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Structural transition in A-15 compounds: Possible Landau theory descriptions

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A comparison is made of Landau theories of the martensitic transition in A-15 compounds involving direct coupling of the electronic order parameter to the lattice dilation (as in the Labbe-Friedel model) or coupling due to pairing of transition-metal atoms (as in Gorkov's Peierls-gap model worked out in a previous paper). It is shown that the predictions of the two *phenomenological* (as distinguished from microscopic) models in respect to existing experimental results are identical in form. Consequently, on the basis of current data, the A-15 compounds are amenable to a generalized Landau description involving either or both types of couplings. Tests of microscopic models based on either or both mechanisms are proposed.

I. INTRODUCTION

It is well known that the same phenomenological Landau theory can be obtained from more than one microscopic model. Consequently, the success of a Landau theory of the martensitic transition in the A-15 compounds[1] Nb_3Sn and V_3Si based on the Gorkov model,[2] while implying that the model was a viable picture of the structural instability of these materials, did not single it out as the correct model. Indeed, another microscopic model, due to Labbe and Friedel,[3] had been in existence even before the Gorkov model, and has been successful to roughly the same degree as the Gorkov model.

Both models attribute the structural instability to a degeneracy of the electronic bands formed of the d orbitals of the transition-metal atoms in the cubic A-15 phase [Fig. 1(a)] which is removed in the tetragonal phase in which the transition-metal atoms pair up in two of the three chains [Fig. 1(b)]. Both models use one-dimensional bands, but differ in the placement of the Fermi level and consequently in details of the instability mechanism. The Labbe-Friedel model puts the Fermi level just above the bottom of the band of Γ, the center of the Brillouin zone, where there is a threefold degeneracy of the one-dimensional (1D) bands, which is split in the tetragonal phase. The transition is thus pictured as a second-order Jahn-Teller effect. In the Gorkov model, the bands are filled up to the zone boundary (X point), where because of the symmetry of the A-15 phase (the periodicity of the linear chains being twice that of the unit cell) two bands meet linearly with opposite slopes. At low enough temperatures, the system transforms to the tetragonal phase where the transition-metal atoms are paired up because the pairing creates a gap at the Fermi surface and lowers the electronic energy, like in the Peierls 1D chain.[4]

Both models can explain the basic features of the martensitic transition but have drawbacks, most of which are due to the one dimensionality. One of the major problems is the existence of the large Kohn singularity in one dimension which would drive the acoustical mode coupled to the $2k_f$ mode soft before the $k=0$ mode. In the Labbe-Friedel model this is circumvented by placing the Fermi level very close to the bottom of the band so that $E_F \sim T_m$, the martensitic transition temperature, and little movement of the Fermi level is possible without destroying the $k=0$ distortion.[5] The X-point Gorkov model in fact uses the Kohn singularity as the instability mechanism, since the $2k_F$ mode for a half-filled 1D band is the $k=0$ mode in the A-15 structure, but as in the Labbe-Friedel case, much movement of the Fermi energy is not possible unless large commensurability terms are present which would make the transition heavily first order. Thus, for example, the results[6] of doping Nb_3Sn with Sb and Al are not well accounted for. In addition, the drop in magnetic susceptibility below the transition is predicted to be 5–10 times the observed result.[7,8] The noninteracting chain Gorkov model also faces problems due to the extreme shortness of the zero-temperature coherence length (determined from the marked phonon softening for the transverse mode in the [110] direction[9]), since the result for the Peierls model is $\xi_0/a \sim E_F/T_m$ ($>>1$). Additional evidence against the one dimensionality of the bands comes from the Mattheiss band-structure calculation[10] which shows neigher a threefold degeneracy at the Γ point nor Gorkov-like bands near the Fermi surface.

The problems arising on account of the Kohn anomaly, susceptibility drop below the transition and phonon softening, can be remedied significantly by considering interactions among the linear chains. An attempt in this direction has been made for the Gorkov model by Gorkov and Dorokhov[11] by including inter-

chain interactions to the lowest order. However, the bands used by the above authors do not resemble those of Mattheiss near the Fermi energy. Any connection of their results with the real situation in A-15 compounds is therefore, on the basis of present evidence, purely speculative. A tight-binding model with interchain interactions,[8,12] based in part on the Mattheiss work has been formulated by the present author, and shown to yield results which agree with experiment at least as well as the other models. The model is three dimensional so the Kohn singularity is weak and not as much of a problem. The model exhibits both a Jahn-Teller degeneracy splitting and a Peierls gap which are found to be jointly responsible for the martensitic transition. The model is capable of explaining the drop in susceptibility below the transition[12] and the extensive softening of the [110] transverse phonon.[13]

Thus electronic models to date attribute the martensitic transition in A-15 compounds to either a direct coupling of the electronic order parameter to the strain tensor or a coupling via the mode which pairs the transition-metal atoms in the linear chains on the faces (Fig. 1).

