solution,

$$\psi(z,t) = \psi_0(z) + \zeta(z,t). \tag{3.1}$$

Expanding the free energy and a kinetic term to second order in ζ, we determine the Lagrangian governing the dynamics of $\zeta(z,t)$ to be

$$\mathcal{L}[\zeta] = \int dz \left(\frac{1}{2} M \left| \frac{\partial \zeta}{\partial t} \right|^2 \right) - F[\zeta], \tag{3.2}$$

$$F[\zeta] = \int dz [\, \gamma |(i\nabla + \delta_I)\zeta|^2 + v|\zeta|^2 - \tfrac{3}{2}(\psi_0 \zeta^2 + \psi_0^* \zeta^{*2}) + 2|\psi_0|^2 |\zeta|^2 + \tfrac{1}{2}(\psi_0^2 \zeta^{*2} + \psi_0^{*2} \zeta^2)]. \tag{3.3}$$

M is the effective mass per unit length of the charge-density wave. Since the original free energy contains terms higher than quadratic in the order parameter, the dynamics of ζ depend on the static field. For the normal and commensurate states, ψ_0 is independent of z and the collective modes are easily found using a method similar to that presented below.

For the incommensurate state analysis, it is useful to introduce the rotated fields ϕ and ξ, $\psi_0(z) + \zeta(z,t) = \exp(i\delta z)\,[\phi(z) + \xi(z,t)]$, a two-component vector

$$\Xi_M = \begin{pmatrix} \xi(z,t) \\ \xi^*(z,t) \end{pmatrix}, \tag{3.4}$$

and a corresponding 2×2 matrix notation. The subscript M indicates that the vector is in Majorana form, self-conjugate under "charge" conjugation. If K is the complex conjugation operator and σ_i, $i = 1, 2, 3$, are the Pauli matrices, then the Majorana form implies $\sigma_1 K \Xi_M = \Xi_M$. Rewriting the free energy we find

$$F = \tfrac{1}{2} \int dz\, \Xi_M^\dagger H \Xi_M \tag{3.5}$$

with the "Hamiltonian" operator

$$H[z, \phi(z)] = \gamma(i\nabla\sigma_3 + \delta_I - \delta)^2 + v + V(z), \tag{3.6}$$

$$V(z) = \begin{pmatrix} 2|\phi|^2 & \phi^2 - 3e^{-3i\delta z}\phi^* \\ \phi^{*2} - 3e^{+3i\delta z}\phi & 2|\phi|^2 \end{pmatrix}. \tag{3.7}$$

The Hamiltonian is periodic in z with period $\Lambda/3 =$

$2\pi/3\delta$, is Hermitian and, since $\phi^*(z) = \phi(-z)$, commutes with $\sigma_1 K$. The equation of motion is

$$-\frac{M}{2}\frac{\partial^2}{\partial t^2}\Xi_M(z,t) = H[z,\phi(z)]\Xi_M(z,t). \tag{3.8}$$

Because of the off-diagonal elements of $H(z)$ that couple $\xi(z,t)$ to $\xi^*(z,t)$ in Eq. (3.8), time dependence cannot be simply chosen as $\xi(z,t) = \exp(-i\omega t)\xi(z)$. To pursue this, let us first investigate the static *general* solutions of

$$H[z,\phi(z)]\Xi(z) = E\Xi(z)\ , \tag{3.9}$$

where Ξ no longer has the restricted symmetry. Since H is periodic, we can think of $\Xi(z)$ as a two-component "spinor" in a Schrödinger equation with a periodic potential. Solutions can be chosen and labeled by a Bloch momentum $k \in [-3\delta/2, +3\delta/2]$, and we can then write $\Xi^k(z) = \sum_m e^{i(k-3\delta m)z}\Xi_{k-3\delta m}$. (The "band" index labeling different Bloch states with momentum k has been dropped.)

Suppose the set of two-component solutions, which we call Bloch states, can be determined. Then the time dependence of the Bloch-state solution to

$$-\frac{M}{2}\frac{\partial^2}{\partial t^2}\Xi^k(z,t) = H[z,\phi(z)]\Xi^k(z,t) \tag{3.10}$$

can be taken as the usual oscillatory $\Xi^k(z,t) = e^{-i\omega t}\Xi^k(z)$, and the Majorana form (3.4) that we seek is obtained by projection using

$$\Xi^k_M(z,t) = \begin{pmatrix} \xi^k(z,t) \\ \xi^{k*}(z,t) \end{pmatrix} = \frac{1+\sigma_1 K}{2} e^{-i\omega t}\Xi^k(z). \tag{3.11}$$

Since $\Xi^k(z)$ has the spectrum E_k, and the spectrum is not changed under the projection (3.11), order parameter vibrations $\xi(z,t)$ will have the identical spectrum $\frac{1}{2}M\omega^2 = E_k$, albeit half the degrees of freedom. In particular, the location of the zone boundaries and the size of the band gaps for Bloch solutions are those dispersion curves that we seek.

Two points concerning the time dependence are worth noting. First, the phase of a Bloch state, defined as a solution to (3.9), was chosen arbitrarily. Had one instead chosen $e^{i\theta}\Xi^k(z)$, it is easily seen that the projection (3.11) can be written with t replaced by $t - t_0$, $\theta = \omega t_0$. This phase degree of freedom of the Bloch state corresponds simply to a shift in the time coordinate. Second, time-reversed displacement modulations are given by the two states ψ^k and $\sigma_1 K\psi^k$. This follows by substituting the latter for the former into Eq. (3.11) and then commuting $\sigma_1 K$ with $\exp(-i\omega t)$ to find $\xi(z,-t)$.

