Structural phase transitions with little phonon softening and first-order character

J. A. Krumhansl and R. J. Gooding
Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York, 14853-2501
(Received 14 September 1988)

We review a number of features of diffusionless structural transformations in materials where phonon dispersion or elastic constants are highly anisotropic and have anomalously low values in a few directions. Though those may change with temperature, they neither soften significantly nor become harmonically unstable at a transition. Standard soft-mode theory is not applicable. Instead, a generic first-order Landau-model free energy describes most of the features found experimentally, including limited phonon softening and precursor fluctuations (e.g., "central peak"). The microscopic basis of such models is demonstrated using anharmonic many-body phonon theory. The ideas are illustrated for ω phase transitions in zirconium.

I. INTRODUCTION

A significant fraction of solid-solid phase transitions are purely structural, i.e., they occur at constant composition and are diffusionless.[1] A significant conceptual advance was made, independently, by Cochran[2] and Anderson.[3] Given that these transformations are structural, they proposed that a phonon became unstable at temperature T_0, its (effective) frequency being $\omega_s^2 = a(T - T_0)$, whence the lattice displaced spontaneously in this mode to a finite amplitude which was limited by higher-order nonlinear contributions to the free energy. The eigenvector pattern for this mode defined the new crystal structure. This mechanism has been called the "soft-mode" model, and a large amount of effort has been devoted experimentally[4] (particularly inelastic neutron scattering) and theoretically[5] (many-body anharmonic phonon theory) toward verifying the predictions of the model. In specific respects, for a small percentage of structural transformations (e.g., Nb_3Sn, $SrTiO_3$, and K_2SeO_4), the predicted features have been verified. However, of the hundreds of transformations studied, true soft-mode systems can almost be counted on the fingers of one hand. The problem is thus that soft-mode theory is simply inapplicable; it is the purpose of this paper to discuss why, and outline by an example (the ω phase in Zr and its alloys) the nature of alternative, relevant models.

For orientation, we itemize particular features of the soft-mode model; they are as follows. (1) One phonon, or several equivalent phonons, has an anomalously low frequency compared to most of the modes. In fact, at low temperatures this mode would be harmonically unstable. (2) Anharmonic effects stabilize the higher-temperature phase and yield $\omega_s^2 \simeq a(T - T_0)$, where $T_0 > 0$, and is approximately the transition temperature. (3) Below T_0, in terms of an order parameter η_s, the static amplitude of a frozen-in soft mode, the simplest theory (widely used) is that the Landau-type free-energy expansion is $F(\eta_s) = a(T - T_0)(\eta_s^2/2) + b(\eta_s^4/4) + \cdots$. (4) From this free energy several results follow: (i) above T_0, $\langle \eta_s \rangle = 0$, (ii) below T_0, $\langle \eta_s \rangle \sim (T - T_0)^{1/2}$, i.e., the amplitude of the distortion increases "continuously" from zero, therefore corresponding to a second-order transformation, and the lattice displaces smoothly into the new structure, and (iii) the susceptibility diverges at T_0. (5) The Landau theory does not include fluctuations; when these are introduced and properly treated by renormalization-group theory,[6] there are modifications in the dependence of the order parameter, and critical fluctuations show the proper universality class behavior.[7] (6) Other than critical fluctuations, there is observed a "central peak," i.e., an essentially static amplitude of the oncoming phase, above T_c. Soft-mode theory in itself provides no explanation.

Are these features characteristic of structural phase transformations? The answer is not very. A survey of a number of alloys[8] and ferroelectrics,[9] and reports on several metallic elements[10] show the following. (1) Phonon frequencies soften only slightly, and do not indicate harmonic instability.[11] (2) Though frequently nearly continuous, there is a finite discontinuity in the microscopic order parameter at the transition, i.e., first order. (3) Critical fluctuations are usually missing, and susceptibilities do not diverge. (4) Strong precursors[12] of the "new" phase, or a distorted form of it, are observed far above the transition temperatures; these provide a mechanism for a central peak. These features are significantly different from the soft-mode doctrine, and have led to reservations[13] about the relevance of soft-mode theory to most structural transitions. Metallurgists are not surprised, and alternatives have been proposed; we show here that those may be placed in generic form and have similar microscopic origins; moreover, intrinsically nonlinear features characterize the physics of these transformations. Quasiharmonic concepts are not applicable.

Finally, in this introductory section, further features need to be mentioned. Many transitions involve both spatially modulated displacements with wavelengths near that of an anomalous (i.e., low-frequency) phonon, as well as elastic distortions [i.e., $q = (2\pi/\lambda) \rightarrow 0$]. They can be purely the former, or latter, or a mixture, and can even be incommensurate with the lattice. Such modulated phases must be regarded as true equilibrium phases, *not as due to defects*, and they can play an important intermediate role