The purpose of this paper is to examine *from the point of view of a phenomenological Landau-type description* of the structural transition in the A-15 compounds, what the differences in the predictions of the two kinds of models are, and to see how a hybrid model, such as the one of Ref. 12, works on a phenomenological basis. The result is that all three models yield the same *form* for anomalies in the elastic moduli and ultrasonic attenuation, for nonlinear stress-strain effects and impurity effects, and differ mainly in the softening of the $\Gamma_{12}(+)$ optical mode. This implies that both the Jahn-Teller triple-degeneracy splitting and the Peierls-gap models in suitably modified form are viable models for the martensitic transition in the A-15 compounds and the question as to which model is appropriate depends on details of the band structure near the Fermi surface in these compounds.

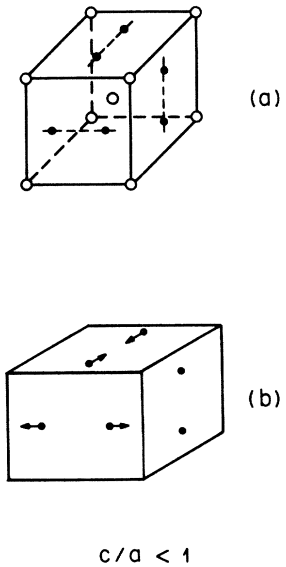


FIG. 1. (a) Schematic structure of the A-15 compounds A_3B, with the B (○) atoms forming a bcc lattice and transition-metal A (●) atoms forming linear chains on the faces. (b) Tetragonal distortion of the unit cell below the martensitic transition, accompanied by a $\Gamma_{12}(+)$ sublattice distortion, with $c/a < 1$, as in Nb_3Sn.

Section II reviews the results of the Landau theory based on the Gorkov model expounded in Ref. 1. In Sec. III, the Landau theory for a triple-degeneracy splitting where the electronic order parameters are directly coupled to the strain tensor is worked out. Calculational details have been left out at places where the procedure is analogous to that used for the Gorkov model, and the reader is referred to Ref. 1 for those. Lattice-dynamical models of the A-15 compounds based on the Labbe-Friedel or other Jahn-Teller models with phenomenological electronic density of states[14,15] exist in literature. However, the present work, being a pure Landau-type description, is independent of any microscopic model of the electronic bands, and analytic results are obtained under the same assumptions as the Landau theory of the Gorkov model,[1] which offers direct comparison of the results. Section IV contains a formulation of the Landau free-energy functional appropriate to the tight-binding model of Ref. 12 and arguments are given as to its results. Some other possible models are also discussed. Since the fits to experimental results are the same as in Ref. 1, the reader is referred to that paper for comparison with experiment. The paper ends with a summary of the results along with qualitative remarks on alloying and pressure effects, on superconductivity, and on some experimental checks of the microscopic nature of the transition.

II. LANDAU THEORY OF THE GORKOV MODEL

In Ref. 1, where the Landau theory of the Gorkov model of the A-15 compounds is worked out, the electronic order parameters are the amplitudes of the three charge-density waves of wave vector $k = 2\pi/a$ along the three chains of transition-metal atoms which open up gaps at the three X points. The order parameters $\phi_\mu(\vec{r})$ ($\mu = x,y,z$) may be taken to be real since we wish to discuss only the case where the charge-density wave is commensurate with the lattice. The electronic part of the free energy is then taken to be

$$F_{\rm el} = \frac{1}{2}\int d^3r \sum_\mu \{a_\mu \phi_\mu^2(\vec{r}) + b'\phi_\mu^4(\vec{r}) + c_1[\partial_\mu \phi_\mu(\vec{r})]^2 + c_2[\nabla\phi_\mu(\vec{r})]^2\} \ . \quad (1)$$

As usual, the parameters a_μ are approximately linear in temperature near the transition temperature

$$a_\mu = a'(T - T_{m0}^{\mu}) \ , \tag{2}$$

while the other parameters are temperature independent. The transition temperature T_{m0}^{μ} for each chain is maximum for placement of the Fermi energy at the X-point energy which is strain dependent, so that for E_F near the X-point energy

$$T_{m0}^{\mu} = T_{m0}^{\max} - \alpha(E_F - E_{x\mu})^2 \ , \tag{3a}$$

where

$$E_{x\mu} = E_{x0} + \lambda_1 \epsilon_{\mu\mu} + \lambda_2 \sum_{\nu} \epsilon_{\nu\nu} \tag{3b}$$

and $\epsilon_{\mu\nu}$ is the strain tensor. The charge-density waves are coupled in the Gorkov model to the optical modes Q_μ which pair the atoms in the three chains, and thus

$$F_{\text{el-ph}} = f \int d^3r \sum_{\mu} Q_\mu(\vec{r}) \phi_\mu(\vec{r}) \ . \tag{4}$$

Finally one includes the relevant portion of the elastic energy (in the harmonic approximation)

$$F_{\text{ph}} = \frac{1}{2} \int d^3r \left[\sum_{\mu} K_{11} \epsilon_{\mu\mu}^2 + \sum_{\mu \neq \nu} (2K_{44} \epsilon_{\mu\nu} \epsilon_{\mu\nu} + K_{12} \epsilon_{\mu\mu} \epsilon_{\nu\nu}) + 2h \left[\epsilon_{xx}(Q_y - Q_z) + \epsilon_{yy}(Q_z - Q_x) + \epsilon_{zz}(Q_x - Q_y) \right] \right.$$
$$\left. + \sum_{\mu} (K_0 + G) Q_\mu^2 + G \sum_{\mu \neq \nu} Q_\mu Q_\nu - 2 \sum_{\mu} \zeta_\mu \epsilon_{\mu\mu} \right] \ . \tag{5}$$

The last term is the coupling to external stresses and permits calculation of elastic constants. The elastic constants K_{11}, K_{12}, and K_{44} are unrenormalized values of the conventional cubic elastic constants c_{11}, c_{12}, and c_{44}, respectively.