To summarize the above procedure of determining the collective modes, one, given a static solution $\psi_0(z)$, rotates by the phase $\exp(i\delta z)$ to find $\phi(z)$, calculates all solutions of Eq. (3.9), projects out using (3.11), reads off the component $\xi^k(z,t)$, and rotates back to find the order-parameter vibrational state $\zeta(z,t)$. In the normal and commensurate phases, the rotations are not necessary, since the order-parameters have no spatial dependence. To investigate the incommensurate phase, we assume $\phi(z)$ to be known from the static field solution, where numerical work has provided a good understanding of its behavior,[11–13,19] and expand our eigenvalue problem using Bloch states $\Xi^k(z)$ and $V_m = \int_0^{\Lambda/3} dz\, \exp(-3i\delta mz)V(z)$ to find

$$\tfrac{1}{2}M\omega^2\Xi_{k-3\delta m} = \gamma\left[(k-3\delta m)\sigma_3 - (\delta_I - \delta)\right]^2\Xi_{k-3\delta m} + \sum_n V_n\,\Xi_{k-3\delta(n+m)}. \tag{3.12}$$

This equation will be studied in the next section for the incommensurate region near the normal phase and at large γ, a region which is analytically tractable and where certain properties characteristic of the incommensurate region are already apparent.

Before continuing, we mention the special case of the zero-frequency solution. The degree of freedom that corresponds to the independence of the origin of the charge-density wave in the incommensurate state is the $k = 0$ phason mode,[20] the Goldstone mode of the broken translational symmetry. In our formalism above, one takes the spatial derivative of the constraint equation (2.3), couples it with the complex conjugate equation, and finds that $\zeta \propto \psi'$ is a solution of energy $E = 0$. This mode is particularly important for the later discussion of soft modes in three dimensions.

IV. ORDER-PARAMETER VIBRATIONS IN ONE DIMENSION

We begin with the one-dimensional study, applicable to a single column in $NbTe_4$, by discussing the spectrum in the normal and commensurate regions of the phase diagram.

In the normal phase, $\psi_0 = 0$ and the frequencies and collective modes are easily found. The vibrations in the order parameter, up to a real coefficient a, are $\zeta^k(z,t) = a\exp i(kz - \omega t)$, where k is measured from Q, have frequencies given by

$$\frac{M}{2}\omega^2 = \gamma(k-\delta_I)^2 + v, \tag{4.1}$$

and correspond to displacements $u^k(z,t) = a\sin[(Q+k)z - \omega t]$. The second-order transition at $v = 0$ is evident: The lattice distortion with wave-vector $Q + \delta_I$ costs no energy to excite and a transition to the incommensurate phase occurs.

The commensurate case, $\phi_0 = A_c\exp(i2\pi n/3)$ with $A_c = \frac{3}{4} + [(\frac{3}{4})^2 - (\gamma+v)]^{1/2}$, is also straightforward. Modes with frequencies[13]

$$\tfrac{1}{2}M\omega^2 = \gamma(k^2+\delta_I^2) + v + 2A_c^2 \pm\sqrt{(2\gamma k)^2 + (A_c^2 - 3A_c)^2} \tag{4.2}$$

correspond to displacements (we set $n = 0$ for clarity)

$$u^k(z,t) = \begin{cases} A_c\sin(Qz) + a\sin(Qz)\cos(kz-\omega t) \\ A_c\sin(Qz) + a\cos(Qz)\sin(kz-\omega t). \end{cases} \tag{4.3}$$

An understanding of the two branches is found by considering the variation Δu with respect to the amplitude and phase of the order parameter $\psi = A\exp(i\theta)$, $\Delta u = \Delta A \sin(Qz) + \Delta\theta A_c \cos(Qz)$. We then can see that the higher-frequency branch corresponds to an amplitude modulation and the lower frequency branch to a phase modulation, termed the amplitudon and phason, respectively. In the incommensurate phase, it is customary to continue using these terms although they no longer correspond strictly to phase and amplitude vibrations.

A. States at the zone boundary and the single-harmonic limit

The modes can be found by solving a Schrödinger equation with a periodic potential with period $2\pi/3\delta$ determined by the static field solution. This implies a Brillouin zone of size 3δ and the usual band and gap structures. We will investigate the nature of the states in the zone center near Q ($k = 0$) in Sec. IV B, but first look at the states at the zone boundaries.

To do this, we need the order parameter. It can be obtained by taking the fundamental harmonic and from (2.3) generating the sequence

$$\psi_0(z) = e^{i\delta z}\left(\phi_0 + e^{-3i\delta z}\phi_{-1} + e^{+3i\delta z}\phi_1 + \cdots\right). \tag{4.4}$$

We consider the purely sinusoidal incommensurate state, or single-harmonic limit, and keep only the first term as the static solution, valid for $\gamma \gg \frac{1}{2}$ and $-v/\gamma(\gamma-\frac{1}{2}) \ll 1$. The free energy in this limit is minimized when $\phi_0^2 = -v$ and $\delta = \delta_I$. The static displacements $u(z) = \phi_0 \sin(Q + \delta_I)z$ are characterized by a wave vector $Q + \delta_I$, which has no particular rational ratio with respect to the wave vector Q of the commensurate state.