in the thermodynamics of structural transformations and in their precursors.[14] There is a class of transitions in martensites and ferroelectrics, for which de Gennes[15] has used the term "nucleation type," which can be continuous (in some control parameter, e.g., stress field) yet not be of the "mode-instability" type. There is then structure at two length and time scales, one being the atomistic and associated with anomalous phonons, but the other at the mesoscopic scale, that is, domain structure, twin arrays, antiphase patterns, etc. The actual structures achieved by transformation are then determined by minimization of a free energy consisting of both a local and long-range (elastic, Coulombic, magnetic, etc.) contribution. In this case both the local (free) energetics and the geometry of the mesoscopic structure (i.e., domain-wall energy) determine the transition. Reviews of such transformations have been given by Khatchaturyan[16] and by Pushin, Kondrat'yev, and Khachin.[17] The richness of the general phenomena is remarkable, as metallurgists have realized for some time. Indeed the phenomenology of a generic formalism appropriate to first-order structural phase transitions was developed in detail by Cook,[18] who also illustrated the model for the ω phase transition in zirconium alloys extending earlier work of deFontaine.[19] Phenomenologically, Cook's concepts are in substantial agreement with many recent experiments, but have not been cited adequately. The work presented here complements Cook's ideas by extending the theoretical microscopic foundation, and by relating results of recent nonlinear theories of displacive transition regions (e.g., twin boundaries) to heterophase fluctuations. In addition, the nature of nonlinear coupling between anomalous phonon modulations and elastic distortion is noted; these more general, intrinsically nonlinear models have been applied by us[20] to martensitic transformations in the alkali metals, and by Lindgard and Mouritsen.[21]

II. GENERIC MODEL FOR DISPLACIVE FIRST-ORDER TRANSFORMATIONS

We discuss now the generic features of one anharmonic Landau-type model appropriate to displacive structural transitions. Motivation has been discussed by Cook,[18] and Kondrat'yev,[22] and by one of us.[13] In a great majority of cases the transition is dominated by one member of a small set of anomalously "soft" distortive modes, which because of great anisotropy occupy only narrow regions of the phonon-dispersion Brillouin zone. The former consideration suggests writing a Landau-type free energy in terms of only a few order parameters, i.e., static expectation of amplitudes or phases of the distortive modes; the latter results in the physics being essentially one dimensional, except possibly for higher-order effects. One more absolutely essential point needs to be made at the outset; unlike soft-mode models for second-order transitions, where as temperatures are lowered below T_c the new phase builds homogeneously from infinitesimal amplitude and can be described by quasiharmonic theory, for first-order transitions, as the transition is approached the "phonon" concept loses meaning because of the finite jump and large anharmonic content in order parameter. Fourier modes continue to have validity as a spatial basis set for displacements, however, if translational symmetry is effectively valid.

Consider a model free energy for a single-component order parameter η,

$$F=\frac{A}{2}\eta^2+\frac{B}{3}\eta^3+\frac{C}{4}\eta^4+\cdots . \tag{1}$$

If B is negative, A and C positive, for certain values of the parameters a first-order transition is possible, from $F=0$ at $\eta=0$ to some finite value of η where F is also zero. Various discussions of the physical origins of A, B, and C have been given[13,18,22] and will be discussed further below. A is *approximately* the quasiharmonic force constant, B and C are third- and fourth-order generalized force constants. The general behavior of F is shown in Fig. 1. Various fittings of the coefficients A, B, and C and their variation with temperature have been studied; because of the large value which η may take on, it has been noted that the conditions for the transition are far more sensitive to parameter variations than for second-order transitions. A generic functional representation does not seem to have been given; it is instructive to do so. Equation (1) contains three parameters; by scaling energy and displacement it can be reduced to a standard form with one control parameter a, which may vary with temperature

$$(F/F_0)=a\frac{\bar{\eta}^2}{2}-\frac{\bar{\eta}^3}{3}+\frac{\bar{\eta}^4}{4} , \tag{2}$$

where

$$F_0=(B^4/C^3),\quad \bar{\eta}=(C/|B|)\eta,\quad a=(AC/B^2) . \tag{3}$$

This generic form is plotted in Fig. 1. Its significant behavior is found by locating the extrema. The condition $\bar{\eta}=0$ corresponds to the parent phase. There are several regimes depending on the parameter a; the condition $(\partial F/\partial\bar{\eta})=0$ yields

$$\bar{\eta}=0,\quad \bar{\eta}=\frac{1\pm\sqrt{1-4a}}{2} . \tag{4}$$

Then the following conditions apply.

If $a>\frac{1}{4}$, F has a real minimum at $\bar{\eta}=0$, only.

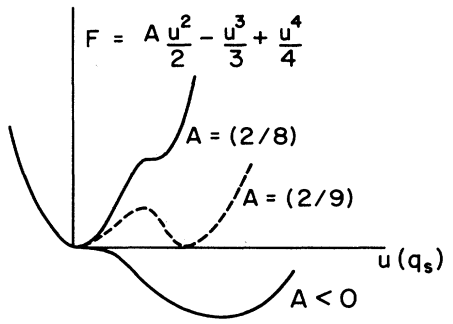

FIG. 1. A generic-model free-energy function for a single-order-parameter first-order phase transformation. Critical parameter values are indicated.

If $a=\frac{1}{4}$, F has a real minimum at $\bar{\eta}=0$, and an inflection at $\bar{\eta}=\frac{1}{2}$.

