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Theory of Phase Transitions in the β-Tungsten Structure Induced by the Band Jahn-Teller Effect

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A dynamic theory of the cubic-to-tetragonal transformation in the β-tungsten structure is presented starting with a Hamiltonian describing the interaction between static strain and acoustic phonons with the electrons in the triply degenerate *d* bands. For this model the elastic constants are strongly temperature dependent in the low-frequency limit. However, for frequencies in the neighborhood of the Debye frequency, they are nearly temperature independent.

I. INTRODUCTION

The cubic-to-tetragonal structural-phase transition in the intermetallic A_3B compounds with the β-tungsten (β-W) structure has been the subject of a number of recent theoretical and experimental papers.[1–37]

These phase transitions are believed to be induced by the interaction of a triply degenerate *d* electron band with the elastic strain.[6] The distortion from cubic symmetry splits the *d* bands into a singlet and a doubly degenerate band lying, respectively, below and above the bands in the undistorted structure. The energy gained by the increased occupation of the lower band is balanced by the increase in the elastic energy. The soft mode associated with the transition is an acoustic shear mode propagating in a [110] direction polarized in the $[1\bar{1}0]$ direction.

The transitions in the β-W structures have been described in terms of a one-dimensional linear-chain model to calculate the *d*-band structure in the tight-binding approximation.[6–10] The coupling of the electronic system to the elastic strain was discussed using a free-energy approach. A simpler constant-density-of-states model was introduced by Cohen, Cody, and Halloran[11] in terms of which good quantitative agreement could be obtained with experimental values.[11,12,29,38] Very recently Klein and Birman[14] revived an early suggestion by Anderson and Blount[5] that the transition might be driven by an optical-phonon instability.

In this paper a dynamic theory is presented for the band Jahn-Teller mechanism based on the electron-phonon interaction. The distortion from cubic symmetry is described in terms of static contributions to the strain and electron-density operators. From the requirement that the static parts of the equations of motion must vanish, expressions are obtained from which the static strain, the shift in the band edges, and the repopulation of the electron bands may be calculated. From the coupled-mode dispersion relation for the acoustic phonons and the electron-density fluctuations, renormalized sound frequencies may be obtained for arbitrary frequency and wave vector. A preliminary account of this approach has already been presented.[15]

II. HAMILTONIAN

The Hamiltonian for the noninteracting d electrons will be written

$$H_d = \sum_{n=1}^{3} \sum_{k} \epsilon_n^0(k) a_n^\dagger(k) a_n(k) \quad , \tag{1}$$

where the index n refers to the three d bands, degenerate at $k=0$. The operators $a_n(k)$ and $a_n^\dagger(k)$ satisfy the usual Fermi commutation relations

$$\{a_n(k),\ a_{n'}^\dagger(k')\} = \delta_{nn'}\,\delta_{kk'} \quad . \tag{2}$$

The Hamiltonian describing static distortions and long-wavelength acoustic phonons may be expressed in terms of localized strain-tensor components. For cubic symmetry we obtain

$$\begin{aligned} H_e = \tfrac{1}{2} \textstyle\sum_l M \dot{u}^2(l) + \tfrac{1}{2}\, C_{11}^0 \textstyle\sum_l [\,e_{11}{}^2(l) + e_{22}{}^2(l) + e_{33}{}^2(l)] \\ + C_{12}^0 \textstyle\sum_l [e_{11}(l)\, e_{22}(l) + e_{11}(l)\, e_{33}(l) + e_{22}(l)\, e_{33}(l)] \\ + 2C_{44}^0 \textstyle\sum_l [e_{12}{}^2(l) + e_{13}{}^2(l) + e_{23}{}^2(l)] \quad , \end{aligned} \tag{3}$$

where $u(l)$ is the c.m. coordinate for the lth unit cell. M is the mass of the unit cell. The constants C_{ij} have units of energy and are related to the usual elastic constant c_{ij} by

$$C_{ij} = a^3 c_{ij} \quad , \tag{4}$$

where a is the lattice constant of the cubic structure.