For states near the zone boundary, we neglect terms of order $\sqrt{-v}/\gamma$ in Eq. (3.12) and solve a matrix equation for the four coupled states to find the frequencies

$$\tfrac{1}{2}M\omega^2 = \tfrac{1}{2}\gamma[(k-3\delta)^2 + k^2] - v$$
$$\pm\left(\tfrac{1}{4}\gamma^2[(k-3\delta)^2 - k^2]^2 + -\tfrac{9}{2}v + v^2 \pm \{(v\gamma)^2[(k-3\delta)^2 - k^2]^2 + (-\tfrac{9}{2}v + v^2)^2 - v^4\}^{1/2}\right)^{1/2}, \tag{4.5}$$

which we label 1 (highest frequency) through 4 (lowest). The behavior of the bands near $k = 3\delta/2$ is sketched in Fig. 3 (along with interpolated results from below).

At $k = 3\delta/2$, the four frequencies and the corresponding displacement fields can be found using the prescription Eq. (3.11) and are listed in Table I. The relative amplitudes of the vibrations depend on temperature through the parameter $\sigma = -v/(\sqrt{-9v/4} + \sqrt{-9v/4 + v^2})$. We find that on top of the incommensurate charge-density wave with wave number $Q+\delta$ is a long-wavelength modulation, which has four standing wave modes that consist of mixed amplitude and phase vibrations.

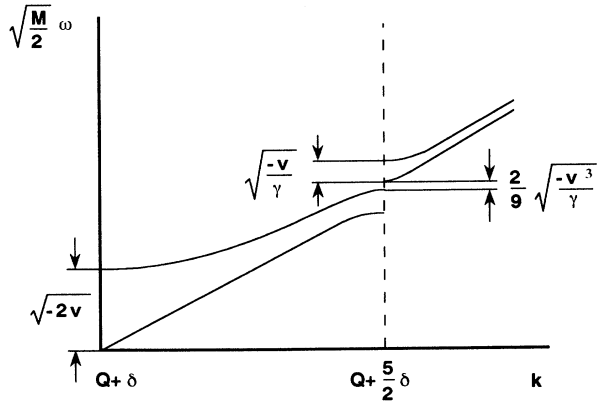

FIG. 3. Dispersion relations in an extended scheme near the normal to incommensurate phase boundary. Frequency and states near the zone boundary are given in Table I. Gap sizes are given in first nonzero order in $\sqrt{-v}$.

B. The zone center and the two-harmonic limit

In this subsection, we again demonstrate the method of Sec. III, now for states near $k = 0$ and in the two-harmonic limit. This allows us to calculate energies and states to a nontrivial order and therefore better understand the limits of the first-harmonic approximation. It will also provide a consistency check on our method via the known symmetry form of the phason mode. We expect the two-harmonic approximation to be qualitatively good for much of the incommensurate phase domain as long as one is not too close to the commensurate boundary where the effects of yet higher harmonics become significant.[12,13]

In Eq. (4.4), we let ϕ_{-1} be of order ϕ_0^2, drop higher-order terms, and find the free energy is minimized with the following consistent set ($\delta_I = 1$):[11,12]

$$\phi_0 = \left(\frac{-v\gamma}{\gamma - \frac{1}{2}}\right)^{1/2}, \tag{4.6}$$

$$\phi_{-1} = \frac{-v}{6(\gamma - \frac{1}{2})} = \frac{\phi_0^2}{6\gamma}, \tag{4.7}$$

$$1 - \delta \equiv \varepsilon = \frac{-v}{6\gamma(\gamma - \frac{1}{2})} = \frac{\phi_0^2}{6\gamma^2}. \tag{4.8}$$

This is valid in the incommensurate domain when $\gamma - \frac{1}{2} \gg |-v|$, a good approximation near the normal-state phase boundary away from the triple point. Numerical results indicate that the ratio ϕ_{-1}/ϕ_0 goes from zero at the normal to incommensurate transition to approximately $\frac{1}{3}$ at

TABLE I. Frequencies and displacements for modes at $q = Q + \frac{3}{2}\delta$ near the normal to incommensurate transition. The $a_1, a_2, a_3, a_4 \ll 1$ are arbitrary real coefficients. See text for definition of σ.

$$\tfrac{1}{2}M\omega_1^2 = \tfrac{9}{4}\gamma\delta^2 - v + \sqrt{-\tfrac{9}{4}v} + \sqrt{-\tfrac{9}{4}v + v^2}$$
$$\tfrac{1}{2}M\omega_2^2 = \tfrac{9}{4}\gamma\delta^2 - v - \sqrt{-\tfrac{9}{4}v} + \sqrt{-\tfrac{9}{4}v + v^2}$$
$$\tfrac{1}{2}M\omega_3^2 = \tfrac{9}{4}\gamma\delta^2 - v + \sqrt{-\tfrac{9}{4}v} - \sqrt{-\tfrac{9}{4}v + v^2}$$
$$\tfrac{1}{2}M\omega_4^2 = \tfrac{9}{4}\gamma\delta^2 - v - \sqrt{-\tfrac{9}{4}v} - \sqrt{-\tfrac{9}{4}v + v^2}$$
$$u_1(z,t) = \sqrt{-v}[1 + a_1(1+\sigma)\sin(\omega_1 t)\sin(\tfrac{3}{2}\delta z)]\sin[(Q+\delta)z + a_1(1-\sigma)\sin(\omega_1 t)\cos(\tfrac{3}{2}\delta z)]$$
$$u_2(z,t) = \sqrt{-v}[1 + a_2(1+\sigma)\sin(\omega_2 t)\cos(\tfrac{3}{2}\delta z)]\sin[(Q+\delta)z + a_2(1-\sigma)\sin(\omega_2 t)\sin(\tfrac{3}{2}\delta z)]$$
$$u_3(z,t) = \sqrt{-v}[1 - a_3(1-\sigma)\sin(\omega_3 t)\sin(\tfrac{3}{2}\delta z)]\sin[(Q+\delta)z + a_3(1+\sigma)\sin(\omega_3 t)\cos(\tfrac{3}{2}\delta z)]$$
$$u_4(z,t) = \sqrt{-v}[1 + a_4(1-\sigma)\sin(\omega_4 t)\cos(\tfrac{3}{2}\delta z)]\sin[(Q+\delta)z - a_4(1+\sigma)\sin(\omega_4 t)\sin(\tfrac{3}{2}\delta z)]$$

