Theory of the bcc-to-9R structural phase transformation of Li

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We present a Landau theory of the martensitic structural phase transformation undergone by bcc Li into the 9R phase. We propose that the transition occurs via incomplete softening of the $(\frac{1}{3}\frac{1}{3}0)$ Σ_4 phonon. Even though this branch does not soften to zero frequency (or even close to zero frequency), because the system is strongly anharmonic, a first-order transition can occur. Coupled to this distortion are the two homogeneous strains possessing the soft Zener elastic constant $\frac{1}{2}(c_{11}-c_{12})$. These strains shear and stretch the (110) planes. As a result of our studies, we propose that Li may transform into any member of a family of displacement patterns, the 9R stacking sequence corresponding to one solution within this family. In addition, our theory describes the stacking faults that are known to occur in terms of (i) domain-wall structures, which model twin faults, and (ii) a multiple domain-wall solution of the double sine-Gordon equation (an equation that describes the phase-modulation equilibrium condition around defects), which models deformation faults. We also discuss the possible extension of this theory to other β-cubic structures that undergo martensitic phase transformations, viz., the other alkali metals, and the TiNi(Fe) alloy system.

I. INTRODUCTION

The low-temperature phases of the alkali metals Li, Na, and K have been a subject of considerable controversy, and at present it must be admitted that the structures assumed by these materials have not been conclusively resolved. According to the theory of Alexander and McTague[1] one would expect that these materials solidify into a bcc structure, and then at low temperatures transform into some close-packed configuration. This latter observation follows immediately from the spherical symmetry of the s^1 electronic configuration of these nearly-free-electron systems. However, the specific form of these close-packed structures need not correspond to either of the familiar hcp or fcc lattices. In this paper we propose a theory of the low-temperature, long-period, close-packed 9R phase of Li (see note added in proof). In particular, we obtain a displacement pattern that represents the bcc-to-9R transition for particular values of the Landau parameters, although the general displacement pattern that we obtain corresponds to a family of possible distortions into which the bcc phase could transform. We also suggest that stacking faults can be modeled by allowing for spatial modulations of the order parameter. We then discuss the possible extension of this formalism to describe the low-temperature phases of some of the other β-cubic structures, including Na and K.

Initially[2] it was believed that around 75 K Li underwent a martensitic structural phase transformation from the bcc to the hcp structure, where the hcp lattice possessed a large number of stacking faults. This hypothesis, as well as any notions of describing the low-temperature phase of Li by the fcc structure, or possibly a matrix consisting of a mixture of hcp, fcc, and bcc phases, were shown to be inadequate in the work of McCarthy *et al.*[3] In 1984 Overhauser[4] proposed that it was possible for the elastic diffraction pattern of McCarthy *et al.*[3] to be understood in terms of a long-period close-packed lattice, in particular, the so-called 9R structure. This configuration corresponds to a unit cell possessing nine layers with the stacking of close-packed planes given by the sequence *ABABCBCAC*..., in contrast to the *AB*... hcp or *ABC*... fcc structures. Overhauser's conjecture was subsequently verified by the very precise work of Berliner and Werner,[5,6] and Smith.[7] The remaining task for the diffractionists seems to be the characterization of the stacking faults that are present.[7]

A number of other important experimental results have been found for this phase transition and we now review these. Firstly, the thermal capacity studies of Martin[8] showed a large hysteresis loop, extending up to 65 K above the transition. Further, Smith[7] found that the satellite peaks that were obtained when the Li sample was cooled to just below the transition temperature were still present when the crystal was heated up to 160 K. Thus, this data provides conclusive evidence for the strongly first-order nature of the transition.

Secondly, the phonon spectra of Li corresponds to a strongly anharmonic ionic Hamiltonian, a feature that may be substantiated by a number of independent results. This behavior is consistent with the large linear expansion coefficients of all of the alkali metals.[9] Also, McCarthy *et al.*[3] found that a harmonic Debye-Waller factor was inadequate to describe the temperature dependence of the bcc Bragg spots, and showed that a theory which included anharmonicities did suffice. In fact, on the basis of their work these authors suggested that the large anharmonicity they observed would prove to be an important feature of the phase transition. Further, Ernst *et al.*[10] have found that the $(\xi\xi 0)$ phonon branch, corresponding to a $[1\bar{1}0]$ polarization [which shall be denoted by the $(\xi\xi 0)$ Σ_4 branch from now on], is temperature dependent near the transition. To be specific, as the tem-

perature is lowered from 200 K to just above the transition, for $0.3 \leq \xi \leq 0.5$, although far from softening completely this phonon branch does decrease by as much as 15%. The softening is most pronounced below 100 K and thus does not seem to be in contradiction to the dynamical study of Smith,[7] which only extended down to 100 K. (An earlier study by Beg and Nielsen[11,12] also found a very small dip around $\xi \approx \frac{1}{3}$ at 293 K. Further, they were able to model this behavior using a five-neighbor general force Born–von Kármán model. Unfortunately, they did not study the variation of this branch with temperature.) We consider the above collection of results ample evidence for the strongly anharmonic character and incomplete phonon softening of the $(\xi\xi 0)$ Σ_4 phonon branch of Li.

Thirdly, Li possesses a so-called Zener mode,[13] viz., there exists a high degree of elastic anisotropy for which a very weak restoring force corresponds to the $(\xi\xi 0)$ Σ_4 long-wavelength sound wave. The elastic constant of this deformation is $\frac{1}{2}(c_{11}-c_{12})$. As we will discuss in the next section, there are also two homogeneous strains corresponding to this elastic constant. This behavior is characteristic of most β-cubic lattices[13] and has previously been suggested[14] as the driving force of the bcc-to-hcp martensitic structural phase transformation undergone by Zr; we propose here that the transition is driven by a combination of homogeneous elastic strains and incomplete phonon softening. It remains for one to determine how Li takes advantage of this soft elastic constant in its transformation to the 9R structure.