Deviations from cubic symmetry are described by nonvanishing thermal expectation values of the strains $e_{ij}(l)$. We set

$$e_{ij}(l) = \langle e_{ij} \rangle + u_{ij}(l) \quad . \tag{5}$$

For tetragonal distortion,

$$\begin{aligned} &\langle e_{ij} \rangle = 0, \quad i \neq j \\ &\langle e_{11} \rangle = \langle e_{22} \rangle = e_a \;, \quad \langle e_{33} \rangle = e_c \quad . \end{aligned} \tag{6}$$

The fluctuations about the average values of the strain may be expressed in terms of the normal-mode coordinates of the acoustic phonons in the usual way,

$$u_{ij}(l) = (1/N) \sum_{\lambda q} e^{iq\cdot X(l)}\, \alpha_{ij}(\lambda q)\, Q(\lambda q) \quad , \tag{7}$$

with

$$\alpha_{ij}(\lambda q) = (i/2)(\sqrt{N})\, [\,q_i\, e_j(\lambda q) + q_j\, e_i(\lambda q)] \quad , \tag{8}$$

where $Q(\lambda q)$ is the normal-mode coordinate for the λth acoustic branch of frequency $\omega(\lambda q)$, wave vector q, and polarization vector $e(\lambda q)$. $X(l)$ is the center of the lth unit cell and N the number of unit cells.

When Eq. (5) is substituted in Eq. (3), the Hamiltonian separates into static terms, terms which are linear in the fluctuations $u_{ij}(l)$, and terms which are quadratic in the fluctuations. For a tetragonal distortion, the static part of the Hamiltonian takes the form

$$H_e^{(s)} = C_{11}^0(e_a{}^2 + \tfrac{1}{2} e_c{}^2) + C_{12}^0(e_a{}^2 + 2 e_a e_c) \quad . \tag{9}$$

The linear term may be written

$$\begin{aligned} H_e^{(l)} = [(C_{11}^0 + C_{12}^0) e_a + C_{12}^0 e_c\,] \textstyle\sum_l [\,u_{11}(l) + u_{22}(l)] \\ + (C_{11}^0\, e_c + 2C_{12}^0\, e_a) \textstyle\sum_l u_{33}(l) \quad . \end{aligned} \tag{10}$$

The term quadratic in the fluctuations is most conveniently expressed in terms of the acoustic-phonon normal-mode coordinates

$$\begin{aligned} H_e^{(f)} = \tfrac{1}{2}(M) \sum_{\lambda q} P(\lambda q)\, P(\lambda, -q) \\ + \tfrac{1}{2} M \sum_{\lambda q} \omega_0{}^2(\lambda q)\, Q(\lambda q)\, Q(\lambda, -q) \quad , \end{aligned} \tag{11}$$

where $P(\lambda q)$ is the canonical-conjugate momentum to $Q(\lambda q)$

$$[Q(\lambda q),\, P(\lambda' q')] = \delta_{\lambda\lambda'}\, \delta_{qq'} \quad . \tag{12}$$

The linear coupling between the strain and the electron density will be of the form

$$\begin{aligned} H_{\rm int} = G_{11}(1/N) \textstyle\sum_q [e_{11}(-q)\rho_{11}(q) + e_{22}(-q)\rho_{22}(q) + e_{33}(-q)\rho_{33}(q)] \\ + G_{12}(1/N) \textstyle\sum_q \{e_{11}(-q)[\rho_{22}(q) + \rho_{33}(q)] \\ + e_{22}(-q)[\rho_{11}(q) + \rho_{33}(q)] + e_{33}(-q)[\rho_{11}(q) + \rho_{22}(q)]\} \\ + 2G_{44}(1/N) \textstyle\sum_q [e_{12}(-q)\rho_{12}(q) + e_{13}(-q)\rho_{13}(q) + e_{23}(-q)\rho_{23}(q)] \quad , \end{aligned} \tag{13}$$

where

$$\rho_{lm}(q)=\sum_k \rho_{lm}(kq)=\sum_k a_l^\dagger(k)\,a_m(k+q)\quad . \tag{14}$$