the commensurate transition.[11]

To this order the Hamiltonian is $H = H_0 + H_1$, $H_0 = -\gamma\nabla^2$,

$$H_1 = \begin{pmatrix} 2i\gamma\varepsilon\nabla + v + 2\phi_0^2 & \phi_0^2 - 3\phi_{-1} - 3\phi_0 e^{-3i\delta z} \\ \phi_0^2 - 3\phi_{-1} - 3\phi_0 e^{+3i\delta z} & -2i\gamma\varepsilon\nabla + v + 2\phi_0^2 \end{pmatrix}. \tag{4.9}$$

Using a perturbation procedure[21] that finds energies and states of an approximate Hamiltonian, we find, for k not too close to the zone boundary, the eigenvalues

$$E_k = \gamma_k k^2 - \rho \pm \sqrt{(\alpha_k k)^2 + |v|^2}, \tag{4.10}$$

$$\gamma_k = \gamma - \left(\frac{\phi_0^2}{\gamma}\right)\frac{1}{(3\delta/2)^2 - k^2}, \tag{4.11}$$

$$\rho = v + 2\phi_0^2\left(1 - \frac{1}{2\gamma}\right), \tag{4.12}$$

$$\alpha_k = 2\varepsilon\gamma - \left(\frac{3\phi_0^2}{2\gamma}\right)\frac{1}{(3\delta/2)^2 - k^2}. \tag{4.13}$$

Only terms to order ϕ_0^2 have been kept, e.g., $\phi_0^2/\gamma\delta^2 \approx \phi_0^2/\gamma$, and we have left the solution in terms of ϕ's because the harmonics' dependence on system parameters will generalize in the three-dimensional case. Presently, $\rho = -v$, and at $k = 0$ we find the expected zero-energy phason state and the amplitudon with $E = 2|v|$. These and our earlier results for states near the zone boundary have been combined to produce the band structure for the phason and amplitudon branches near the wave vector $Q + \delta$. See Fig. 3.

The displacements are found from the Bloch-form eigenstates of (4.9) and the prescription (3.11). For the phason branch, we find (up to a real coefficient)

$$\zeta(z,t) \propto i\sin(kz - \omega t)e^{i\delta z}\left(1 - \frac{\phi_0}{3\gamma}e^{-3i\delta z}\right). \tag{4.14}$$

At $k = 0$, this result can be checked with the symmetry argument regarding invariance of the static solution under a translation. The amplitudon eigenstate can similarly be computed:

$$\zeta(z,t) \propto \cos(kz - \omega t)e^{i\delta z}\left(1 + \frac{\phi_0}{3\gamma}e^{-3i\delta z}\right). \tag{4.15}$$

At $k = 0$, a heuristic argument for this result can be given. From the static order parameter in the two-harmonic approximation ($\phi_{-1} = \phi^2/6\gamma$), one varies the "amplitude" ϕ_0 and finds the expression (4.15). In first order, the solutions (4.14) and (4.15) correspond to phase and amplitude vibrations of the order parameter. The higher-order terms scramble this strict delineation.

The phason velocity for long wavelengths, $c = \omega/k$, is easily found from our result (4.10):

$$c^2 = \frac{2\gamma}{M}\left[1 - \left(\frac{4}{9} + \frac{\gamma}{18(\gamma - \frac{1}{2})}\right)\left(\frac{\phi_0}{\gamma}\right)^2\right]. \tag{4.16}$$

Although the two-harmonic approximation is valid near the normal-incommensurate phase boundary, the decrease in the sound velocity is expected to continue as the temperature ($v \propto -\phi_0^2$) decreases.

V. ORDER-PARAMETER VIBRATIONS IN $NbTe_4$

Our picture for the $NbTe_4$ crystal consists of a two-dimensional $a \times a$ grid of columns extending along the c axis, with a longitudinal distortional mode that fixes the tellurium ions to the motion of the niobium. To lowest order, the columns act as independent one-dimensional charge-density-wave systems. As a perturbation, we now introduce intercolumn interactions considered weaker than intracolumn interactions.