The fourth experimental result that is important concerns the recurring evidence[2–7,10] that stacking faults are always present in the low-temperature phase of Li. Stacking faults have two specific forms, viz., deformation and twin faults, and are illustrated in Fig. 1. One sees

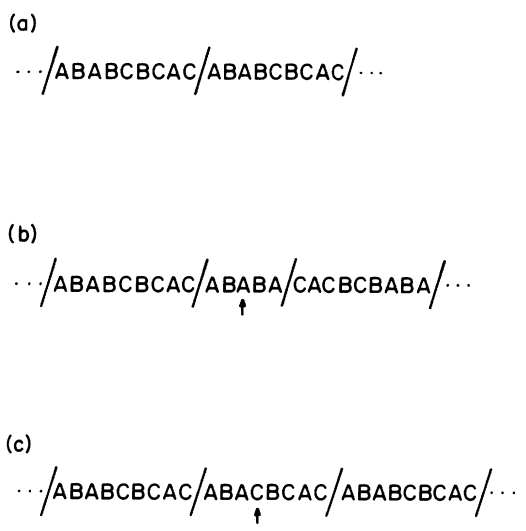

FIG. 1. (a) The 9R stacking sequence. (b) A twin fault in the 9R pattern has occurred at the position denoted by an arrow. Note that the two unit cells shown are mirror reflections of one another. (c) A deformation fault has occurred at the arrow. Note that the two unit cells shown are the same.

that a deformation fault corresponds to an interruption of the perfect 9R stacking, while a twin fault corresponds to a reversal of this stacking, thus producing a mirror-reflection plane at the fault (see Ref. 6 for an excellent discussion of the implications of the presence of stacking faults on the elastic diffraction pattern). At present it does not seem to be resolved[7] what kind of stacking faults are present, viz., whether deformation or twin faults are dominant. However, it is clear that a correct theory of the bcc-to-9R structural phase transformation of Li must allow for a finite density of some kind of stacking faults.

In the present work we propose that the incomplete phonon softening of the interior of the transverse $(\xi\xi 0)$ Σ_4 branch, coupled to the homogeneous strains associated with the soft Zener[13] elastic constant $\frac{1}{2}(c_{11}-c_{12})$, is responsible for the formation of the 9R structure. This is a consequence of the strongly anharmonic ionic Hamiltonian discussed above. Some general consequences of strong anharmonicity and incomplete phonon softening have previously been discussed by one of us.[15,16] We implement the Landau theory of phase transitions in order to describe this change in structure, and show that the transition involves two different components, viz., (i) homogeneous strains that shear and stretch the (110) planes, and (ii) an inhomogeneous modulation corresponding to the static $(\frac{1}{3}\frac{1}{3}0)$ Σ_4 phonon. This is consistent with a recently proposed geometrical model of the transition from the bcc-to-9R structure put forward by Wilson and de Podesta.[17] We find that for a perfect bcc crystal it is necessary in the free-energy expansion of the coupled distortions to include contributions up to eighth order in the Σ_4 mode and that when the other degrees of freedom are eliminated, the amplitude-only free-energy expansion can have a strongly negative sixth-order coefficient. This leads to a first-order phase transition from the bcc phase to the 9R structure, in agreement with experiment. Further, we show that twinning faults are naturally described in terms of domain walls in our model. We also discuss how deformation faults may possibly arise around defects in the bcc phase, viz., regions where the perfect $Im\bar{3}m$ space-group symmetry of the bcc phase is broken.

The paper is organized as follows. In Sec. II we present the free-energy density that describes the transition, as well as an analysis of the general distortion that results. In Sec. III we discuss stacking faults within the framework of our Landau theory. In Sec. IV we discuss the relationship between our work and experiment, and propose the possible extension of this theory to describe martensitic phase transformations undergone by other β-cubic structures. In the Appendix we provide the details of the transformation properties of the distortions under consideration that allow for the determination of the form of the Landau free-energy density.

II. LANDAU THEORY

The structural transformation connecting the bcc and 9R phases involves both intracellular and intercellular distortions (see Ref. 18 for a discussion of some features of these two kinds of ionic displacements). For Li the

relevant distortions may be described by (i) the homogeneous strains e_{ii}, $i=x,y,z$, and (ii) the $\{\frac{1}{3}\frac{1}{3}0\}$ Σ_4 phonons. These strains may be rewritten in terms of the following linear combinations:

$$e_1=\frac{1}{\sqrt{3}}(e_{xx}+e_{yy}+e_{zz}) , \tag{1a}$$

$$e_2=\frac{1}{\sqrt{2}}(e_{xx}-e_{yy}) , \tag{1b}$$

$$e_3=\frac{1}{\sqrt{6}}(e_{xx}+e_{yy}-2e_{zz}) . \tag{1c}$$

Then, as discussed by Cowley,[19] one has that e_1 corresponds to the (lowest-order) volume change undergone near the phase transition, and does not change the structure's symmetry. However, e_2 and e_3 are shear strains corresponding to the elastic constant $\frac{1}{2}(c_{11}-c_{12})$, viz., these are soft Zener modes. Also, the $(\frac{1}{3}\frac{1}{3}0)$ Σ_4 phonon corresponds to the distortion given by

$$\mathbf{u}(\mathbf{r})=A\hat{\mathbf{e}}_{[\bar{1}10]}\sin(\mathbf{k}\cdot\mathbf{r}+\phi) , \tag{2a}$$

$$\mathbf{k}=\tfrac{1}{3}(1,1,0) , \tag{2b}$$

and, as usual, one may describe this mode in terms of the two-component order parameter

$$\psi\equiv Ae^{i\phi} . \tag{2c}$$

In order for one to derive the necessary expansion of the Landau-type free-energy density, one requires a knowledge of the transformation properties of the above distortions. These are given in the Appendix. In this section we focus on just one possible variant of the $9R$ structure, and thus we describe the phase transition in terms of the four-component order parameter (e_2,e_3,A,ϕ). Then, including terms up to fourth order in the e_2 and e_3 strains and eighth order in ψ, we find that the free-energy density is

$$\begin{aligned}\tilde{F}=&\tfrac{1}{2}(c_{11}-c_{12})(e_2^2+e_3^2)\\&+\tfrac{1}{3}c_{333}e_3(e_3^2-3e_2^2)+\tfrac{1}{4}c_{2222}(e_2^2+e_3^2)^2\\&+\tfrac{1}{2}r_0\,|\psi|^2+\tfrac{1}{4}u_0\,|\psi|^4+\tfrac{1}{6}v_0\,|\psi|^6\\&+\tfrac{1}{6}v_1[\psi^6+(\psi^*)^6]+\tfrac{1}{8}w_0\,|\psi|^8+\gamma e_2[\psi^3+(\psi^*)^3]\end{aligned} \tag{3a}$$

where the free energy is given by

$$F=\int\tilde{F}\,dV \tag{3b}$$

[the full expansion is given in Eq. (A14)]. We note that the present discussion refers to a uniform order parameter, i.e., A and ϕ are independent of position; the extension to heterogeneous structures is outlined in the next section.