This model differs from a model recently introduced to discuss transition-metal superconductivity[39] and the electron-phonon interaction in the β-tungsten structures[40] by the presence of the G_{12} and G_{44} terms. We set

$$\rho_{lm}(q)=N\langle \rho_l\rangle\,\delta_{lm}\,\delta_{q,0}+\tau_{lm}(q)\quad , \tag{15}$$

where $\langle \rho_l\rangle$ is the average electron density in the lth d band and τ_{lm} describes the density fluctuations. For tetragonal distortion,

$$\langle \rho_1\rangle=\langle \rho_2\rangle=\rho_a \tag{16}$$

and

$$\langle \rho_3\rangle=\rho_c\quad . \tag{17}$$

III. COUPLED-MODE FREQUENCIES

From the Hamiltonian equations (1), (3), and (13) and the commutation relations [Eqs. (2) and (12)] we calculate the equations of motion for the acoustic normal-mode coordinates $Q(\lambda q)$ and the density fluctuations $\tau_{ij}(q)$. Setting the static parts of the equations of motion for $Q(\lambda q)$ equal to zero gives the following relationships:

$$\begin{gathered}(C_{11}^0-C_{12}^0)(e_c-e_a)+(G_{11}-G_{12})(\rho_c-\rho_a)=0\quad ,\\ (C_{11}^0+2C_{12}^0)(e_c+2e_a)+(G_{11}+2G_{12})(\rho_c+2\rho_a)=0\quad .\end{gathered} \tag{18}$$

For the equations of motion we obtain

$$-\frac{\partial^2}{\partial t^2}Q(\lambda q)=\omega_0{}^2(\lambda q)\,Q(\lambda q)+\frac{1}{MN}\sum G_{ijlm}\,\alpha_{ij}(\lambda,\,-q)\tau_{lm}(q)\quad . \tag{19}$$

The equations of motion for the electron operators $a_n(k)$ have no static parts. We obtain

$$i\frac{\partial}{\partial t}\;a_n(k)=\epsilon_n^0(k)\,a_n(k)+\frac{1}{N}\sum_q G_{ijnm}\,e_{ij}(-q)\,a_m(k+q)\quad . \tag{20}$$

Separating the static and dynamic contributions of the strain $e_{ij}(q)$, this equation may be written

$$i\frac{\partial}{\partial t}\;a_n(k)=\tilde{\epsilon}_n\,a_n(k)+\frac{1}{N}\sum_q G_{ijnm}\,u_{ij}(-q)\,a_m(k+q)\quad , \tag{21}$$

where

$$\tilde{\epsilon}_{1,2}(k)=\epsilon_{1,2}^0(k)+G_{11}\,e_a+G_{12}(e_a+e_c)\quad ,$$

$$\tilde{\epsilon}_3(k)=\epsilon_3^0(k)+G_{11}\,e_c+2G_{12}\,e_a\quad . \tag{22}$$

The coupling shifts the band edges of the d electron bands. In the distorted structure where $e_a\neq e_c$, it splits the triply degenerate $k=0$ mode into a singlet mode and a doubly degenerate mode.

The last term in Eqs. (19) and (21) describes the dynamic electron-phonon interaction. Treating this interaction in the Migdal approximation[41] we obtain a set of equations determining the renormalized acoustic-phonon frequencies of the form

$$\omega^2 Q(\lambda q)=\omega_0{}^2(\lambda q)\,Q(\lambda q)-\frac{1}{M}\,\frac{1}{N}\sum_{ijlm}\;\sum_{i'j'\lambda'}G_{ijlm}G_{i'j'lm}\times\alpha_{ij}(\lambda,\,-q)\,\alpha_{i'j'}(\lambda'q)\,F_{lm}(q\omega)\,Q(\lambda'q)\quad , \tag{23}$$

where

$$F_{lm}(q\omega)=\frac{1}{N}\sum_k\frac{n_m(k)-n_l(k-q)}{\omega-\epsilon_m(k)+\epsilon_l(k-q)} \tag{24}$$

and where $n_l(k)$ is the Fermi-occupation-number factor

$$n_l(k)=1/e^{\beta(\epsilon_l(k)-\epsilon_F)}+1\quad . \tag{25}$$

ϵ_F is the Fermi level and $\beta=1/k_BT$. In these expressions $\epsilon_n(k)$ denotes the electron energies, shifted because of the static strain according to Eqs. (22) and renormalized by the dynamic electron-phonon interaction. The renormalization affects only the k dependence of the electron energy.