If $\frac{2}{9}<a<\frac{2}{8}$ $(=\frac{1}{4})$, F has a stable minimum at $\bar{\eta}=0$, a metastable minimum at $\bar{\eta}=(1+\sqrt{1-4a})/2$, and a relative maximum at $\bar{\eta}=(1-\sqrt{1-4a})/2$.

If $a=\frac{2}{9}$, F has two minimum values with $F=0$, at $\bar{\eta}=0$ and $\bar{\eta}=\frac{2}{3}$, and a maximum at $\bar{\eta}=\frac{1}{3}$. This is the condition for a first-order phase transition.

If $0<a<\frac{2}{9}$, F has a metastable minima at $\bar{\eta}=0$, and is stable at $\bar{\eta}>\frac{2}{3}$, with a maximum $F>0$ for $\bar{\eta}$ between.

The condition $a<0$ is not relevant to first-order transitions.

The microscopic physics of the parameters will be examined further below. Meanwhile, a number of phenomenological features distinctly different from soft-mode theory are found, many discussed by Cook,[18,23] as follows.

(1) Given $a=[AC/4B^2]$. At high temperatures anharmonic many-body theory yields $A=\omega_0^2+RT=\omega^2(T)$, where ω_0^2 is the "bare" harmonic frequency of the order parameter mode. Unlike soft-mode second-order transitions where $a\rightarrow 0$, here $a=\frac{2}{9}$ and $\omega^2(T)$ remains finite at the transition. Assuming that B and C are constant, the quasiharmonic behavior can thus be related to the transitional behavior.

(2) In the case where B and C are constant, the entire change in $\omega^2(T)$ from the first onset of significant anharmonicity, i.e. the inflection condition $a=\frac{2}{8}$ to transition T_1, is only $\omega^2(T_1)=\frac{8}{9}\omega_{\text{inf}}^2$, or ω decreases by only about 6%. This provides a generic explanation of why so many displacive transitions, known to result in modulations related to an anomalous low-frequency phonon, actually show very little softening as temperature is changed to achieve a transition. Note, particularly, $\omega^2(T)=R(T+T_0)$, rather than $R(T-T_0)$ as in conventional soft-mode theory. Thus in this model $\omega^2(T)$ softens to zero only for negative temperatures. This has been noted in many systems, a recent example being the $Ni_{62.5}Al_{37.5}$ alloy,[24] where the martensitic (first-order) transition is around 80 K, but $\omega^2(T)$ goes to zero linearly only at $T\approx -30$ K. However, there are other considerations for this alloy, which will be addressed elsewhere.

(3) Although it is convenient as a first approximation to assign the major temperature dependence of $a(T)$ to A, i.e., $\omega^2(T)$, in general $a=(AC/B^2)$ and $|B|$ and C can also have a temperature dependence. Particularly, if the transition is only weakly first order, B being small can have a strong temperature dependence. Thus, if both A and B are strongly proportional to temperature the quasiharmonic frequency may change by much more (less) than $\frac{8}{9}$ to achieve the first-order transition.

(4) At least *harmonically* the high-temperature structure is stable at all temperatures; the instability is anharmonic in origin, in contrast to soft-mode theory where anharmonicity stabilizes the high-temperature phase. Thus critical fluctuations are not to be expected and linear-response susceptibilities do not diverge at the transition (cf. de Gennes[15]).

(5) Perhaps most significantly this model provides one very clear mechanism for both precursor structure and a "central peak." The term central peak in the context of structural phase transitions simply means the appearance, at positions in reciprocal space for the distortive mode, on an intensity versus scattering energy loss (gain) plot, of a large essentially elastic (static) peak at zero energy loss in addition to the dynamic inelastic scattering. This central peak is found as a precursor to the transition in both second-order and first-order transitions. However, as Cook has pointed out[23] the mechanism in first-order transitions is fundamentally different from that for soft-mode (second-order) transitions.

The rationale is simple; below T_{inf} but above T_1, referring to Fig. 1, there is a metastable minimum. Heterophase fluctuations[25] from $\eta=0$ into this η_{met} are equivalent to the appearance of precursors of the new structure. In principle there is no reason why these fluctuations cannot set in at temperatures far above the actual transition at T_1. Obviously, this mechanism is completely different from second-order critical fluctuations, or defect effects. The spatial shape of such fluctuations was discussed by Cook,[23] in terms of a droplet model; but by extending the concepts proposed by Krumhansl and Schrieffer,[26] recent studies by Barsch and Krumhansl,[27] and similar ideas of Kondrat'yev,[22] it is clear that the fluctuations are not simple waves, but domains of the new phase separated by "domain walls" containing the parent phase, highly anharmonic quasistatic distortions. Thus the presence of a central peak can be a purely intrinsic manifestation of strong displacive nonlinearity in anisotropic materials with first-order transitions. Undoubtedly, such fluctuations can be nucleated by impurities to become locally stable, and there may be several other mechanisms for a central peak. The essential point is that it is an intrinsic property of first-order transitions, whether nucleated or not. Generally, though, the origin of the central peak is still an open question.