From this expansion one notes that up to the order considered the e_3 strain is not directly coupled to the $(\frac{1}{3}\frac{1}{3}0)$ Σ_4 phonon. Instead, to lowest order, the free energy is minimized for e_3 assuming the value given by

$$e_3=\frac{c_{333}}{(c_{11}-c_{12})}e_2^2 . \tag{4}$$

The equilibrium value of e_2 is given in terms of the ψ distortion, viz.,

$$e_2=-\frac{2\gamma}{c_{11}-c_{12}}A^3\cos(3\phi) . \tag{5}$$

One thus obtains an effective free-energy density in terms of ψ that may be written as

$$\begin{aligned}\tilde{F}=&\tfrac{1}{2}r_0A^2+\tfrac{1}{4}u_0A^4\\&+\left[\left[\frac{v_0}{6}-\frac{\gamma^2}{c_{11}-c_{12}}\right]\right.\\&\left.+\left[\frac{v_1}{3}-\frac{\gamma^2}{c_{11}-c_{12}}\right]\cos(6\phi)\right]A^6+\tfrac{1}{8}w_0A^8 .\end{aligned} \tag{6}$$

Since the phonon softening at $(\frac{1}{3}\frac{1}{3}0)$ Σ_4 is weak, which we assume corresponds to the interaction given by v_1 (see the discussion in Sec. IV), and the $\frac{1}{2}(c_{11}-c_{12})$ elastic constant is small, from now on we shall assume that

$$\frac{\gamma^2}{c_{11}-c_{12}}>\frac{v_1}{3} . \tag{7}$$

Then, Eq. (6) is minimized when the phase assumes one of the following values:

$$\phi_+=0,\pm\frac{2\pi}{3} , \tag{8a}$$

$$\phi_-=\pm\frac{\pi}{3},\pi . \tag{8b}$$

Our labeling of these six variants corresponds to the ±1 values taken by $\cos(3\phi)$. Note that the sign of the e_2 shear strain is dependent upon ϕ_+ or ϕ_- [see Eq. (5)], while e_3 is independent of this choice [see Eq. (4)].

Finally, the above analysis yields an effective free-energy density in terms of the amplitude only, viz.,

$$\tilde{F}=\tfrac{1}{2}r_0A^2+\tfrac{1}{4}u_0A^4+\tfrac{1}{6}v_{\text{eff}}A^6+\tfrac{1}{8}w_0A^8 , \tag{9a}$$

with

$$v_{\text{eff}}=v_0+2v_1-12\frac{\gamma^2}{c_{11}-c_{12}} . \tag{9b}$$

Since we are not considering the phase transition to be a soft-mode transition,[15,16] we analyze Eq. (9) subject to the constraint that $r_0>0$ for all temperatures of interest (see Ref. 20 for a discussion of soft-mode theories). Also, for stability one requires $w_0>0$. There seems to be no motivation to consider $u_0<0$, while, on the other hand, owing to the small value of $\frac{1}{2}(c_{11}-c_{12})$ in Li, we suppose that v_{eff} can be negative.[14] Further, if

$$v_{\text{eff}}<v_{\text{crit}} , \tag{10a}$$

where the critical value of v_{eff} is given by

$$v_{\rm crit}=-3\left[\frac{u_0 w_0}{2}\right]^{1/2}, \tag{10b}$$

a first-order transition to a phase characterized by $A\neq 0$ can result (note that if $v_{\rm eff}=v_{\rm crit}$ the transition occurs at $r_0=0$). According to the study of Felice *et al.*,[21] $\frac{1}{2}(c_{11}-c_{12})$ increases very slightly with decreasing temperature just above the transition. Thus, for now we assume that $v_{\rm eff}$ is not strongly temperature dependent, but rather take $r_0=|r|(T-T_0)$ where T_0 is well below the transition temperature. Then, as r_0 decreases a $A\neq 0$ phase can become the state of lowest energy, as is shown in Fig. 2 for $v_{\rm eff}=3v_{\rm crit}$. Further, Ernst *et al.*[10] have pointed out that the softening is quite small, possibly only 15%, and thus this version of the phase transition is consistent with experiment if $v_{\rm eff}\ll v_{\rm crit}$.

This is only one possible scenario for which a transition described by the expansion given in Eq. (9) can result. Others include a temperature-dependent $v_{\rm eff}$, a topic to be discussed in Sec. IV, as well as a defect-induced softening of $\frac{1}{2}(c_{11}-c_{12})$ and/or r_0, a topic to be discussed in a later publication.[22]

The structure arising from this transition may be described by the displacement pattern given by

$$\begin{aligned}\mathbf{u}(\mathbf{r})=&-\frac{|e_2|}{\sqrt{2}}\cos(3\phi_\pm)(x\hat{\mathbf{e}}_x-y\hat{\mathbf{e}}_y)\\&+\frac{|e_3|}{\sqrt{6}}(x\hat{\mathbf{e}}_x+y\hat{\mathbf{e}}_y-2z\hat{\mathbf{e}}_z)\\&+A\hat{\mathbf{e}}_{[\bar{1}10]}\sin(\mathbf{k}\cdot\mathbf{r}+\phi_\pm),\end{aligned} \tag{11}$$

providing that we assume that $\gamma>0$ and $c_{333}>0$. We have explicitly included the $\cos(3\phi_\pm)$ prefactor of the e_2 distortion since e_2 changes sign if ϕ_+ is changed to ϕ_-, while e_3 remains unchanged [see Eqs. (4) and (5)].

It is easily seen that the e_3 distortion can transform the (110) planes into two-dimensional triangular lattices, viz., the $\cos^{-1}(-\frac{1}{3})$ octahedral angle is transformed into the $\cos^{-1}(-\frac{1}{2})$ close-packed angle [see Fig. 1(c) of Wilson and de Podesta[17]]. To be specific, this strain contracts the (110) planes along the [001] direction, while stretching them in the $\pm[1\bar{1}0]$ directions. Also, the e_2 strain shears the (110) planes in either of the $\pm[110]$ directions, depending upon the choice of ϕ_+ or ϕ_-. This strain accounts for the rotation of the $(009)_{9R}$ satellite away from the $[110]_{\rm bcc}$ direction that was observed by Smith.[7] Thus, as seen from Fig. 1 of Ref. 17, for specific values of e_2, e_3, and A the displacement pattern given by Eq. (11) transforms the bcc structure into the ideal $9R$ lattice.

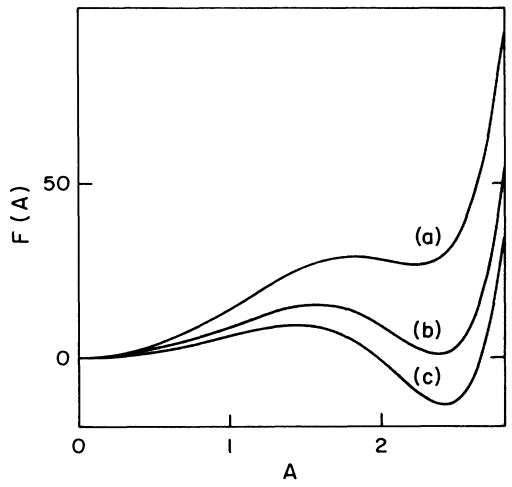

FIG. 2. The function $F(A)$ representing a first-order transition for $v_{\rm eff}=3v_{\rm crit}(u_0=w_0=1)$ with (a) $r_0=30$, (b) $r_0=20$, and (c) $r_0=15$.