IV. DESCRIPTION OF PHASE TRANSITION

The structural transition in Nb_3Sn and V_3Si is to a good approximation volume conserving. Choosing the undistorted structure as reference point, we set

$$e_a=-\tfrac{1}{2}e_c\quad . \tag{26}$$

From Eqs. (18) we then obtain

$$\tfrac{3}{2}(C_{11}^0-C_{12}^0)\,e_c+(G_{11}-G_{12})(\rho_c-\rho_a)=0\quad . \tag{27}$$

Here $(\rho_c-\rho_a)$ is a measure of the difference in the average electron density along the c axis and the a axes in the distorted structure.

These equations have a solution $e_a=e_c=\rho_c-\rho_a=0$ corresponding to the undistorted structure $T>T_m$. For $T<T_m$ Eq. (27) may be written

$$\tfrac{3}{2}(C_{11}^0-C_{12}^0)e_c=-(G_{11}-G_{12})\frac{1}{N}\left(\sum_k\frac{1}{e^{\beta(\epsilon_3(k)-\epsilon_F)}+1}-\frac{1}{e^{\beta(\epsilon_{1,2}(k)-\epsilon_F)}+1}\right)\quad , \tag{28}$$

where from Eqs. (22)

$$\epsilon_{1,2}(k) = \epsilon^0_{1,2}(k) + \Delta \quad ,$$
$$\epsilon_3(k) = \epsilon^0_3(k) - 2\Delta \quad , \qquad (29)$$

with

$$\Delta = -\tfrac{1}{2}(G_{11} - G_{12})e_c \quad . \qquad (30)$$

The Fermi level is determined by

$$n_d = \frac{1}{N} \sum_k \sum_{l=1} n[\epsilon_l(k)] \quad , \qquad (31)$$

where n_d is the number of d electrons per unit cell.

This model gives a first-order transition contrary to the assumption made in Ref. 15. The supercooling temperature T_0 is defined by the limit $e_c \rightarrow 0$, $T \rightarrow T_0$. From Eq. (28) we obtain

$$C^0_{11} - C^0_{12} = (G_{11} - G_{12})^2 K_{11}(\Delta = 0, T_0) \quad . \qquad (32)$$

The superheating temperature T_u is determined by $(de_c/dT)|_{T_u} = \infty$. Making use of Eq. (28),

$$C^0_{11} - C^0_{12} = 3(G_{11} - G_{12})^2 \frac{K_{11}(T_u)K_{33}(T_u)}{2K_{11}(T_u) + K_{33}(T_u)} \quad . \qquad (33)$$

The transition temperature is determined by equating the free energies of cubic and tetragonal phases. An approximate free-energy expression may be written[6,12]

$$F = \tfrac{3}{4}(C^0_{11} - C^0_{12})e_c^2 + n_d\epsilon_F$$
$$- (1/\beta)(1/N)\textstyle\sum_k \left[2\ln(1 + e^{-\beta[\epsilon_{1,2}(k) - \epsilon_F]})\right.$$
$$\left. + \ln(1 + e^{-\beta[\epsilon_3(k) - \epsilon_F]})\right] \quad , \qquad (34)$$

where F is the free energy per unit cell.

So far no assumptions have been made concerning the form of the d bands. The preceding expressions simplify considerably if we use a constant-density-of-states model.[11] We set

$$N(\epsilon) = N_0, \quad \epsilon > 0$$
$$N(\epsilon) = 0, \quad \epsilon < 0 \qquad (35)$$

for the density of states of the unshifted d bands. We assume that $\epsilon_F(T = 0) > 0$. The model then describes nearly empty d bands.