To do dynamics, one includes the kinetic energy of the lattice,

$$K = \frac{1}{2} \int d^3r \left[m \sum [\delta_\mu(\vec{r})]^2 + M \sum [\dot{Q}_\mu(\vec{r})]^2 \right] \ , \tag{6}$$

where δ_μ are the acoustic mode amplitudes, related to the strain tensor by $\epsilon_{\mu\nu} = \frac{1}{2}(\nabla_\mu \delta_\nu + \nabla_\nu \delta_\mu)$, and m and M are the mass densities associated with the acoustic and optic modes, respectively. In addition, dissipative processes associated with the charge-density waves may be represented by a Rayleigh dissipation function[16]

$$D = \gamma \int d^3r \left(\frac{\partial \phi_\mu}{\partial t} \right)^2 \ , \tag{7}$$

and to describe the thermal equilibrium one needs a random thermal force represented by a Gaussian distributed random variable $g_\mu(\vec{r},t)$ with a correlation function

$$\langle g_\mu(\vec{r},t) g_\nu(\vec{r}',t') \rangle = \gamma k T \delta_{\mu\nu} \delta(\vec{r} - \vec{r}') \delta(t - t') \tag{8}$$

The dynamical (Lagrangian) equations of motion for the space Fourier-transformed variables are

$$\frac{d}{dt} \frac{\partial K}{\partial \dot{\psi}_{\mu q}} = - \frac{\partial F}{\partial \psi_{\mu q}} - \frac{1}{2} \frac{\partial D}{\partial \dot{\psi}_{\mu q}} + g_{\mu q} \ , \tag{9}$$

where $\psi = \phi$, Q, or δ.

The results of the above theory are as follows:

(i) The elastic constants c_{44} and $(c_{11} + 2c_{12})$ are temperature independent, while $(c_{11} - c_{12})$ goes to zero at the transition temperature (neglecting cubic terms which are proportional to $(E_f - E_{x0})$, according to

$$c_{11}(T) - c_{12}(T) = (c_{11} - c_{12})[1 - 1/(1 + \beta\theta)] \ , \tag{10}$$

where c_{ij} without argument refer to the high-temperature value, $\theta = (T - T_m)/T_m$, and $\beta = (c_{11} - c_{12}) K_0^2 a' T_m / 3h^2 f^2$. This is in excellent agreement with the data, right from T_m to room temperatures.

(ii) In the absence of cubic terms, the orthorhombic and tetragonal distortion modes have the same transition temperature, but the cubic terms decide in favor of the latter, the sign of tetragonality being given by the sign of $(E_f - E_{x0})$.

(iii) The [110] transverse $[1\bar{1}0]$ polarized phonon has a dispersion which can be represented approximately as

$$\omega_k^2 = \frac{c_{11} - c_{12}}{2m} \left[1 - \frac{1}{1 + \beta\theta + \eta k^2} \right] \ , \tag{11}$$

where η is related essentially to the zero-temperature coherence length, given by the gradient terms. This phenomenological form, with only one adjustable parameter, η, is in excellent agreement with experiment[9] for all temperatures. The large attenuation of the [110] transverse ultrasonic wave, however, seems to be due to impurities and other effects.

(iv) The dynamic acoustic structure function $S_\delta(\vec{k}, \omega)$, which is just the Fourier transform of the correlation function $\langle \delta_k^*(t) \delta_k(t') \rangle$, for the [110] transverse phonon shows no dynamic central peak,

and neutron scattering results are in agreement with results for static impurity scattering.

(v) The optical mode which is coupled to the tetragonal distortion is found to be temperature dependent right up to room temperature. However, it does not become soft at the transition, nor does a central peak appear in the optical structure function, which is in agreement with the total absence of the (300) Bragg reflection above T_m.

(vi) The cubic coupling embodied in Eqs. (2) and (3) implies a correlation between the pressure dependence of T_m and the sign of the tetragonality which is borne out by V_3Si and Nb_3Sn. It also explains the change in sign of tetragonality due to substitution of Sn with Sb in Nb_3Sn, because of change of sign of $E_F - E_{\nu 0}$ (and hence of the cubic term).

(vii) In addition to the above, the theory makes other correlations which are not specific to the type of coupling involved. For example, using parameters determined by fits to the elastic constants and the low-temperature distortion, the theory predicts correctly the nonlinear stress-strain relation in V_3Si just above T_m, and the heat capacity jump at T_m for both V_3Si and Nb_3Sn.