It is to be stressed, however, that what we have shown does not convince us that the transformation must be to the ideal $9R$ structure, but rather the diffractionists[5–7] must determine whether or not the best fit to their satellite peaks does indeed correspond to the $9R$ structure, or to some other values of e_2, e_3, and A. Note that in this sense our theory is similar to that of Ref. 14 in that no symmetry-breaking terms appear in the free-energy expansion that would specifically choose the $9R$ structure (or the hcp lattice in Ref. 14). In view of the considerable effort that has been expended in understanding the stacking faults,[5–7] results that could be influenced by such a (e_2,e_3,A) determination, it seems imperative that this fitting be carried out.

It is very interesting to note that the transition we propose cannot lead from the bcc to the fcc or hcp phases. No values of e_2, e_3, and A lead to the hcp phase (this would require that the phonon minimum occur at the zone boundary), while

$$\begin{aligned}&e_2=0,\\&e_3=\left[\frac{4\sqrt{6}}{5}-\frac{9}{5}\right]\approx 0.16,\\&\frac{A}{a}=\left[\frac{2}{27}\right]^{1/2}\left[1+\frac{e_3}{\sqrt{6}}\right]\approx 0.29,\end{aligned} \tag{12}$$

gives rise to a bcc-to-fcc transition, where a is the bcc lattice constant. However, as shown by Eq. (4), our theory only allows for the development of a nonzero e_3 strain in conjunction with an e_2 strain, and thus the parameters in Eq. (12) are not compatible with this theory.

III. STACKING FAULTS

A. Twin faults

Our discussion of stacking faults begins with the extension of Eq. (6) to include spatial correlations of the order parameter ψ. In order for this aspect of our theory to be valid, these variations must occur over distances large compared with the interplanar spacings. Thus, we do not attempt to model the discrete stacking faults shown in Fig. 1, but rather we examine the low-energy spatial variations of the order parameter that can connect two (or more) regions of the $9R$ phase. Thus, for η being a coor-

dinate describing the [110] direction (viz., the direction parallel to $\mathbf{k}$) we include the term that behaves as $|\partial\psi/\partial\eta|^2$. Then, if we consider the phase-only terms[20] we have that the relevant expansion is

$$\tilde{F}_\phi = \tfrac{1}{2}gA^2\left[\frac{\partial\phi}{\partial\eta}\right]^2 + \left[\frac{v_1}{3} - \frac{\gamma^2}{c_{11}-c_{12}}\right]A^6\cos(6\phi) . \quad (13)$$

Thus, the function $\phi=\phi(\eta)$ is minimized by solutions of

$$\frac{d^2\phi}{d\eta^2} = \frac{1}{6d^2}\sin(6\phi) , \quad (14a)$$

where

$$\frac{1}{d^2} = \frac{36}{g}\left[\frac{\gamma^2}{c_{11}-c_{12}} - \frac{v_1}{3}\right]A^4 . \quad (14b)$$

Note that Eq. (7) ensures that d is purely real. Equation (14a) is recognized[23] as the time-independent sine-Gordon equation, whose solutions, some of which are known as domain walls, discommensurations, kinks, or solitons, are well known. In particular, the single soliton (kink) solution is

$$\phi(\eta) = \tfrac{2}{3}\tan^{-1}\{\exp[\pm(\eta-\eta_0)/d]\} + m\pi/3 \quad (15)$$

where m is some integer which for convenience we set equal to zero, and η_0 is an arbitrary constant. This describes the region of transition from one of the six variants to another, and defines the sequential ordering of variants. Choosing the plus sign of Eq. (15), one sees that $\phi(\eta\rightarrow-\infty)=0$ and $\phi(\eta\rightarrow+\infty)=\pi/3$. Thus, comparison of this result with Eq. (8) shows that for $\eta \ll \eta_0$ a ϕ_+ distortion is obtained, while for $\eta \gg \eta_0$ a ϕ_- distortion occurs. Also, Eq. (5) shows that the e_2 shearing of the (110) planes changes sign at $\eta=\eta_0$.

We now discuss the change in the structural distortion given by Eq. (11) that occurs as a result of this phase modulation. In the previous section it was noted that $v_{\text{eff}} \ll v_{\text{crit}}$ seemed to be compatible with the observed[10] small incomplete softening of the $\xi(110)\Sigma_4$ phonon above the phase transition. Further, the minimum around $\xi=\frac{1}{3}$ is likely to be very shallow, implying a small value for the constant g appearing in Eq. (13). Thus, it seems reasonable to assume that d is very small. This corresponds to the domain-wall thickness ($2d$) separating the ϕ_+ and ϕ_- solutions being small, possibly only a few interlayer spacings of the $9R$ structure. Then, the phase modulation given by Eq. (15) corresponds to the stacking sequence shown in Fig. 3, viz., this phase modulation represents a twin fault, the twinning occurring around $\eta=\eta_0$. To see this more clearly define the three-layer sequences $P_1=ABA$, $P_2=BCB$, and $P_3=CAC$. Then, a ϕ_+ distortion gives a $P_1P_2P_3$ sequence, while a ϕ_- distortion produces a $P_1P_3P_2$ pattern, and thus Eq. (15) corresponds to a $\ldots P_1P_2\text{“}P_3\text{”}P_2P_1\ldots$ stacking fault, where “P_3” represents the twin fault. Larger values of d simply increase the domain-wall thickness, thus further distorting the twin-fault region. (Note that at the twin fault e_2 and thus e_3 go to zero, i.e., locally the structure is still β-cubic. Thus, any crystallographic modeling of these faults should take this into account.) Away from η_0 the homogeneous $9R$ structure is still obtained.

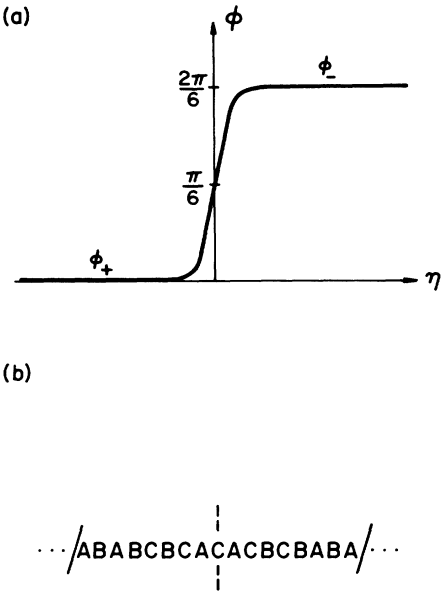

FIG. 3. (a) The phase-modulation function $\phi(\eta)$ corresponding to a single domain wall at $\eta_0=0$ connecting a ϕ_+ state with a ϕ_- state. (b) The stacking sequence corresponding to the above phase. Note that the central C layer is a mirror-reflection plane and represents a twin fault.