If near-neighbor interactions dominate further-neighbor and long-range interactions, the lowest-order Landau term describing the interactions and obeying the crystal symmetries is[1]

$$F_{\rm int} = g_1 \sum_{i,j}{}' \int dz\, {\rm Re}\, \psi_i^* \psi_j + g_2 \sum_{ij}{}'' \int dz\, {\rm Re}\, \psi_i^* \psi_j + g_3 \sum_{i,j}{}''' \int dz\, {\rm Re}\, \psi_i^* \psi_j + \cdots . \quad (5.1)$$

The single, double, etc., primes restrict the sum to nearest-, second-nearest-, etc., neighbor sites. We first consider only nearest-neighbor interactions. Minimization of the full free-energy then gives the variational equation

$$\gamma(i\nabla+1)^2\psi_{0,i} + v\psi_{0,i} - \tfrac{3}{2}\psi_{0,i}^{*2} + |\psi_{0,i}|^2\psi_{0,i} + g_1 \sum_j{}' \psi_{0,j} = 0, \quad (5.2)$$

and solutions $\psi_{0,i}$ to the variational equation can also be expanded in the same general form as the single-column case, Eq. (2.4). The weak interaction will only slightly distort the shape of the columnar density wave. More significantly, it will determine the relative phases of the columns. We can describe the stable state of the crystal by specifying the phases Δ_i, which determine the relative displacements of the charge-density waves along the c axis, $\psi_{0,i}(z + \Delta_i)$.

If g_1 is negative, all columns will have the same phase, and the resulting basal plane is $2a \times 2a$, which does not agree with observation. For positive g_1, the columns shift their phase so as to minimize the free energy. Expanding in a harmonic approximation about small Δ_i gives an effective potential between two columns. A study of $F_{ij}(\Delta_i - \Delta_j)$ finds that the minimum energy solution arises when $\Delta_i - \Delta_j$ is $\Lambda/2$ (mod Λ).[8] This results in two interleaved sublattices of columns, the phases of the odd sites ($n_1 + n_2$ odd) shifted by half the incommensurate period with respect to the phases of the even sites ($n_1 + n_2$ even) resulting in a $\sqrt{2}a \times \sqrt{2}a$ structure, as has been observed.[2,7]

We can then write for the static order parameter of the ith column labeled by n_1^i, n_2^i (and now drop the column superscript when otherwise clear), $\psi_{0,i}(z) = \psi_0[z + (n_1 + n_2)\Lambda/2]$, where ψ_0 is the solution to

$$\gamma(i\nabla + 1)^2\psi_0(z) + v\psi_0(z) - \tfrac{3}{2}\psi_0^*(z)^2 + |\psi_0(z)|^2\psi_0(z) + 4g_1\psi_0\left(z + \frac{\Lambda}{2}\right) = 0. \quad (5.3)$$

In the two-harmonic limit we find the Fourier coefficients and wave vector to be Eqs. (4.6)–(4.8) with the substitutions $v \to v_g = v - 4g_1$ and $\gamma \to \gamma_g = \gamma + 4g_1/9$.

To study the three-dimensional vibrational modes, the methodology of the single-column study easily extends; the resulting equation of motion is

$$-\frac{M}{2}\frac{\partial^2 \Xi_i}{\partial t^2} = H[z, \psi_{0,i}(z)]\Xi_i(z) + g_1 \sum_j{}' \Xi_j(z). \quad (5.4)$$

H is the 2×2 matrix operator of (3.6) that depends on the interaction coupling constant through the static solution $\psi_0(z)$ of Eq. (5.3). Introducing plane-wave states $[i = (n_x, n_y)]$,

$$\Xi_i(z,t) = e^{-i\omega t} e^{i(k_x n_1 a + k_y n_2 a)} \times \begin{cases} \Xi_e \text{ if } n_1 + n_2 \text{ is even} \\ \Xi_o \text{ if } n_1 + n_2 \text{ is odd,} \end{cases} \quad (5.5)$$

the equation of motion reduces to the four-component eigenvalue problem

$$\frac{M}{2}\omega^2 \begin{pmatrix} \Xi_e(z) \\ \Xi_o(z) \end{pmatrix} = \begin{pmatrix} H(z) & c\mathbb{1} \\ c\mathbb{1} & H(z + \frac{\Lambda}{2}) \end{pmatrix} \begin{pmatrix} \Xi_e(z) \\ \Xi_o(z) \end{pmatrix}, \quad (5.6)$$

where we have used the fact that the Hamiltonian (5.4) for the even sites is identical to that of the odd sites except that it depends on $\psi_0(z)$ shifted by $\Lambda/2$ due to the $\sqrt{2}a \times \sqrt{2}a$ structure. Note that because of our method the 4×4 Hamiltonian (5.6) has period $\Lambda/3$. The coupling $c \equiv 2g_1[\cos(k_x a) + \cos(k_y a)]$ isolates the k_x, k_y dependence.

An elegant approach is available at $k_z = 0$ if we consider only phason degrees of freedom. The notation is $\psi_{0,i}(z) = \psi_0((n_1^i + n_2^i)\Lambda/2 + \Delta_i)$. Expanding about small Δ_i, we determine the equation of motion for the phase displacements to be

$$M\frac{\partial^2 \Delta_i}{\partial t^2} = -2\beta g_1 \sum_j{}' (\Delta_i - \Delta_j), \quad (5.7)$$

where we have introduced

$$\beta = \frac{{\rm Re} \int dz\, \psi_0^*(z)\psi_0''(z + \Lambda/2)}{\int dz\, |\psi_0'(z)|^2}. \quad (5.8)$$

The parameter β, a function of the system parameters γ, v, and g_1, is one at the normal-to-incommensurate transition and decreases toward zero as the temperature is lowered and second and higher harmonics increase. In terms of β, the frequencies are

$$\omega^2(k_z = 0) = \frac{4\beta g_1}{M}\{2 \pm [\cos(k_x a) + \cos(k_y a)]\}. \quad (5.9)$$

Not surprisingly, the minus sign solution is found to correspond to the two sublattices of columns moving together in an acoustic mode, while the plus sign is for the sublattices moving π out of phase in an optic mode. Also, because of the factor β, we note that as the temperature is lowered, the frequencies of all modes go to zero.