In summary, essentially all those features which are regarded as anomalies in soft-mode (second-order) models fall out quite naturally within the phenomenological first-order model.

III. AN ILLUSTRATIVE EXAMPLE—THE ω PHASE IN Zr ALLOYS

The previous discussion has been generic. As a result of experimental studies, and microscopic computations of electronic and phonon structure over the past two decades, a good deal is now known about the relevant parameters of a number of materials. Perhaps the ideal candidate for application of the present ideas is Zr and its alloys which display the formation of the ω phase. Its phonon spectrum is highly anisotropic. Figure 2 shows the phonon dispersion for Zr,[28] exhibiting a low-frequency longitudinal (1,1,1) branch with an anomaly at $\mathbf{q}_a=\frac{2}{3}(1,1,1)$. The dispersion surfaces are highly anisotropic, in such a sense as to be pseudo-one-dimensional. As discussed previously[13] various response functions and diffuse diffraction would mirror this anisotropy. Although this phonon broadens markedly in ω-transforming zirconium alloys as temperature is lowered to the transition,[29] it cannot be said to soften appreciably.

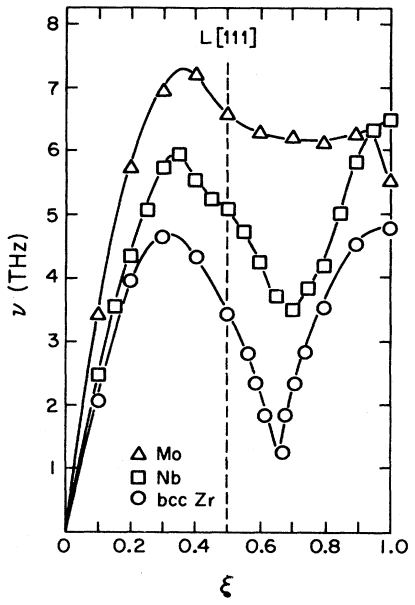

FIG. 2. Phonon dispersion data (Ref. 28) for Zr, Nb, and Mo. Note the pronounced difference in the $\frac{2}{3}(1,1,1)$ anomaly. This is attributed (Ref. 31) to differences in the role of bond-bending interactions between materials.

The least stable mode is the longitudinal $\frac{2}{3}(1,1,1)$, and the Landau-type free energy is developed in terms of the amplitude $A(\underline{x})$ and phase $\varphi(x)$ of a modulating function

$$\psi(\underline{x};\mathbf{q}_a)=A(\underline{x})e^{i\varphi(\underline{x})} \tag{5}$$

such that particle displacements are

$$\underline{u}(\underline{x})=\hat{e}^{\,L}_{\mathbf{q}_a}A(\underline{x})\sin[\mathbf{q}_a\cdot\underline{x}+\varphi(\underline{x})]\,, \tag{6}$$

where $\hat{e}^{\,L}_{\mathbf{q}_a}$ is the longitudinal eigenvector for this mode. Following the nonlinear Landau phenomenology for first-order transitions, and imposing that F must be invariant under lattice translations as well as the $\mathrm{Im}\bar{3}m$ space-group symmetry of the bcc phase, if $\mathbf{q}_a=\frac{2}{3}(1,1,1)$ then ψ must enter as ψ^3 and $(\psi^*)^3$ as well as $|\psi|^2$ and $|\psi|^4$. The arguments are similar to those in the Appendix of Ref. 20. The result to fourth order is that

$$F=\frac{1}{2}\omega_a^2(T)|\psi|^2+\frac{B}{3}[\psi^3+(\psi^*)^3]+\frac{C}{4}|\psi|^4+\cdots\,, \tag{7}$$

or

$$F=\frac{1}{2}\omega_a^2(T)|\psi|^2+\frac{B}{3}|\psi|^3\cos(3\varphi)+\frac{C}{4}|\psi|^4\,. \tag{8}$$

For a uniform ω phase, ψ=const, and the choice of phase determines the patterns of the modulation with respect to the bcc {111} planes. The lowest free energy is for (3φ) equal to an odd multiple of π; there are three equienergetic variants. Letting $|\psi|=\eta$ then

$$F=A\frac{\eta^2}{2}-B\frac{\eta^2}{3}+C\frac{\eta^4}{4}$$

as in Eq. (1). The consequences physically are as discussed in the previous section. With suitable choice of $|\psi|$ and φ the ω-phase displacement pattern may be obtained. The rationale for the amplitude $|\psi|$ to yield just the right magnitude of [111] displacements to produce the "perfect" ω phase is another matter, recently studied by Toledano *et al.*,[30(a)] as well as Horovitz, Gooding, and Krumhansl.[30(b)] The ω phase is a topic with many facets; the intent here was to relate the transition to a generic first-order Landau-type model.