The only other solutions of Eq. (14) are $\phi=m\pi/3$, viz., the homogeneous $9R$ structure [note that $\phi=(2m+1)\pi/6$ are relative maxima of Eq. (6)], and the soliton lattice solution that may be cast in the form of elliptic sine functions.[24] One such solution is shown schematically in Fig. 4, from which it follows that the stacking sequences regularly alternate between ϕ_+ and

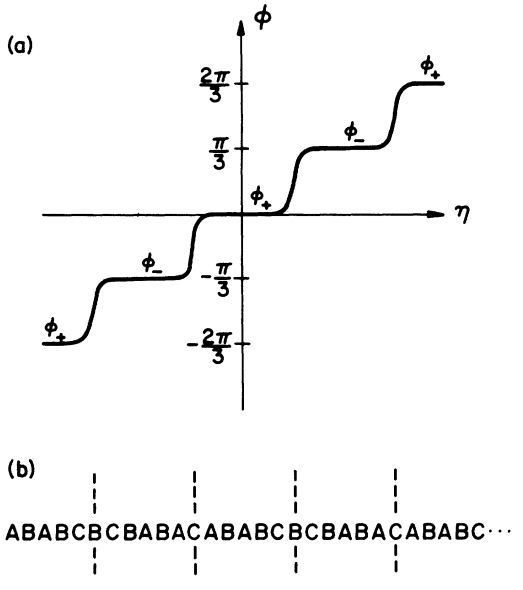

FIG. 4. (a) The phase-modulation function pertaining to the soliton lattice. Note the regular alteration between ϕ_+ and ϕ_- regions. (b) The stacking sequence representing the soliton lattice. The ϕ_+ and ϕ_- regions are separated by twin faults.

ϕ_- solutions. Thus, a regular twin-fault lattice would occur, and would be consistent with the highly correlated stacking faults proposed by Smith.[7]

In addition to a spatially-varying phase, one may also consider the amplitude-modulation[20] condition given by

$$g\frac{d^2A}{d\eta^2}=r_0A+u_0A^3+v_{\rm eff}A^5+w_0A^7 . \tag{16}$$

Then, for $\pm A_{9R}$ being the solutions minimizing Eq. (9) in the $9R$ phase, a domain-wall solution can connect $\pm A_{9R}$ states at $\eta\rightarrow-\infty$ with $\mp A_{9R}$ states at $\eta\rightarrow+\infty$. Thus, these may be viewed as being like multiple-phase solitons connecting the $\phi=0$ and $\phi=\pi$ states. Like a phase soliton, this solution also models twin faults if one includes in Eq. (11) the dependence of e_2 on the sign of the amplitude, as shown in Eq. (5).

Which of these two types of domain walls will be found in Li, viz., amplitude or phase modulations, is determined by the energies of these structures. The solution of Eq. (16) may only be obtained numerically,[25] and as seen from Eq. (14b) and Ref. 24, the energy of the phase solitons involves a large number of parameters occurring in the free-energy expansion. Consequently, based on the present theory, the determination of the lower energy domain wall cannot be made.

B. Deformation faults

As seen from Fig. 1, a deformation fault is simply represented as an interruption of the regular $9R$ sequence. The stacking fault shown occurs over only one layer, although more complicated multilayer defects are also possible. In our model this corresponds to ϕ_+ or ϕ_- solutions being present on both sides of the deformation fault. However, it is to be stressed that there are no solutions to Eq. (14) possessing this property. For example,

$$\phi(\eta)=\tfrac{4}{3}\tan^{-1}[\exp(\pm\zeta\eta)] , \tag{17}$$

is not a solution to Eq. (14) for any value of ζ. Thus, if one only considers the four-component order parameter (e_2,e_3,A,ϕ), deformation faults are not predicted to arise from the phase transition. We consider this to be an important conclusion of our theory. However, in view of the result provided by Berliner and Werner,[6] viz., that they were able to model their powder-diffraction profiles using only deformation faults, we have extended our theory in search of deformation faults.

Suppose that at some location the perfect $Im\bar{3}m$ space-group symmetry of the bcc phase is broken by the presence of a defect.[22] Then, the symmetry restrictions may no longer be enforced on the free-energy density expansion near the defect. Thus, Eq. (3) must be augmented by terms that were disallowed in the analysis presented in the Appendix. This leads to the introduction of the (lowest-order) term which is of the form

$$\tilde{F}_{\rm def}=\frac{\delta}{3}[\psi^3+(\psi^*)^3] , \tag{18a}$$

where the free energy in the region of the defect is given by

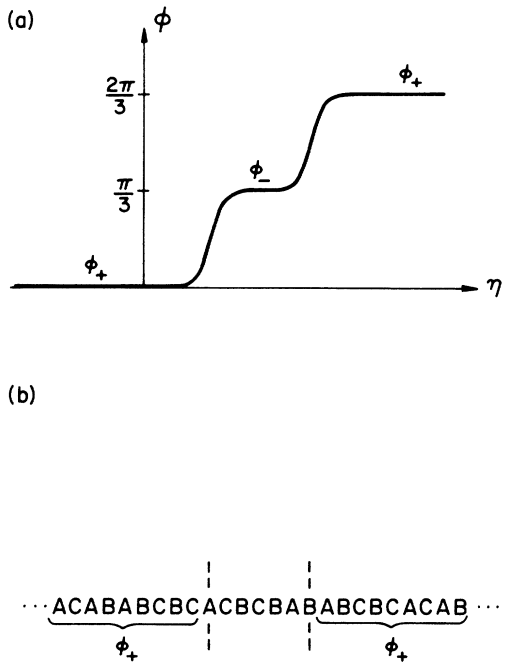

FIG. 5. (a) The phase-modulation function solving the double sine-Gordon equation. The width of the ϕ_- plateau varies as $O(\ln(\epsilon^{-1}))$. (b) The stacking sequence corresponding to a deformation fault.

$$F_{\rm def}=\int_{V_{\rm def}}(\tilde{F}+\tilde{F}_{\rm def})dV , \tag{18b}$$

$V_{\rm def}$ being the volume of the region around the defect. [Note that we are approximating that the Landau coefficient δ, which appears in Eq. (18a), is independent of "position."[22]] Consequently, Eq. (14) becomes

$$\frac{d^2\phi}{d\eta^2}=\frac{1}{6d^2}\sin(6\phi)+\epsilon\sin(3\phi) \tag{19}$$

where ϵ represents that local perturbation induced by the defect on the phase-modulation equilibrium condition. Equation (18) is a double sine-Gordon equation, and has one particular solution[26] that is shown schematically in Fig. (5a). To be specific, one sees that a double domain wall can occur connecting the ϕ_+ or ϕ_- solutions on both sides of the domain-wall structure. Thus, the phase modulation corresponds to deformation faults, as shown in Fig. (5b), and we predict that this form of faulting will only occur around defects.[6]

The effect of terms such as $\tilde{F}_{\rm def}$ on the phase transition will be discussed in a later publication.[22] For now we simply note that it has previously been suggested[27] that martensitic instabilities seed around defects.