(viii) The results do not however, bear out the connection with the one-dimensional Peierls-chain model—the coherence length needed to fit the phonon dispersion curves is much smaller than that for the Peierls model ($\xi_0/a \sim E_F/T_m$). In addition, identifying the quadratic term a' with the density of states involved in the charge-density-wave transition gives a susceptibility drop below T_m five times the experimental value for Nb_3Sn.[8]

III. LANDAU THEORY OF A THREEFOLD DEGENERATE JAHN-TELLER MODEL

Another picture of the electronic instability in A-15 compounds is that of three degenerate bands in the cubic phase which get split in the tetragonal phase (second-order Jahn-Teller effect). The gain in electronic free energy due to depopulation of electrons from the higher band(s) to the lower one(s) is large enough at low temperatures to offset the expense of lattice elastic energy and warrant a phase transition provided the electronic density of states near the Fermi surface is sharply peaked (or sharply varying). This is the case in the Labbe-Friedel one-dimensional model with three noninteracting chains, and other calculations with phenomenological models of the electronic density of states[12,15] which yield essentially similar results. The Landau theory, therefore, naturally has three electronic order parameters Φ_μ, which represent the electronic energy levels of bands, which change as a result of the transition; in the Labbe-Friedel model these would be the bands due to the three chains. As in the Labbe-Friedel model, where the electronic energy at the Γ point for the chain in the μ (x, y, or z) direction ($E_k^\mu = -2|M|\cos k_\mu a$, M being the nearest-neighbor hopping integral and a the lattice spacing) is dependent on the longitudinal chain $\epsilon_{\mu\mu}$ (through M), the electronic order parameters Φ_μ in the Landau theory are coupled to the strain $\epsilon_{\mu\mu}$. *However, it must be emphasized that it is not necessary to make restrictions such as one dimensionality of the bands for the present study.* In fact it is possible, for relatively general bands, to divide the Brillouin zone into regions and categorize them into three groups whose motions are coupled, respectively, to the three diagonal components of the strain, as required by cubic symmetry. Thus, for example, in the tight-binding model of Ref. 12, the M point in the k_1-k_2 plane and the saddle point between Γ and X along k_3 (which are the two important features of the band as far as the Fermi-level density of states is concerned) are coupled to a longitudinal [100] strain, while the strains along [010] and [001] are coupled to their permutations. Thus the three order parameters Φ_μ represent three regions of the cubic Brillouin zone which are degenerate by cubic symmetry. The temperature-dependent part of the electronic free energy relevant to the transition may be written in terms of these order parameters, along the lines of Eq. (1) (see Ref. 1 for details),

$$F_{\rm elec} = \frac{1}{2}\int d^3r \sum_\mu \{A_\mu \Phi_\mu^2(\vec{r}) + B'\Phi_\mu^4(\vec{r}) + C_1[\partial_\mu \Phi_\mu(\vec{r})]^2 + C_2[\nabla \Phi_\mu(\vec{r})]^2\} \ , \qquad (12)$$

where, for comparsion, all relevant symbols have been replaced by their capital counterparts. The gradient terms have been written in a manner analogous to the Landau theory of the Gorkov model, and is of the general form permitted by cubic symmetry for softening of a $q=0$ mode. By comparison, the Labbe-Friedel model, being one dimensional, would have $C_2 = 0$.[13]

As in Eq. (2), near the transition temperature,

$$A_\mu = A'(T - T_{m0}^\mu) \ , \qquad (13)$$

and the variation of T_{m0}^μ is taken to be of the phenomenological form given by Eq. (3), with $E_{\nu 0}$ representing the energy corresponding to the bands filling for which the transition temperature is maximum in the absence of stress. Such a maximum would be expected for peaked density-of-states models, such as the one in Ref. 12.

The electron-phonon coupling is provided, in this case, by the direct response of the bands to strain, which is in contrast with the coupling in the Gorkov model [Eq. (4)]. By cubic symmetry, this is of the form

$$F_{\text{el-ph}} = \int d^3r \sum_{\mu} \epsilon_{\mu\mu}(\vec{r}) \left[F_1 \Phi_\mu(\vec{r}) + F_2 \sum_{\nu \neq \mu} \Phi_\nu(\vec{r}) \right] .$$

However, it should be remembered that only those strains couple with the temperature-dependent part of the electronic free energy, which split the cubic degeneracy of the bands near the Fermi surface and result in a reshuffling of the electrons. A uniform bulk strain, ($\epsilon_{xx} = \epsilon_{yy} = \epsilon_{zz}$) for example, shifts all three regions of the Brillouin zone equally and therefore does not couple to the temperature dependent part of the electronic free energy. This implies $F_2 = -\frac{1}{2} F_1$, and thus the electron-phonon interaction becomes[17]

$$F_{\text{el-ph}} = F \int d^3r \sum_{\mu} \left[\Phi_\mu(\vec{r}) - \frac{1}{3} \sum_{\nu} \Phi_\nu(\vec{r}) \right] \epsilon_{\mu\mu}(\vec{r}) , \tag{14}$$

where $F = \frac{3}{2} F_1$. Equation (14) is written in a form which clearly exhibits the physics that only the relative position of the bands enters the temperature dependence, so the relevant order parameters are the position of the bands relative to their mean, i.e., $\Psi_\mu = \Phi_\mu - \sum_\nu \Phi_\nu/3$. The elastic energy, of course, remains the same [Eq. (5)].