IV. MICROSCOPIC CONSIDERATIONS

In the above $\omega_a^2(T)$ was taken to be $\omega_0^2+\alpha T$, where $\omega_0^2,\alpha>0$. This implies that for small displacements the high-temperature lattice is metastable at $T=0$, unlike the conventional soft-mode model where $\omega_0^2<0$.[3] On the other hand, for $T<T_1$ the free energy can have a lower energy minimum for finite displacements. Is there microscopic justification for this view? The answer is affirmative and explicitly demonstrated in the frozen phonon "first-principles" $T=0$ calculations by Ho, Fu, and Harmon.[31] Figure 3 exhibits their $T=0$ energy versus displacement amplitude in the $\frac{2}{3}(1,1,1)$ longitudinal mode for Zr, Nb, and Mo. For small displacments the upward curvature is >0, but the stable minimum is at a finite displacement which produces an ω-like distortion.

In addition to the energetics there is the question of how the coefficients in the Landau expansion relate to dynamical qualities, e.g., phonon frequencies as observed by neutron scattering.

The issues of principle involved here are not simple, but have already been discussed in connection with the anharmonic phonon many-body perturbation theory of soft modes, particularly in its application to displacive ferroelectrics by Cowley.[32] The difference in the present

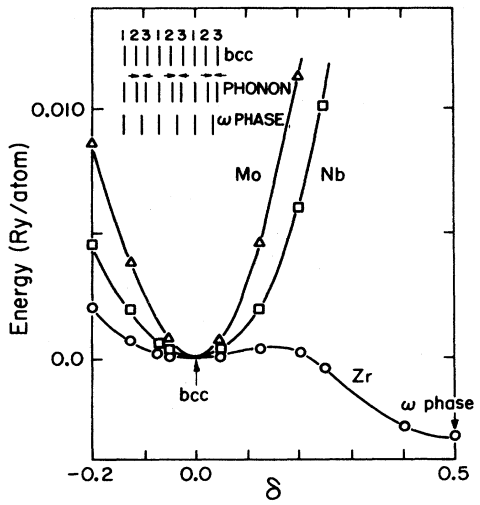

FIG. 3. The "frozen-phonon" zero-temperature energy of the $\frac{2}{3}(111)$ mode vs amplitude (Ref. 31) in Zr. The mode is harmonically metastable but unstable with respect to the ω phase for large amplitude displacements.

case, which makes the development of the theory straightforward, is that $\omega_a^2(0)>0$. By contrast, in soft-mode models the bare quadratic potentials yield negative $\omega_a^2(0)$, i.e., an imaginary frequency; the stability of the high-temperature lattice form is entirely dependent on anharmonicity.

In the present discussion the objective for microscopic theory is to determine how a Landau-type free energy of the form Eq. (1) may be obtained. The derivation must go far beyond the harmonic approximation for atomic motion in order to properly include the anharmonic contributions to the free energy. At present the only systematic method for doing this, because anharmonic interactions mix any harmonic lattice vibration with many others, is the "many-body" formalism developed by Maradudin and Fein,[33] and Cowley.[34] All of the many-body methods develop the theory in a perturbation series; it is most convenient and systematic, however, to use the method of thermodynamic Green's functions because, in addition to thermodynamic properties, correlation functions and scattering cross sections for neutrons can be computed within the same formalism, thus allowing cross checking between parameters in the free energy and other experimental data.

There is a conceptual similarity between a displacive transitions of the type being discussed, sometimes referred to as "ferroelastic," and "ferroelectric" transitions. Three types of displacements are involved: thermal phonons, elastic strain, and one or more lattice distortive modes (e.g., polarization, in the case of ferroelectrics). We have transcribed the principles of the microscopic analysis of ferroelectrics[32] to the present case.

Before proceeding to the details of the microscopic theory we note in briefest terms the main physical motivating elements of the method of thermodynamic Green's functions, as treated by perturbation theory. The microscopics of physical systems may be studied by (a) measuring average properties, i.e., energy, thermodynamic parameters, and elastic properties, and (b) by scattering experiments. Typically, then, one chooses some operator $B(0)$ which couples to a microscopic excitation at $t=0$ and then observes some property $A(t)$ at a later time t. At finite temperature, experimentally, the experiment samples a thermal distribution of configurations of the system under study, so that a thermally averaged correlation function $\langle A(t)B(0)\rangle_T$ would contain useful information. The development of the formalism for the response function (cf. Sec. 2.2, Cowley[34]) focuses on a retarded Green's function

$$G^R(AB,t)=\theta(t)\langle\psi|[A(t)B(0)]|\psi\rangle_T\ , \tag{9}$$

where $\theta(t)=1$, $t>0$; and zero, $t<0$. The Fourier transform $(2\pi)^{-1}\int dt\, G^R(A,B,t)\exp(i\Omega t)$ exhibits typical resonant behavior at the excitation frequencies of the system. If, for a Hamiltonian H, the exact states $|\nu\rangle$ and excitation energies E_ν are known then

$$G^R(A,B;\Omega)\propto\sum_\nu\frac{f(AB,\nu)}{(\Omega+i\epsilon)-(E_\nu/\hbar)} \tag{10}$$

exhibiting response when the probe frequency Ω is at resonance with any of the excitation energies of the system; in Eq. (10) ϵ is a positive infinitesimal quantity which ensures a retarded response.