IV. DISCUSSION

We now discuss the relationship between a number of aspects of our theory and experiment. Firstly, consider the small dip in the $(\xi\xi0)$ Σ_4 phonon dispersion curve obtained by Ernst *et al.*[10] In this paper we have asserted that this incomplete softening (viz., the increased anhar-

monic content of this branch near $\xi=\frac{1}{3}$) occurs as a manifestation of an incipient low-temperature instability of the bcc phase relative to the phase corresponding to the displacement pattern stated in Eq. (11). In order for us to explain our motivation for this assumption we must make the connection between the anharmonic phonon Hamiltonian and the measurement of phonon dispersion relations. The formal aspects of this problem involve the renormalization of the harmonic phonon frequencies by the phonon self-energy correction.[28] In terms of our formalism we compare the expansion given by Eq. (3a) to that describing the incomplete phonon softening of the $(\xi\xi\xi)$ L (longitudinal) mode of Zr,[29] which is represented by Eq. (18a) if ψ is taken to represent the $(\frac{1}{3}\frac{1}{3}\frac{1}{3})$ L mode.[16,30] Clearly, the analogous term in Eq. (3a) is the $v_1\psi^6$ term. The $(\xi\xi 0)$ Σ_4 phonon of Li is renormalized by a sixth-order term in the anharmonic phonon Hamiltonian, while the $(\xi\xi\xi)$ L phonon of Zr is renormalized by a cubic term, and thus the lesser degree of softening of the Li branch that is observed is to be expected.

In spite of this, it still remains for the $\xi=\frac{1}{3}$ minimum to be proven. Apparently there are difficulties with the experimental verification of this point (note that Refs. 7 and 10 obtain different conclusions regarding any dip being present). One possible resolution to this problem could come from the work of Harmon and collaborators. Their first-principles frozen-phonon calculation for some bcc metals[31] verified the instability of bcc Zr relative to the ω-phase, and a similar investigation of Li (and possibly the other alkali metals) could prove invaluable in testing our assertion. In particular, if such a calculation obtained an energy-versus-amplitude curve for the $(\frac{1}{3}\frac{1}{3}0)$ Σ_4 phonon that mirrored Fig. 2, we would consider this a verification of this aspect of our theory.

Secondly, we discuss how the amplitude-only free-energy expansion of Eq. (9) can account for the transition to the $9R$ phase if v_{eff} is temperature dependent. This version of the phase transition requires that an association be made between precursor states occurring above the transition (obtained on cooling) and the experimental determination of the elastic constants. For r_0 being nearly temperature independent and v_{eff} decreasing with decreasing temperature Eq. (9) still behaves (approximately) as shown in Fig. 2, although the evolution of the $A\neq 0$ minimum is considerably more sensitive to changes in v_{eff} than it is to changes in r_0. Thus, from Fig. 2 one sees that above the transition temperature metastable $A\neq 0$ states may occur, regions of the crystal that are known as precursors. (This is not true for second-order transitions where the $A\neq 0$ minima do not occur until below the phase transition.) Some evidence for this has already been reported above the bcc-to- (presumably) hcp transition (see note added in proof) undergone in Na (Ref. 32) in studies of the diffuse scattering, as well as possibly in Li.[10]

If the softening of the elastic constant that we are suggesting does indeed occur one cannot utilize the results of inelastic neutron scattering studies to determine this since one must probe the elastic behavior right at the zone center, not out in the interior of the zone [note the stiffening of $\frac{1}{2}(c_{11}-c_{12})$ reported by Smith[7] followed from neutron studies that only extended down to $\xi\approx 0.1$ and is not a zone-center study]. The most dramatic evidence of this latter assertion comes from studies of the $A15$ compounds[33] where the neutron results were found to be completely inadequate in displaying the pronounced softening of the $\frac{1}{2}(c_{11}-c_{12})$ elastic constant that is found in V_3Si and Nb_3Sn just above their cubic-to-tetragonal structural phase transformations. Further, ultrasonic techniques would also suffer from the difficulty that they would not be sampling just the bcc structure's elastic moduli, but rather those of a bcc-precursor matrix, if precursors do indeed occur. To be specific, the pulse-overlap method employed by Felice *et al.*[21] found a small stiffening of $\frac{1}{2}(c_{11}-c_{12})$ with decreasing temperature just above the transition, a result that could be interpreted as the stiffening of the measured elastic modulus due to the presence of precursors. In fact, a stiffening of the measured elastic constant seems to be consistent with the appearance of precursors taking advantage of the small resistance to the e_2 and e_3 distortions given in Eq. (11).

Unfortunately, a satisfactory theory describing the effects of precursors on ultrasonic experiments (including the resonant method, which may also suffer from these problems) is presently unavailable. This is certainly required before the above assertions could be tested. For now we simply note the apparent consistency of the softening of this elastic constant above the transition with (i) Eq. (9) describing the bcc-to-$9R$ transformation, (ii) the existence of precursors above T_c and their subsequent effect on the experimental determination of this elastic constant, and (iii) the discussion of the $9R$ phase presented by Wilson and de Podesta.[17]

We now turn our attention to the relation between our theory and the modulation of the electronic density that would occur at the transition, viz., what about charge-density waves in Li? For the electron density $\rho(\mathbf{r})$ being modulated according to

$$\rho(\mathbf{r})=\rho_0+(\rho_{\mathbf{k}}e^{i\mathbf{k}\cdot\mathbf{r}}+\text{c.c.})\ , \tag{20}$$

where ρ_0 is a constant and $\mathbf{k}$ is given by Eq. (2b), the coupling of ρ with the structural distortions that we have been discussing is given by

$$\tilde{F}_\rho=\tfrac{1}{2}\alpha\,|\,\rho_{\mathbf{k}}\,|^2+\tfrac{1}{3}\beta_1(\rho_{\mathbf{k}}^3+\text{c.c.})+\tfrac{1}{3}\beta_2(\rho_{\mathbf{k}}\psi^2+\text{c.c.})\ . \tag{21}$$

One may then show that providing $\beta_1>0$, both u_0 and the prefactor of $\cos(6\phi)$ in Eq. (6) are reduced by the β_2 coupling, viz., v_{crit} becomes less negative while v_{eff} becomes more negative. Thus, the consequences of this coupling are (i) that a commensurate, charge-density modulation occurs below the transition such that $\rho_{\mathbf{k}}\sim A^2$, and (ii) the conditions under which the transition can take place are enhanced (the degree to which this occurs cannot be estimated from the present theory). We wish to stress that the charge-density modulation that occurs is parasitic, and simply represents the response of the electron distribution to the structural distortion that Li undergoes, and that in no way does our theory rely on the presence of some electronic instability in the bcc phase.[34] [An identical analysis also applies to the coupling of the $\{\frac{1}{3}\frac{1}{3}0\}\Sigma_1$ (longitudinal) phonons with the Σ_4 phonons.]