The present Landau description is valid under essentially the same restrictions as that in Ref. 1. Critical fluctuations are neglected, as are anharmonic and k-dependent terms in the lattice part of the free energy. The former is unimportant, and many of the effects of the latter cause trivial renormalization of the Landau parameters.

Static theory

In order to get the transition temperature, elastic constants, and symmetry of the low-temperature phase, only the quadratic and uniform part of the free energy need be considered:

$$\frac{F_0}{V} = \frac{1}{2} \left\{ \sum_{\mu} \left[A \Phi_\mu^2 + K_{11} \epsilon_{\mu\mu}^2 + (K_0 + G) Q_\mu^2 + 2F \epsilon_{\mu\mu} \left(\Phi_\mu - \sum_{\nu} \frac{\Phi_\nu}{3} \right) \right] + \sum_{\mu \neq \nu} (2K_{44} \epsilon_{\mu\nu} \epsilon_{\mu\nu} + K_{12} \epsilon_{\mu\mu} \epsilon_{\nu\nu} + G Q_\mu Q_\nu) + 2h [\epsilon_{xx}(Q_y - Q_z) + \cdots] \right\} , \tag{15}$$

where the dots indicate permutations. $A = A'(T - T_m^0)$ in this approximation. As in Ref. 1, the modes separate by defining

$$\begin{aligned} \epsilon_1 &= (\epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz})/\sqrt{3} , \\ \epsilon_2 &= (\epsilon_{xx} - \epsilon_{yy})/\sqrt{2} , \\ \epsilon_3 &= (\epsilon_{xx} + \epsilon_{yy} - 2\epsilon_{zz})/\sqrt{6} , \end{aligned} \tag{16}$$

and similarly Φ_i and Q_i ($i = 1, 2, 3$) in terms of the Φ_μ and Q_μ. The off-diagonal components of the strain tensor (ϵ_{xy}, ϵ_{yz}, and ϵ_{zx}), the bulk strain ϵ_1 and the symmetric optical mode Q_1 become uncoupled and therefore have temperature-independent elastic constants. The remaining part of the free energy becomes

$$\begin{aligned} F/V = \tfrac{1}{2} [& A(\Phi_1^2 + \Phi_2^2 + \Phi_3^2) + (K_{11} - K_{12})(\epsilon_2^2 + \epsilon_3^2) \\ & + K_0(Q_2^2 + Q_3^2) + 2F(\Phi_2 \epsilon_2 + \Phi_3 \epsilon_3) \\ & + 2\sqrt{3} h (\epsilon_2 Q_3 - \epsilon_3 Q_2)] \end{aligned} \tag{17}$$

Two modes "condense" simultaneously in this approximation—one a linear combination of Φ_2, Q_3, ϵ_2 and the other of Φ_3, Q_2, ϵ_3 at a "Gaussian" transition temperature (see Ref. 1 for calculational procedures),

$$T_m^* = T_m^0 + \frac{F^2/A'}{K_{11} - K_{12} - 3h^2/K_0} . \tag{18}$$

By adding the stress coupling term $-2\zeta_3 \epsilon_3$ to (17) from (5), the temperature dependence of the elastic modulus is easily worked out to be

$$c_{11}(T) - c_{12}(T) = (c_{11} - c_{12})[1 - 1/(1 + B\theta)] , \tag{19}$$

where $c_{11} - c_{12} = K_{11} - K_{12} - 3h^2/K_0$ is the value far from the transition,

$$B = a'(c_{11} - c_{12}) T_m^*/F^2 \tag{20}$$

is a dimensionless coupling constant not to be confused with B' in Eq. (12), and $\theta = (T - T_m^*)/T_m^*$ is the reduced temperature. The bulk and shear elastic constants are temperature independent, since those modes do not couple,

$$c_{44}(T) = K_{44} , \tag{21a}$$

$$c_{11}(T) + 2c_{12}(T) = K_{11} + 2K_{12} . \tag{21b}$$

Comparing Eqs. (19) and (21) with Eq. (10) and the preceding statements, it follows immediately that the *form* of the temperature dependences of the elastic moduli in the two models are *identical*, and since the parameters β or B are determined by a fit to experiment, so are the results.

Inclusion of cubic terms, as in the Gorkov model, renders the transition first order and selects the tetragonal (ϵ_3) mode over the orthorhombic (ϵ_2) mode. (In fact, anharmonic terms in the elastic free energy would do the same.) Thus the entire discussion of cubic and higher-order terms in Ref. 1 can be carried

through with only trivial redefinition of the Landau parameters. The correlation between pressure dependence of the transition temperature and sign of tetragonality follows from a coupling like that in Eqs. (1) and (3), and its appropriateness depends on the microscopic model. For example, the peaked density of states model in Ref. 12 would have such terms present.