The real problem, however, is that the proper states are usually not known. Specifically, if $H=H_0+H_a$, where H_0 is a harmonic phonon term whose states can be found, then H_a is a general anharmonic perturbation which mixes many of the states of H_0. The formal many-body methods were applied by Cowley in detail up to third- and fourth-order anharmonic terms in atomic displacements. The formalities of the expansion are discussed in Sec. 2.3 of Ref. 34; also in Sec. 4 of Ref. 34 it is shown that a very similar perturbation series can be used to compute the equilibrium free energy, thus providing a microscopic basis for relating response and thermodynamic parameters.

To develop the complete microscopic theory, say, for the [111] distortions of Zr, in the framework of anharmonic perturbation theory, the normal phonon modes and static elastic strains need to be included, as well as static distortions in the $\frac{2}{3}(111)$ mode. The general distortions of the lattice then fall into the following three classes.

(1) The large majority of displacements are nearly harmonic; at finite temperature these yield the usual thermal fluctuations. We denote them as $\{\hat{a}_q,\hat{a}_q^\dagger\}$, the set of harmonic phonons. (2) But a few important phonons can freeze out to produce static distortions described by order parameters like ψ_a in the Landau expansions above. Denote these as $\{\psi_a\}$. (3) Elastic strains may produce distortions. Denote these as $\{e_\alpha\}$. (4) Then denote the ensemble of all contributions to displacements $\{\underline{u}(\underline{x})\}=f[\{\hat{a}_q,\hat{a}_q^\dagger\},\{\psi_a\},\{e_{\alpha\beta}\}]$.

The potential for atomic motions is taken to be a power series of nth order terms in displacements $V=V_2+V_3+V_4+\cdots$. The following steps are then to be taken.

(i) Determine the normal modes of V_2 and a bare harmonic phonon basis set; in the case of Zr, expanding about the β-cubic lattice would yield phonons with $\omega_q^2>0$, i.e., ω_q real.

(ii) Determine the finite-temperature time-ordered Green's function for the anharmonic lattice. With translational symmetry, the phonon transform of the displacements can be used as variables, denoted for brevity $A(q,j,t)$, wave number q, branch j, and time dependent. Symbolically,

$$A(q,j,t)\equiv\left[\frac{\hbar}{2Nm\omega_q}\right]^{1/2}[a_{qj}^\dagger(t)+a_{-q,j}(t)] + A_q(\{\psi_a\})+A_q(\{e_{\alpha\beta}\})\ . \tag{11}$$

(iii) When the Green's function

$$G(q,j,j';t)=\langle TA(q,j,t)A(q,j',0)^*\rangle$$

for the purely harmonic phonons only is evaluated its Fourier transform satisfies the equation [$\beta=(k_BT)^{-1}$]

$$\beta\hbar\sum_{j'}\{[\omega^2(qj)-\Omega^2]\delta_{jj'}G(qj'j'',\Omega)\}=\delta_{jj''}2\omega(qj)\ , \tag{12}$$

where $\omega(qj)$ is the harmonic frequency for the jth branch. It is apparent, as expected, that in the harmonic approximation $\delta_{jj'}$ does not mix branches, so

$$\beta\hbar G(q,j,j;\Omega)=2\omega(q,j)[\omega^2(q,j)-\Omega^2]^{-1}$$

and the response is resonant at all $\Omega=\pm\omega(q,j)$. This simple physical result is as expected.

(iv) What about the phonon response of an anharmonic system? For most of the phonons, which are only slightly perturbed, it is possible and experimentally useful to modify the above by a self-energy correction. *Approximately*, a quasiharmonic representation is then of the form

$$G(q,j,j';\Omega)\simeq\delta_{jj'}2\omega(q,j)\{[\omega^2(q,j)-\Omega^2]+2\omega(qj)D\}^{-1}\ , \tag{13}$$

where $D=\Delta+i\Gamma$ is an anharmonic "self-energy" correction which shifts the harmonic resonances via Δ, and introduces decay into other phonons via Γ. In general, in the present case,

$$D=D(q,j,j';\Omega;T;\{\psi_a\};\{e_{\alpha\beta}\})\ , \tag{14}$$

where it is seen that both static modulations $\{\psi_a\}$ and static elastic strains $\{e_{\alpha\beta}\}$ can contribute to changes in the phonon spectrum. Inelastic neutron scattering experiments give specific information[4,34] about the shifts and lifetimes; in this case $\hbar\Omega$ is equal to the neutron scattering energy change. From such data information about V_3 and V_4 can be inferred. Such an analysis provided a formal basis for the soft-mode model. At a reasonably high temperature one may expect the anharmonic correction Δ to be proportion to T, in which case for the special mode, designated by $q_{a,j}$, the quasiharmonic frequency becomes $[\omega^2(q_{a,j})+aT]$. If the mode $q_{a,j}$ is harmonically unstable at zero temperature, i.e., $\omega^2(q_{a,j})$ is negative, then the quasiharmonic frequency satisfies

$$\bar{\omega}^2(q_{a,j})=\alpha(T-T_0)\ ,$$

where $\alpha T_0=|\omega^2(q_{a,j})|$. However if the reference lattice is harmonically stable or metastable at $T=0$, i.e., $\omega^2(q_{a,j})>0$, then

$$\bar{\omega}^2(q_{a,j})=\alpha(T+T_0)\ .$$

In the former case anharmonicity *stabilizes* the high-temperature lattice; in the latter case anharmonicity may *destabilize* the lattice.