For $k_z \neq 0$, we turn to perturbation theory. A direct expansion about $g_1 = 0$, the free-column case, has the consequence that "turning on" g_1 also perturbs $H(z)$, and so the zero-order solutions and energies also change. This leads us rather to consider the formal expansion about $c = 0$. The zero-order energies $E_{\rm k}^{(0)}$ are the eigenvalues of H and are not the free column solutions; in particular there is no zero-energy eigenvalue. In this present analysis, $E_{\rm k}^{(0)}$ depends only on k_z, since the k_x and k_y dependence is contained entirely in c.

The form of the interaction is such that a particular $c = 0$ eigenstate on one column couples only to states on

other columns. The largest contribution to the change in the energy of a state due to the interaction comes from a mixing with degenerate states on the four nearest columns. To lowest order in g_1 over the energy separation between two zero-order states (where our expansion procedure is valid), we apply degenerate perturbation theory to Eq. (5.6). Let $\Xi^{k_z}(z)$ be an eigenstate of $H(z)$ (for any band, whose index we do not carry) with eigenvalue $E_{\mathbf{k}}^{(0)}$ for the $c=0$ case. Then we find for the frequencies

$$E_{\mathbf{k}} = \tfrac{1}{2}M\omega_{\mathbf{k}}^2 = E_{\mathbf{k}}^{(0)} \pm 2g_1[\cos(k_x a)+\cos(k_y a)] \times \left(e^{-ik_z\Lambda/2}\int dz\,\Xi^{k_z\dagger}(z)\Xi^{k_z}(z+\tfrac{1}{2}\Lambda)\right). \quad (5.10)$$

By considering the dependence of the displacements u on the corresponding Bloch states, it is found that the solution with the plus sign corresponds to a vibrational mode with the columns moving in phase and the minus sign to the columns moving out of phase.

We have seen how in the case of only nearest-neighbor interactions that, as the temperature is lowered and we approach the commensurate part of the phase diagram (Fig. 2), the frequencies of all modes in the basal plane go to zero. This is consistent with the observation that the effective restoring force between columns becomes weaker and weaker.[8] The following analysis applies only to the lower part of the phase boundary where the transition is second order[12] and our mode analysis can provide information about the transition. The conclusion that all modes go to zero simultaneously is unphysical, although it does indicates a possible instability of the $\sqrt{2}a \times \sqrt{2}a$ phase. To break the degeneracy, second-nearest neighbor interactions must be considered as their restoring force becomes comparatively more important. In the case that this is still not sufficient to completely determine an outcome, the effects of third-nearest neighbors must be considered, and so forth. We wish to see if there exists a particular soft mode that drives the second-order phase transition to the low-temperature incommensurate state and what our model can say about the phase structure.

After adding interaction terms between second- and third-nearest neighbors to the free energy, the earlier methods can be used with only slight modification. [To describe the incommensurate (and commensurate) phase, it has been determined that both g_1 and g_2 must be positive.[1,22]] There is a simplification because of the fact that for the $\sqrt{2}a \times \sqrt{2}a$ phase, the phases of the charge-density-wave on the second- and third-nearest neighbors from column i is that of column i, as opposed to π out of phase as in the nearest-neighbor case. The variational equation is Eq. (5.3) with $v \to v + 4(g_2+g_3)$. The calculation of the frequencies is repeated, and we again find Eq. (5.10), now with

$$E_{\mathbf{k}}^{(0)} = E_{k_z} + 2g_2\{\cos[(k_x+k_y)a]+\cos[(k_x-k_y)a]\} + 2g_3[\cos(2k_x a)+\cos(2k_y a)], \quad (5.11)$$

where E_{k_z}, an eigenvalue of $H[z,\psi_0(z)]$, depends on g_2 and g_3. For example, near the normal-to-incommensurate phase boundary, E_{k_z}, for $k_z \approx 0$ in the two-harmonic approximation, is Eq. (4.10) with k set to k_z. Similarly, at $k_z = 3\delta/2$ in the single-harmonic approximation, the four solutions are

$$E_{k_z=3\delta/2} = \frac{9}{4}\gamma\delta^2 + v + 2\phi_0^2 \pm \frac{3}{2}\phi_0 \pm \left[\left(\frac{3\phi_0}{2}\right)^2 + \phi_0^4\right]^{1/2}. \quad (5.12)$$

In both cases, the coefficients ϕ_0, ϕ_{-1} are now functions of $v_g = v - 4(g_1 - g_2 - g_3)$ and $\gamma_g = \gamma + 4g_1/9$.

In the search for a soft mode near the commensurate transition, we restrict ourselves to the basal plane in reciprocal space, since this is where such a mode would arise. At low temperatures in the incommensurate domain, higher harmonics play a more important role, and calculating $E_{\mathbf{k}}^{(0)}(k_z=0)$ analytically is difficult. Rather, we use the symmetry of the k_z state and expand about small variations in the phase of the order parameter for each column as was done for the nearest-neighbor only case. This approach contains the following approximation. Since the interaction couples free-column states with states of other columns, we are neglecting through consideration of only the variation of the CDW phases the interaction to any states other than those states on each column with the lowest frequency. For example, the matrix element between the lowest band solution on the ith column and second-lowest band solution on the jth column is neglected, as was not done, for example, when we calculated $E_{\mathbf{k}}$. This amounts to neglecting terms on the order of g^2 over the energy separation between the two lowest nondegenerate states on different columns. As the temperature is lowered, v becomes larger, and so for small intercolumn coupling g this approach is expected to be good.