Dynamics

As in Ref. 1, it is convenient to go over to the acoustic mode amplitudes. δ_μ, related to the strain tensor by $\epsilon_{\mu\nu}=\frac{1}{2}(\nabla_\mu\delta_\nu+\nabla_\nu\delta_\mu)$ for dynamic calculations. The free energy can be written as a sum of independent Fourier components over half of k space (since the real-space functions are real) as

$$F_{\vec{k}}=\sum_\mu\{(A+C_1k_\mu^2+C_2k^2)|\Phi_{\mu\vec{k}}|^2+(K_0+G)|Q_{\mu\vec{k}}|^2+[(K_{11}-K_{44})k_\mu^2+K_{44}k^2]|\delta_{\mu\vec{k}}|^2\}$$
$$+\sum_{\mu\neq\nu}[(K_{12}+K_{44})k_\mu k_\nu\delta_{\mu\vec{k}}{}^*\delta_{\nu\vec{k}}+GQ_{\mu\vec{k}}{}^*Q_{\nu\vec{k}}]+\{ih[k_x\delta_{x\vec{k}}{}^*(Q_{y\vec{k}}-Q_{z\vec{k}})+\cdots]+\text{c.c.}\}$$
$$+[iF(k_x\Phi_{x\vec{k}}{}^*\delta_{x\vec{k}}+k_y\Phi_{y\vec{k}}{}^*\delta_{y\vec{k}}+k_z\Phi_{z\vec{k}}{}^*\delta_{z\vec{k}})+\text{c.c.}]\ , \tag{22}$$

where the dots indicate permutations.

In addition, one needs the lattice kinetic energy [Eq. (6)] and electronic relaxation processes and random thermal forces represented by terms exactly of the form given in Eqs. (7) and (8). The dynamical equations (9), in the absence of the random thermal force g, yield the mode frequencies. In order to compute the dynamic structure factor, the Eqs. (9) are solved for a given random force g, and an ensemble average performed according to Eq. (8). The results are (see Ref. 1 for calculation details): (i) For the wave vector $\vec{k}$ in the [100] direction, the transverse-acoustical modes are uncoupled, while the longitudinal mode for $\vec{k}\to 0$ shows the softening expected from the temperature dependence of $c_{11}(T)$, and exactly the same as Ref. 1 with β replaced by B; and (ii) For $\vec{k}$ along [110], the transverse mode polarized along [001] shows no softening, while the longitudinal sound velocity varies exactly as obtained from Eq. (58) of Ref. 1. The interesting $[1\bar{1}0]$ polarized acoustical-mode frequency can be obtained from the dynamical structure factor $S_\delta(k,\omega)$ which is the Fourier transform of $\langle\delta_k{}^*(t)\delta_k(t')\rangle$. For small k, when the acoustical-mode frequency is much smaller than the optical frequency, the structure factor may be written in a form exactly like in Ref. 1,

$$S_\delta(k,\omega)=\frac{2\Omega k_BT/(c_{11}-c_{12})k^2}{[(1/\tau_k)(1-x^2)-\Omega x^2]^2+\omega_{k\infty}^2x^2(1-x^2)^2}\ , \tag{23}$$

where

$$\tau_k=\gamma/[A'(T-T_m{}^*)+(C_1/2+C_2)k^2] \tag{24}$$

is a relaxation time characteristic of the dissipation process which diverges like $(T-T_m{}^*)^{-1}$ at the transition temperature for vanishing k (in the absence of cubic terms),

$$\Omega=f^2/\gamma(c_{11}-c_{12}) \tag{25}$$

is a frequency characteristic of the coupling terms, $\omega_{k\infty}=[(c_{11}-c_{12})/2m]^{1/2}k$ is the acoustical frequency far from the transition, and $x=\omega/\omega_{k\infty}$ is the reduced frequency.

Since this result is identical in form to that in Ref. 1, the expressions for the phonon frequency and mean free path have the same form as in Ref. 1,

$$\omega_k^2=\omega_{k\infty}^2\left(1-\frac{1}{1+B\theta+Nk^2}\right) \tag{26}$$

where B is defined in Eq. (20), θ the reduced temperature is defined just below that, and

$$N=\frac{(C_1/2+C_2)-\gamma v_\infty/2\Omega}{2\Omega\gamma}\ ,$$

$v_\infty=[(c_{11}-c_{12})/2m]^{1/2}$ is the [110] transverse sound velocity far from the transition. The mean free path near the transition diverges as $\Lambda_k\sim\omega_k^2/(T-T_m{}^*)^{3/2}$.

One result that is different in this model from Ref. 1 is the optical-mode frequency which is, in fact, temperature independent in the $k\to 0$ limit. This may be seen without computing optical structure factor, from Eq. (22). The optical-mode frequency is shifted by coupling terms $\sim k$, so that simple perturbation theory gives

$$M\omega^2\sim K_0+O(k^2)/[K_0-(K_{11}-K_{12})k^2]\sim K_0$$

(for $k\to 0$), which is independent of temperature.

Finally, by adding on coupling to an impurity potential of the form $-\int d^3r\,u_\mu(\vec{r})\Phi_\mu(\vec{r})$ in Eq. (12), a static central peak with an intensity diverging like $(T-T_m{}^*)^{-2}$, and a $(T-T_m{}^*)^{-1}$ dependence of the ultrasonic attenuation would be obtained, just as in Ref. 1.

Thus, the form of the results of the present Landau theory are the same as those of Ref. 1 for most of the quantities related to the martensitic transition and experimental results to date may be fit to exactly the same extent as done in Ref. 1. The one major

difference in the predictions—partial softening of the $\Gamma_{12}(+)$ optical mode—is not known experimentally.