(v) As noted above, the same formalism can be used to compute the finite-temperature free energy, if a "zero-temperature" harmonic phonon set is used as a starting basis, viz., for H_0. The procedure is summarized in Cowley's paper on ferroelectrics.[34] It is readily seen that if the atomic displacements, in general, are functions of phonons $A(q,j)$, modulations $\{\psi_a\}$, and strains $\{e_{\alpha\beta}\}$, when V_3 and V_4 are evaluated there will be all sorts of mixed terms. These can be collected systematically.

The form of F will then be

$$\begin{aligned}F=&F_1(\text{phonons},T)+F_2(\{\psi_a\},T)+F_3(\{e_{\alpha\beta}\},T)\\&+F_4(\{\psi_a\},\{e_{\alpha\beta}\},T)\\&+F_5(\{\psi_a\},\{e_{\alpha\beta}\},\text{phonons},T)\ .\end{aligned} \tag{15}$$

If $\{\psi_a\}=0$ and $\{e_{\alpha\beta}\}=0$, then F_1 is the free energy of phonons, only. The term F_2 yields the finite-temperature (phonon-renormalization) free energy for modulations $\{\psi_a\}$ of an unstrained crystal; up to fourth order the functional form can be related directly to terms in the Green's function, as for the ferroelectric case. F_3 determines finite-temperature elastic constants. F_4 couples modulation order parameters and elastic strain, generally important,[20] but not included in the previous pedagogical discussion. F_5 couples phonons, elastic strain, and order parameter, relating to such effects as thermal expansion, shift of phonon frequencies when static order parameters develop, and other mixed effects.

Thus, there is a systematic formalism relating microscopic (e.g., zero-temperature) computations of electronic and lattice-distortive energies to Landau forms of the finite-temperature free energy, within the framework of finite-temperature many-body perturbation theory.

This may seem mostly to be an issue of principle. However, there is one important question: In fact, should the coefficient of $\eta^2/2$ in the static F_2 [i.e., Eq. (1)] be the quasiharmonic frequency observed in dynamical experiments? The Green's function formalism provides an answer, as follows.

We are discussing transitions beginning from a high-temperature phase where $\langle\psi_a\rangle$ and $\langle e_{\alpha\beta}\rangle$, i.e., static distortions, are zero. For small deviations from this condition the dominant form in $F(\{\psi_a\})$ is the quadratic, for which the coefficient was taken to be $\omega_a^2(T)$. The necessary link between the microscopic theory and the free-energy function equation (1) now is to determine how (whether) $\omega_a^2(T)$ is related to other measurable quantities determined by V_2, V_3, and V_4. The result (see Ref. 32, p. 680) is the following: the quasiharmonic frequency, which is determined by neutron scattering if the damping Γ is small, is $\omega_a^2(\text{neutron})\simeq\omega_a^2(0)+2\omega_a(0)\Delta(q_a,T,\Omega)$, where $\omega_a^2(0)$ is the bare harmonic frequency and $(\hbar\Omega)$ is the neutron energy loss (gain). But the free-energy coefficient $\omega_a^2(T)$ is the same except $\Omega=0$ (*static*). In many cases the dependence of Δ on Ω is weak, so the neutron result is a good approximation to the free-energy coefficient. At high temperature $\omega_a^2(T)\simeq\omega_a^2(0)+cT$ comes out of the theory directly, for either neutron scattering or the free energy.

Of course, it is also possible by this approach to determine the higher-order anharmonic terms in the free energy, and strain-order parameter coupling terms. However, as long as the issues of principle are settled, this is probably better done directly from experiment.

V. DISCUSSION

The main purpose of this paper has been to discuss why first-order displacive transitions are so different conceptually from soft-mode second-order transitions.

First, a phenomenological-model free energy like

$$F=\frac{a}{2}\eta^2-B\frac{\eta^3}{3}+C\frac{\eta^4}{4}+\cdots$$

can describe transitions in which there is only small phonon softening, and in which precursor structures, "heterophase fluctuations" and "central peaks," are intrinsic features.

Our second objective was to show how, in principle, this static and apparently phenomenological free energy can be related by many-body phonon perturbation theory to first principles microscopic computations. In particular, we expect A to have the form $\omega_{q_a}^2(0)+RT$, where both terms are positive, unlike $A=r(T-T_0)$.

For illustration, we noted some of the features of the ω phase transition in Zr alloys, and that recent calculations[31] of electronic structure extended to finite (static) displacements in the Zr $\mathbf{q}=\frac{2}{3}(1,1,1)$ longitudinal-phonon mode produced just the kind of double-minimum anharmonic potential (for zero temperature) which would lead to the model proposed.