We continue as before and include terms from the second- and third-nearest neighbor. As with the nearest-neighbor case, the coupling constants for the second- and

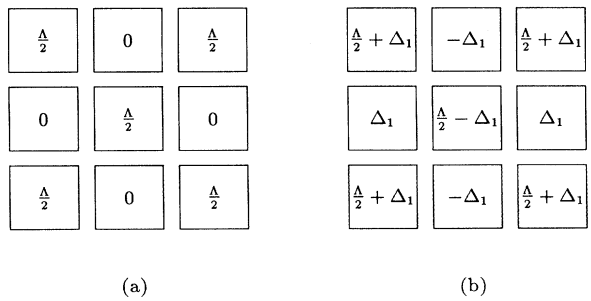

FIG. 4. Basal-plane projections for the two incommensurate phases of $NbTe_4$: (a) $\sqrt{2}a \times \sqrt{2}a$ and (b) $2a \times 2a$. The quantities label relative c axis displacement of the charge-density wave for each column. Λ is the period of the discommensurations, and $\Delta_1 \ll \Lambda/2$ is a small phase shift.

third-nearest-neighbor terms are again modified. Since the interaction in this case is between two sites with the same relative mean position [Fig. 4(a)], we find g_2 and g_3 to be multiplied by

$$\frac{\mathrm{Re}\int dz\,\psi_0^*(z)\psi_0''(z)}{\int dz\,|\psi_0'(z)|^2}=-1. \tag{5.13}$$

The frequencies are subsequently found to be

$$\begin{aligned}\frac{M}{2}\omega^2 = {}& 4\beta g_1\left[\sin^2\left(\frac{k_x a}{2}\right)+\sin^2\left(\frac{k_y a}{2}\right)\right]\\ & -4g_2\left[\sin^2\left(\frac{k_x+k_y}{2}a\right)+\sin^2\left(\frac{k_x-k_y}{2}a\right)\right]\\ & -4g_3\left[\sin^2(k_x a)+\sin^2(k_y a)\right].\end{aligned} \tag{5.14}$$

Consider for the moment the (possibly sufficient) case of only the first two nearest neighbors (set $g_3 = 0$). As the temperature drops β decreases, and we find the possibility of zero-frequency modes arising. There exists a critical temperature $v_c(\gamma)$, defined through

$$\beta(v_c,\gamma,g_1,g_2)=\frac{2g_2}{g_1} \tag{5.15}$$

at which the $\sqrt{2}a\times\sqrt{2}a$ phase becomes unstable. The wave vectors that label the distortions whose frequency goes to zero are those for which $k_x = 0$ or $k_y = 0$. This is unphysical and one looks to higher-order couplings to break this degeneracy.

Incorporation of third-nearest neighbors gives the dispersion relation (5.14). As the temperature is lowered in this case, there are two possibilities to consider. First, the velocity of the state $\mathbf{k} = 0$ goes to zero and suggests that the crystal may become unstable under homogeneous phason strain. Second is the case of a soft mode occurring at $\mathbf{k} = (\pi/a, 0, 0)$ [or similarly $\mathbf{k} = (0, \pi/a, 0)$]. The frequencies at these wave vectors are

$$\frac{M}{2}\omega^2=\begin{cases}(\beta g_1-2g_2-4g_3)(k_x^2+k_y^2)a^2, & \mathbf{k}\approx\mathbf{0}\\ 4(\beta g_1-2g_2), & \mathbf{k}=(\pi/a)\hat{\mathbf{x}}.\end{cases} \tag{5.16}$$

Since strain couples to the coordinate of a modulation and the frequency near $\mathbf{k} = 0$ is linear in k, the coefficient coupling to the phason strain parameter is $\beta g_1 - 2g_2 - 4g_3$. This is to be compared with $\beta g_1 - 2g_2$ for the wave vector at the zone boundary. As the temperature is lowered, which coefficient goes to zero first determines which instability occurs.

The sign of g_3 is crucial at this stage. If g_3 is positive, the strain coefficient goes to zero first as the temperature is lowered and the crystal becomes unstable under homogeneous phason strain. This would occur at a critical temperature defined through $\beta(v_{\mathrm{st}}) = (2g_2 + 4g_3)/g_1$. For g_3 negative, a soft mode at $\mathbf{k} = (\pi/a, 0, 0)$ arises and drives a transition from the $\sqrt{2}a\times\sqrt{2}a$ phase into a new structure characterized by the wave vector of the soft mode. The new state would have alternate layers of columns in the x (or y) direction shifted by an additional phase $\pm\Delta_1$ and, upon checking the relative charge-density-wave phase symmetry of the columns, would describe a $2a \times 2a$ incommensurate structure [Fig. 4(b)]. The phase boundary lies at the critical temperature defined in Eq. (5.15), which lies to the right of the incommensurate-commensurate boundary by an amount dependent on g_2 (Fig. 2). These conclusions are in agreement with the free-energy analysis,[8] where in addition a Landau theory for the incommensurate-to-incommensurate transition has been presented, and the new state is described in terms of the Fourier modes at $\mathbf{k} = \frac{\pi}{a}\hat{\mathbf{x}}$ and $\mathbf{k} = \frac{\pi}{a}\hat{\mathbf{y}}$.