The marked similarity of the results, which may appear surprising at first, is directly ascribable to the A-15 crystal structure. Symmetry considerations show that in the A-15 structure a bilinear coupling between the "pairing" modes and the dilation of the unit cell is allowed; consequently, the normal modes of the system are their linear combinations. It is precisely this coupling [Eq. (5)] which ensures that when modes separate out as ones with orthorhombic and tetragonal symmetry, the modes Q_2 and ϵ_3 (or Q_3 and ϵ_2) are coupled in the same way, and the one driven soft first is the lowest energy, i.e., acoustic branch. The temperature dependence of the elastic constants comes from that of a_μ or A_μ [Eqs. (2) and (13)], the only temperature-dependent parameters of the model, and consequently have identical form, though the parameters β and B look rather different in terms of the original Landau coefficients. The temperature dependence of the $k=0$ optical-mode frequency, though, is different, depending on whether the pairing mode serves as an intermediary between the electronic and acoustical modes or not.

Once the soft mode frequency in the two models has been shown to have the same form, the similarity of other results follows immediately. The acoustical phonon softening at finite wave vector is governed by the gradient terms in the electronic free energy, which has been taken to be of the same form, permitted by cubic symmetry, in the two models. The central peak and ultrasonic attenuation due to impurities near T_m is dominated by the coupling to the soft mode; consequently, the two models predict the same temperature dependence. The pressure dependence of T_m and sign of tetragonality, on the other hand, depend on the assumption of an ideal placement of the Fermi level which maximizes the transition temperature—which is expected both for Peierls-gap model and Jahn-Teller splitting of a peak in the density of states.[12]

Consequently, the excellent agreement between existing experimental data and the phenomenological theory of Ref. 1 is not capable of deciding in favor of either type of coupling in the phenomenological description.

IV. LANDAU THEORIES BASED ON THREE-DIMENSIONAL BAND MODELS

In the one-dimensional models of the electronic bands of the A-15 compounds, the symmetry points—Γ (zone center) and X (zone edge)—being coupled to the dilation and pairing mode, respectively, were obvious candidates for placement of the Fermi energy. Once interchain coupling is taken into account, the threefold degeneracy at Γ for bands near the Fermi surface (as determined by Mattheiss[10]) is split by the crystal field, and the singular one-dimensional density of states is washed out, too. Symmetry points such as M and R also become likely candidates for placement of the Fermi energy, as do other points of somewhat lower symmetry, such as those along lines joining Γ, X, M, and R, provided the relevant portions of the bands couple to either the dilation or the pairing mode (or both, as will be shown below). This section reviews, in a qualitative way, the Landau energy functionals needed to describe the martensitic transformation for some of these models. It is assumed for simplicity, as in the previous cases, that the bands can be divided into distinct regions and represented by k-independent coupling parameters.

A description of the martensitic instability, using simplified three-dimensional bands, has been given in Ref. 12, based on the result of Mattheiss[10] that the density of states at the Fermi surface is dominated by the $\delta_1(x^2-y^2)$ orbitals at the transition metal (A) sites [Fig. 1(a)], and that two bands lie consistently close to the Fermi energy in many A-15s. The model uses two bands resembling those of Mattheiss formed using only the above orbitals with nearest-neighbor (intrachain) and next-nearest-neighbor (interchain) interactions. The model has a sharp peak in the density of states due to two triplets of saddle points (for the three symmetry directions of the cubic lattice)—one at the three M points and another along the three ΓX directions (Fig. 2), which are close in energy. In the tetragonal phase, the triplet degeneracy (at both M and ΓX) required by cubic symmetry is removed; in each triplet two of the saddle points move one way and the third in the opposite direction. This motion can be adequately represented by just three order parameters Φ_μ by pairing the saddle points (the ΓX saddle point along k_x with the M point in the $k_y k_z$ plane). In addition (though not of as great importance as the saddle-point motion), pairing of the atoms in the chains causes gaps at the X points which are also close in energy to the saddle points, and three additional electronic order parameters ϕ_μ are needed to describe the charge-density wave, which couple to the pairing mode. If the Fermi energy lies near the peak in the density of states, a feature required by all electronic models of the A-15 compounds, the structural instability is ascribable to both types of instabilities—the Jahn-Teller splitting at the saddle points and the X-point Peierls gap. Thus a Landau free-energy functional for the tight-binding model would have both the electronic parts, Eqs. (1) and (12), with the electron-phonon couplings, Eqs. (4) and (14), respectively. Such a theory in the absence of coupling to the off-diagonal components of the strain tensor (which are actually present in the microscopic model to the extent of interchain coupling) would predict temperature independent bulk and shear moduli, and temperature dependence of $(c_{11}-c_{12})$ of the form

$$c_{11}(T)-c_{12}(T)=(c_{11}-c_{12})-\frac{c}{1+\beta\theta}-\frac{c_{11}-c_{12}-c}{1+B\theta}\ , \tag{27}$$

where β and B are dimensionless coupling constants defined in Secs. II and III, respectively, $\theta=(T-T_m{}^*)/T_m{}^*$ is the reduced temperature, and c is another (adjustable) parameter of the Landau theory. Comparison of Eq. (27) with Eq. (19) for the Jahn-Teller model,

$$c_{11}(T)-c_{12}(T)=(c_{11}-c_{12})-\frac{c_{11}-c_{12}}{1+B\theta}\ ,$$

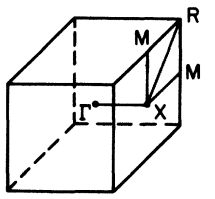
or that for the Gorkov model which is the same except for replacing B by β, shows immediately that the forms are very similar. Both start linearly with temperature above $T_m{}^*$ and saturate as $T\to\infty$, and with the two additional parameters in (27), it is clear that the fit of (27) to experiment will be at least as good as that for either of the earlier models.