It seems likely to us that this theory may be extended to describe the martensitic phase transformations of other β-cubic materials. Both Na (Ref. 35) and K (Refs. 34 and 36) have been reported to exist in incommensurate charge-density-wave states, while others have refuted these claims.[17,37–39] The low-temperature martensitic phase transition undergone by Na is first order and strongly hysteretic. Also, an incomplete phonon softening of the $(\xi\xi 0)$ Σ_4 branch has already been observed,[32] and even though these authors suggested that the phonon minimum occurred at the zone boundary (leading to the transition to the hcp phase), the strongest temperature dependence just above the transition could well be taken to occur at $\xi=\frac{1}{3}$. Further, as mentioned previously, diffuse scattering was observed,[32] consistent with the presence of precursors. Thus, it seems possible (see note added in proof) that Na may undergo a transformation to the $9R$ phase, instead of either the reported[32] hcp phase, or the alleged incommensurate charge-density-wave state.[35]

The notion of K undergoing a transition to the $9R$ phase has been discussed at length by Wilson and de Podesta.[17] Of particular importance is the study of Dolling and Meyer[40] examining the possibility of anomalous Σ_4 phonons at 4.3 K. It is clear that a minimum at $\xi=\frac{1}{3}$ was not observed. Note, however, the similarity between the data points of Beg and Nielsen's study[11,12] of the Σ_4 phonons in Li and those of Ref. 40. To be specific, in each case a fitted smooth curve passing through the data points may be found, although the data points at $\xi=\frac{1}{3}$ clearly are (slightly) beneath such curves (but within experimental resolution) for both these materials. Further, no $9R$ satellites have been confirmed,[38,39] and satellites at other positions (see Fig. 3 of Smith[7]) have yet to be observed (however, see the discussion of Ref. 41 provided by Wilson and de Podesta[17]). Thus, the proposition of Wilson and de Podesta[17] cannot be justified (at this time) by our theory, although it is possible that many of the low-temperature anomalies[42] observed in K are due to an incompletely transformed bcc-$9R$ matrix, viz., precursors.

Some β-phase alloys are also candidates for undergoing their martensitic transitions according to the theory we are proposing for Li in this paper, and for now we consider its application to the TiNi(Fe) alloy system. It has been established[43] that there is an incomplete softening of the $(\xi\xi 0)$ Σ_4 branch for $\xi=\frac{1}{3}$, and that the $\frac{1}{2}(c_{11}-c_{12})$ elastic constant decreases with decreasing temperature by about 10% from room temperature to the transition temperature, which is approximately 230 K. Further, the symmetry of the ordered TiNi structure ($Pm\bar{3}m$) also allows for it to be described by the free-energy expansion given in Eq. (3a). Below the transition an anomalous satellite pattern has been observed[44] that may not simply be described by a commensurate phase transition at $\xi=\frac{1}{3}$ relative to the untransformed bcc Bragg spots. It has been proposed[45] that this satellite pattern may be explained by the presence of a discommensuration lattice that does not significantly alter the bcc spots, but does modify the location of the satellites. One may show that the displacement pattern that follows from the v_4 term of Eq. (A14), with or without discommensurations such as those given in Eq. (15), can provide an alternate explanation of this data.

Note added in proof. It has recently been shown[47] that Na also transforms to the $9R$ phase with a transformation temperature above 18 K.

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APPENDIX: TRANSFORMATION PROPERTIES OF THE ORDER PARAMETERS

Firstly, we determine the transformation properties of the displacements of wave vector $\mathbf{k}_1=\xi(1,1,0)$. The little cogroup of wave vector $\mathbf{k}_1$, corresponding to the Σ line of symmetry, is given by $G_0(\mathbf{k}_1)=\{E,C_{2(xy)},\sigma_{\bar{x}y},\sigma_z\}$ (we follow the labeling of space-group operators given in Ref. 46), and its irreducible representations are given in Table I. There is one ion per primitive unit cell and for these three branches one may show that the displacement representation decomposes according to $\Sigma=\Sigma_1+\Sigma_2+\Sigma_4$. The $\Sigma_4(\mathbf{k}_1)$ phonon corresponds to a transverse mode propagating in the [110] direction polarized along the $[\bar{1}10]$ direction. For $\xi=\frac{1}{3}$, this distortion is given in Eq. (2). The star of $\mathbf{k}_1$ may be denoted by $\pm\mathbf{k}_1,\ldots,\pm\mathbf{k}_6$, where $\mathbf{k}_2=\xi(0,1,1)$, $\mathbf{k}_3=\xi(1,0,1)$, $\mathbf{k}_4=\xi(1,\bar{1},0)$, $\mathbf{k}_5=\xi(0,1,\bar{1})$, and $\mathbf{k}_6=\xi(\bar{1},1,0)$. Then we introduce the other Σ_4 order parameters $\psi_2,\ldots,\psi_6$, with $\psi_j=A_j e^{i\phi_j}$, according to

$$\begin{aligned}
\mathbf{u}_2(\mathbf{r})&=A_2\hat{\mathbf{e}}_{[0\bar{1}1]}\sin(\mathbf{k}_2\cdot\mathbf{r}+\phi_2)\ ,\\
\mathbf{u}_3(\mathbf{r})&=A_3\hat{\mathbf{e}}_{[10\bar{1}]}\sin(\mathbf{k}_3\cdot\mathbf{r}+\phi_3)\ ,\\
\mathbf{u}_4(\mathbf{r})&=A_4\hat{\mathbf{e}}_{[110]}\sin(\mathbf{k}_4\cdot\mathbf{r}+\phi_4)\ ,\\
\mathbf{u}_5(\mathbf{r})&=A_5\hat{\mathbf{e}}_{[011]}\sin(\mathbf{k}_5\cdot\mathbf{r}+\phi_5)\ ,\\
\mathbf{u}_6(\mathbf{r})&=A_6\hat{\mathbf{e}}_{[101]}\sin(\mathbf{k}_6\cdot\mathbf{r}+\phi_6)\ .
\end{aligned}\tag{A1}$$

Having defined these distortions, we determine their

TABLE I. The irreducible representations (irreps) of the little cogroup of wave vector $\mathbf{k}_1$. In the last column we have displayed the association of these representations with the phonon modes that transform under them, viz., the longitudinal mode (L) transforms under the identity irrep, while the transverse mode polarized along the z direction (T_z) transforms under Σ_2 irrep, and $T_{\bar{x}y}$ transforms under the Σ_4 irrep.