Our result that one of two possibilities is expected fits well with the observation of a transition to a $2a \times 2a$ incommensurate phase.[6,7] This indicates that, within the context of our phenomenological model, the third-nearest-neighbor coupling is negative. This is consistent with the identical conclusion arrived at for the low-temperature $2a \times 2a$ *commensurate* phase.[22]

While looking for these modes, one must contend with dissipation that enters, for example, through commensuration effects or impurities. We can phenomenologically include this with the addition of a dissipation function

$$F_{\mathrm{diss}}=\frac{M}{2}\sum_i \mathrm{Re}\int dz\,\frac{1}{\tau}\frac{\partial\psi_i^*}{\partial t}\frac{\partial\psi_i}{\partial t}. \tag{5.17}$$

By repeating the derivation of the frequencies, one finds that instead of solving for ω^2, one is solving for $\omega^2 + i\omega/\tau$. Therefore, if the undamped frequencies are ω_0, the damped frequencies are given by

$$\omega_\pm=-i\frac{1}{2\tau}\pm\sqrt{\omega_0^2-\left(\frac{1}{2\tau}\right)^2}. \tag{5.18}$$

For short wavelengths k such that $\omega_0(k) > 1/2\tau$ we still have propagating modes. At long wavelengths, $\omega_0^2 = (ck)^2$ and

$$\omega_\pm=\begin{cases}-i/\tau\\ -i\tau(ck)^2.\end{cases} \tag{5.19}$$

These correspond, respectively, to a rapidly damped mode and a diffusive phason mode.

To search for the soft mode, we finally note that the wave vectors of the zero-frequency phason modes are those of the superlattice spots, i.e., the Fourier components of the term $|q_z u(\mathbf{q})|^2$. This follows from the fact that the phason is a vibration that changes only the origin of the displacement. Specifically,[2,23]

$$q_x=\pm\left(n_1+\frac{3m+1}{2}\right)a^*, \tag{5.20}$$

$$q_y=\pm\left(n_2+\frac{3m+1}{2}\right)a^*, \tag{5.21}$$

$$q_z=\pm\left[\left(n_3+\frac{2}{3}\right)c^*+(3m+1)\delta\right], \tag{5.22}$$

where, because of systematic absences due to glide planes, n_3 must be even at $q_x = 0$, $q_y = 0$, and $q_x = \pm q_y$. In addition, the relative diffraction peak intensities, being proportional to $|\phi_m|^2$, provide information about the magnitude of the Fourier components.[11]

VI. SUMMARY

A phenomenological charge-density-wave Landau model has been used to study the order-parameter vibrations in $NbTe_4$. We have assumed that the tellurium atoms move with the niobium in longitudinal vibrational modes, and so the essential properties can be modeled by the location of the niobium ions.

We first investigated the one-dimensional CDW model, a column in $NbTe_4$, by mapping the equation of motion into a two-component Schrödinger equation with a periodic potential and then used Bloch-state analysis to determine the modes for the normal, commensurate, and, near the normal-to-incommensurate boundary, incommensurate states. The spinor notation is the first that we know of in the context of collective modes in charge-density-wave systems. This formalism makes manifest a band structure centered about the incommensurate wave vector due to the discommensurate periodicity, in agreement with previous work. The expected zero-frequency phason mode corresponds to invariance of the free-energy with respect to a translational shift of the charge-density wave. The modes at the zone boundary consist of a mixed motion of amplitude and phase oscillations.

Our three-dimensional work on the collective modes of $NbTe_4$ is new. Our model relies on the assumption that the relative phases of single CDW modulations determine the crystal structure. The three-dimensional nature is described by a weak coupling between neighboring columns exhibiting charge-density waves. We find the presence of a soft mode that drives a continuous incommensurate-to-incommensurate transition.

In the $\sqrt{2}a \times \sqrt{2}a$ incommensurate phase, as the temperature is lowered and the commensurate domain is approached, the frequency of all modes in the reciprocal-space basal plane decreases if only nearest-neighbor interactions are considered. This agrees with the result[8] that the restoring force between nearest neighbors becomes weaker and weaker. One must then take into account second-nearest neighbors. The critical temperature at which the $\sqrt{2}a \times \sqrt{2}a$ phase becomes unstable is distinct from the commensurate phase boundary and the possibility of a second-order transition to another phase is considered. There still remains a degeneracy, and one must then take into account third-nearest neighbors. We find that the $\sqrt{2}a \times \sqrt{2}a$ phase can become unstable with respect to a modulation of wave vector $\mathbf{k} = (\pi/a, 0, 0)$ or $(0, \pi/a, 0)$ and consequently a $2a \times 2a$ basal-plane phase if the sign of the third-nearest-neighbor coupling constant is negative, or homogeneous phason strain if the constant is positive. Since a low-temperature incommensurate phase with a $2a \times 2a$ basal-plane structure has been observed, one can then conclude that the model is consistent, and that within the framework of our analysis the sign of the third-nearest-neighbor interaction is negative, in agreement with the analysis of the low-temperature commensurate phase.[22]

Finally, we have briefly described where in reciprocal space one would hope to find these soft modes and have phenomenologically incorporated possible dissipation effects.

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