Other results of the Landau theory such as the [110] transverse acoustic phonon frequency, attenuation, central peaks in neutron scattering, etc., can be worked out in a fashion similar to Ref. 1, and shown to have forms that are similar to, and in as good agreement with, existing experimental data as the previous models. The temperature dependence of the optic mode frequency, as would be expected, is in between the results of the two earlier models.

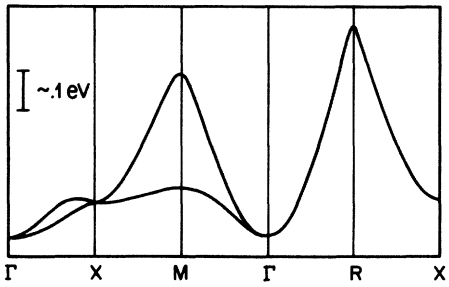
A recent three-dimensional model[18] puts the Fermi energy at the R point, where in the actual band structure (as in tight-binding model of Ref. 12) there is a six-fold degeneracy. In that case (at least for the tight-binding bands of Ref. 12) pairs of bands are coupled to each pairing mode, creating a gap as in the Gorkov model. Consequently, the Landau description would be as in Ref. 1.

V. CONCLUDING REMARKS

To summarize, the experimental data on elastic softening, phonon dispersion, central peaks, ultrasonic attenuation, heat capacity jump, etc., are not in conflict with phenomenological theories based on either a Jahn-Teller triplet splitting or a Peierls-type gap (or a combination). Results of alloying such as change in sign of the tetragonality of Nb_3Sn with Sb doping can be explained by the assumption of an optimum positioning of the Fermi level for which the transition temperature is a maximum, such as that in Eqs. (3), which is expected in peaked density-of-states models.[19] The same assumption also explains the correlation between sign of tetragonality and pressure dependence of the transition temperature, as is observed in V_3Si and Nb_3Sn. Consequently, many microscopic models which exhibit either type of coupling would be suitable on a qualitative basis. Calculation



(a)



(b)

FIG. 2. (a) Brillouin zone of the cubic phase with some high-symmetry points labeled. (b) The two bands used in the tight-binding model of Ref. 12.

of Landau parameters from the microscopic model yield important clues as to the microscopics of the transition. One such parameter is η (Eq. 11) which determines the recovery of the [110] transverse acoustical phonon, and is related to the zero temperature coherence length, ξ_0. For the 1D Peierls model $\xi_0/a\sim E_B/T_m$, where E_B is the bandwidth and a is the lattice spacing, while for the Labbe-Friedel model (with $E_F\sim T_m$) $\xi_0/a\sim\sqrt{E_B/T_m}$.[13] Neutron scattering data give $\xi_0/a\sim 1$, which is in serious disagreement with both the above (less for the Labbe-Friedel model). The tight binding model of Ref. 12, on the other hand, gives a much shorter coherence length,[13] in good agreement with experiment. Another check is the susceptibility drop below the transition which may be obtained from the parameters a' and A' [Eqs. (2) and (13)] which govern the motion of the bands and hence the change in density of states in the tetragonal phase. As before, models with interchain coupling[11,12] fare much better than the 1D models.[2,3]

As has been stated earlier,[1] the martensitic transition affects the superconducting transition in two ways. First, the significant softening of the phonon raises the superconducting transition temperature T_c if it is in the vicinity of T_m, by increasing the electron-phonon coupling constant λ. After the martensitic transition has taken place, though, the electronic density of states drops and this depresses the superconducting temperature. Consequently, in both models (or the hybrids) the maximum superconducting tem-

perature is expected when the two transition temperatures are equal, and this indeed appears to be the case, both for the variation of T_c of V_3Si with pressure[20] and of $Nb_3Sn_{1-x}Al_x$ with Al doping.[6(b)]

One more check of the nature of the band structure near the Fermi surface could possibly come from infrared absorption data in the cubic and tetragonal phase above the superconducting transtion. In addition to a decrease in absorption due to a decrease in the density of states[21] in the tetragonal phase, in the Gorkov model, a structure should develop at the energy of the X-point gap. For the Jahn-Teller triplet splitting model, the splitting would be at different points in k-space in general (such as the M points in the tight-binding model of Ref. 12) and so the possibility of low energy ($\sim 5T_m$) direct (vertical) transitions would not exist in the tetragonal phase (except in such cases as Γ- point or R-point splitting). Experimental results[22] on the infrared reflectivity of V_3Si in the range 6–25 meV show no change to within 0.5% due to the martensitic transition; however, these do not extend down to low enough energies to detect the Gorkov gap, and absolute absorption measurements would be better suited to observe changes in density of states at the Fermi surface.

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