	E	$C_{2(xy)}$	$\sigma_{\bar{x}y}$	σ_z	
Σ_1	1	1	1	1	L
Σ_2	1	−1	1	−1	T_z
Σ_3	1	1	−1	−1	
Σ_4	1	−1	−1	1	$T_{\bar{x}y}$

transformation properties under the action of the bcc space-group symmetry in order that the correct form of the free-energy expansion may be constructed. The space group of bcc Li is $Im\bar{3}m$, and the generators of this group may be taken to be (i) the bcc primitive translation vectors, and (ii) the elements[46] $i, C_{31}^{+}, C_{4z}^{+}$. The transformation properties of the ψ_j may be determined by noting that a vector function $\mathbf{U}(\mathbf{r})$ transforms under the operator $\hat{O}$ according to

$$\hat{O}(\mathbf{U}(\mathbf{r}))\rightarrow(\hat{O}\mathbf{U})(\{\hat{O}^{-1}\mathbf{r}\}) . \tag{A2}$$

Thus, we find

$$\{E\mid\mathbf{t}\}\psi_j\rightarrow\psi_j\exp(-i\mathbf{k}_j\cdot\mathbf{t}) , \tag{A3}$$

$$\{i\mid\mathbf{0}\}\psi_j\rightarrow\psi_j^{*} , \tag{A4}$$

$$\{C_{31}^{+}\mid\mathbf{0}\}\begin{bmatrix}\psi_1\\ \psi_2\\ \psi_3\\ \psi_4\\ \psi_5\\ \psi_6\end{bmatrix}\rightarrow\begin{bmatrix}\psi_2\\ \psi_3\\ \psi_1\\ \psi_5\\ \psi_6\\ \psi_4\end{bmatrix} , \tag{A5}$$

$$\{C_{4z}^{+}\mid\mathbf{0}\}\begin{bmatrix}\psi_1\\ \psi_2\\ \psi_3\\ \psi_4\\ \psi_5\\ \psi_6\end{bmatrix}\rightarrow\begin{bmatrix}\psi_4^{*}\\ \psi_6\\ -\psi_2\\ \psi_1\\ \psi_3^{*}\\ -\psi_5^{*}\end{bmatrix} . \tag{A6}$$

The transformation properties of e_1, e_2, and e_3 defined in Eq. (1) may be determined from those of the e_{ii}, $i=x,y,z$. We find

$$\{E\mid\mathbf{t}\}e_{ii}\rightarrow e_{ii} , \tag{A7}$$

$$\{i\mid\mathbf{0}\}e_{ii}\rightarrow e_{ii} , \tag{A8}$$

$$\{C_{31}^{+}\mid\mathbf{0}\}\begin{bmatrix}e_{xx}\\ e_{yy}\\ e_{zz}\end{bmatrix}\rightarrow\begin{bmatrix}e_{yy}\\ e_{zz}\\ e_{xx}\end{bmatrix} , \tag{A9}$$

$$\{C_{4z}^{+}\mid\mathbf{0}\}\begin{bmatrix}e_{xx}\\ e_{yy}\\ e_{zz}\end{bmatrix}\rightarrow\begin{bmatrix}e_{yy}\\ e_{xx}\\ e_{zz}\end{bmatrix} . \tag{A10}$$

The free-energy density must be invariant under the action of the space group of the bcc phase of Li, viz.,

$$\hat{O}(\tilde{F})\rightarrow\tilde{F},\quad \hat{O}\in Im\bar{3}m \tag{A11}$$

and this restricts the form of the expansion. For example, consider $\xi=\frac{1}{3}$ and the term

$$\tilde{F}_{13}=\sum_{i=x,y,z}\sum_{j=1}^{6}A_{ij}e_{ii}(\psi_j^3+\text{c.c.}) . \tag{A12}$$

Then, Eq. (A11) requires that $\tilde{F}_{13}$ assume the form

$$\tilde{F}_{13}=A_{11}[(e_{xx}-e_{yy})(\psi_1^3-\psi_4^3)+(e_{yy}-e_{zz})(\psi_2^3-\psi_5^3)+(e_{zz}-e_{xx})(\psi_3^3-\psi_6^3)+\text{c.c.}] . \tag{A13}$$

Applying similar analysis to all terms up to sixth order in the ψ_j and third order in e_2 and e_3, and including the lowest order coupling term between these distortions, we find

$$\begin{aligned}\tilde{F}=&\sum_{j=1}^{6}(\tfrac{1}{2}r_0\mid\psi_j\mid^2+\tfrac{1}{4}u_0\mid\psi_j\mid^4+\tfrac{1}{6}v_0\mid\psi_j\mid^6+\tfrac{1}{6}v_1[\psi_j^6+(\psi_j^{*})^6]+\tfrac{1}{8}w_0\mid\psi_j\mid^8)+\tfrac{1}{4}u_1\sum_{j=1}^{6}\sum_{k=1}^{6}{}'\mid\psi_j\psi_k\mid^2\\&+\tfrac{1}{6}v_2\sum_{j=1}^{6}\sum_{k=1}^{6}{}'\mid\psi_j\mid^2\mid\psi_k\mid^4+\tfrac{1}{6}v_3\sum_{j=1}^{6}\sum_{k=1}^{6}{}'\sum_{l=1}^{6}{}''\mid\psi_j\psi_k\psi_l\mid^2\\&+\tfrac{1}{6}v_4[(\psi_4\psi_5\psi_6)^2+(\psi_4\psi_2\psi_3^{*})^2+(\psi_5\psi_1^{*}\psi_3)^2+(\psi_6\psi_1\psi_2^{*})^2+\text{c.c.}]\\&+\tfrac{1}{2}(c_{11}-c_{12})(e_2^2+e_3^2)+\tfrac{1}{3}c_{333}e_3(e_3^2-3e_2^2)+\tfrac{1}{4}c_{2222}(e_2^2+e_3^2)^2+\tilde{F}_{13} .\end{aligned} \tag{A14}$$

We have included the w_0 and c_{2222} terms such that the high-temperature ground state pertains to $e_2=e_3=\psi_j=0$. It is to be noted that the term given in Eq. (18a) does not appear in the above expansion. This follows immediately from application of Eq. (A6) to

$$\tilde{F}_3=\frac{\delta}{3}\sum_{j=1}^{6}[\psi_j^3+(\psi_j^{*})^3] . \tag{A15}$$

Since this term is not an invariant under the space-group symmetry of bcc Li, one must set $\delta=0$ in the ordered phase.

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