There are in general, many further aspects of models,[20,21,30] depending on application; multicomponent order parameters are probably needed in most cases; coupling to strain fields is always present to a degree; symmetry restrictions (i.e., group theory) must always be incorporated into determining the form of F.[20] For transverse modes in a β-cubic structure F cannot contain cubic terms, but must be written in terms of η^2, η^4, and η^6. Each case must be examined on its own. Finally we note that the complete description of *nearly* second-order transitions, such as the martensitic transformations in the superconducting A-15 compounds, is a provocative problem yet to be addressed.

ACKNOWLEDGMENTS

We wish to express our thanks for stimulating discussions with N. Ashcroft, G. Barsch, R. Berliner, B. Harmon, B. Horovitz, S. Shapiro, H. Smith, and L. Tanner. One of us (R.J.G.) acknowledges partial support from the National Sciences and Engineering Research Council of Canada. This work was supported by the National Science Foundation through the Cornell Material Science Center, and by the U.S. Department of Energy.

[1]J. W. Christian, *Theory of Phase Transformations in Metals and Alloys* (Pergamon, Oxford, 1965).
[2]W. Cochran, Adv. Phys. **9**, 387 (1960).
[3]P. W. Anderson, *Fizika Dielectrikov,* edited by G. I. Skanavi (Acad. Nauk SSR, Moscow, 1960).
[4]*Structural Phase Transitions,* edited by A. D. Bruce and R. A. Cowley (Taylor and Francis, London, 1981).
[5]A. A. Maradudin, Phys. Status Solidi **2**, 1493 (1962).
[6]Reference 4, Pt. II, pp. 112–214.
[7]Reference 4, p. 194.
[8]S. M. Shapiro, *Competing Interactions and Microstructures: Statics and Dynamics,* Vol. 27 of *Springer Proceedings in Physics,* edited by R. Le Sar, A. Bishop, and R. Heffner (Springer, Berlin, 1988).
[9]J. D. Axe, M. Lizumi, and G. Shirane, in *Incommensurate Phases in Dielectrics: 2,* edited by R. Blinc and A. P. Levanyuk (Elsevier, Amsterdam, 1986).
[10]H. G. Smith, Phys. Rev. Lett. **58**, 1228 (1987); O. Blaschko *et al., ibid.* **60**, 2800 (1988); see the discussion in O. Blaschko, M. de Podesta, and L. Piutschovias, Phys. Rev. B **37**, 4258 (1988).
[11]Cf. Ref. 8 (unpublished).
[12]L. E. Tanner, p. 74 of Ref. 8.
[13]J. A. Krumhansl, p. 50 of Ref. 8.
[14]G. R. Barsch, J. A. Krumhansl, L. E. Tanner, M. Wuttig, Scr. Metall. **21**, 1257 (1987).
[15]P. G. de Gennes, in *Fluctuations, Instabilities, and Phase Transitions,* edited by T. Riste (Plenum, New York, 1973).
[16]A. G. Khatchaturyan, *Theory of Structural Transformations in Solids* (Wiley, New York, 1983).
[17]V. G. Pushin, V. V. Kondrat'yev, and V. N. Khachin, Izv. Vuzov. Fiz. **3**, 5 (1985).
[18]H. E. Cook, Acta Metall. **23**, 1027 (1975); loc. cit. 1041 (1975).
[19]D. deFontaine, Acta Metall. **18**, 275 (1970).
[20]R. J. Gooding and J. A. Krumhansl, Phys. Rev. B **38**, 1695 (1988).
[21]P. A. Lindgard and O. G. Mouritsen, Phys. Rev. Lett. **57**, 2458 (1986).
[22]V. V. Kondrat'yev, Fiz. Met. Metalloved. **41**, 256 (1976) [Phys. Met. Metallogr. (USSR) **41**, 22 (1976)]; loc. cit. **47**, 102 (1979) [**47**, 82 (1979)].
[23]H. E. Cook, Phys. Rev. B **15**, 1477 (1977).
[24]Cf. Ref. 11; in $Ni_{62.5}Al_{37.5}$ the [???]-TA mode frequency softens by $\sim 30\%$ from well above down to the transition.
[25]J. Frenkel, *Kinetic Theory of Liquids* (Oxford University, New York, 1946).
[26]J. A. Krumhansl and J. R. Schrieffer, Phys. Rev. B **11**, 3535 (1975).
[27]G. R. Barsch and J. A. Krumhansl, Mettal. Trans. **19A**, 761 (1988).
[28]C. Stassis, J. Zaretsky, and N. Wakabayashi, Phys. Rev. Lett. **41**, 1726 (1978).
[29]J. D. Axe, D. T. Keating, and S. C. Moss, Phys. Rev. Lett. **35**, 530 (1975).
[30](a) V. P. Dmitriev, S. B. Bochal, Yu M. Gufan, and P. Toledano, Phys. Rev. Lett. **41**, 702 (1978); (b) B. Horovitz, R. J. Gooding, and J. A. Krumhansl (unpublished).
[31]K. M. Ho, C. L. Fu, and B. N. Harmon, Phys. Rev. B **29**, 1575 (1984).
[32]R. A. Cowley, Philos. Mag. **11**, 673 (1964).
[33]A. A. Maradudin and A. E. Fein, Phys. Rev. **128**, 2589 (1962).
[34]R. A. Cowley, Adv. Phys. **12**, 421 (1964).