The definitions of the stability limits take the form

$$C^0_{11} - C^0_{12} = \tfrac{1}{3}(G_{11} - G_{12})^2 N_0 n(0, T_0) \quad , \qquad (36)$$

$$C^0_{11} - C^0_{12} = (G_{11} - G_{12})^2 N_0 \frac{n(\Delta, T_u)n(-2\Delta, T_u)}{2n(\Delta, T_u) + n(-2\Delta, T_u)} \quad . \qquad (37)$$

The definition of the transition temperature T_m may be written

$$(C^0_{11} - C^0_{12})\, e_c^2(T_m) = \tfrac{4}{9} k_B T_m N_0[2f(\Delta, T_m)$$
$$+ f(-2\Delta, T_m) - 3f(0, T_m)] \quad ,$$

where

$$f(\Delta, T) = \int_\Delta^\infty d\epsilon \ln(1 + e^{-\beta(\epsilon - \epsilon_F)}) \quad . \qquad (38)$$

The Fermi level is determined by

$$n_d = 2\rho_a + \rho_c \quad , \qquad (39)$$

where

$$\rho_a = \tfrac{1}{3}N_0[(\epsilon_F - \Delta) + (1/\beta)\ln(e^{-\beta(\epsilon_F - \Delta)} + 1)] \quad ,$$
$$\rho_c = \tfrac{1}{3}N_0[(\epsilon_F + 2\Delta) + (1/\beta)\ln(e^{-\beta(\epsilon_F + 2\Delta)} + 1)] \quad . \qquad (40)$$

The Fermi level at $T = 0$ for the case $\Delta > 0$ is given by

$$n_d = N_0\epsilon_F(0) \qquad \text{for } \epsilon_F(0) > \Delta(0) \quad , \qquad (41)$$

$$n_d = (N_0/3)[\epsilon_F(0) + 2\Delta(0)] \quad \text{for } \epsilon_F(0) < \Delta(0) \quad . \qquad (42)$$

The static part relationships Eqs. (27), (39), and (40), derived by the equation-of-motion method, may be obtained alternatively from the free-energy expression Eq. (34).

V. BEHAVIOR OF SOUND FREQUENCIES

The renormalization of the sound frequencies given by Eq. (23) has been obtained by considering fluctuations about the static thermally averaged quantities. This assumes that the sound wave does not induce any repopulation of the electron bands. This calculation, therefore, applies in the limit $\omega\tau \gg 1$, where τ is the relaxation time for electron transfer. For the very low frequencies used in conventional ultrasonic experiments, then, $\omega\tau \ll 1$, and the corresponding low-frequency elastic constants may be calculated thermodynamically. It is nevertheless of interest to consider the static $\omega = 0$ and small q limit of Eq. (23) in order to compare with the results obtained thermodynamically. For sound propagation along particular symmetry directions Eq. (23) is diagonal in $\lambda\lambda'$. Making use of the relationship between the sound velocities and the elastic constants, we may deduce the corresponding changes in the elastic constants. We obtain[42]

$$C_{11} = C^0_{11} - [G_{11}{}^2 K_{11} + G_{12}{}^2(K_{11} + K_{33})] \,,$$
$$C_{33} = C^0_{11} - [G_{11}{}^2 K_{33} + 2G_{12}{}^2 K_{11}] \,,$$
$$C_{12} = C^0_{12} - [G_{12}{}^2 K_{33} + 2G_{11}G_{12}K_{11}] \,, \qquad (43)$$
$$C_{13} = C^0_{12} - [G_{12}{}^2 K_{11} + G_{11}G_{12}(K_{11} + K_{33})] \,,$$
$$C_{44} = C^0_{44} - G_{44}{}^2 (K_{13} + K_{31}) \,,$$

$$C_{66}=C^0_{44}(K_{12}+K_{21})\ ,$$

where the functions K_{lm} are defined by

$$K_{lm}=\lim_{q\to 0}F_{lm}(q,\ 0)\ . \tag{44}$$

The diagonal elements have the simple form

$$K_{ll}=-\frac{1}{N}\sum_k \frac{\partial n(\epsilon_l)}{\partial \epsilon_l(k)}\ . \tag{45}$$

For the constant-density-of-states model,

$$K_{11}=K_{22}=(N_0/3)n(\Delta,\ T),\quad K_{33}=(N_0/3)n(-2\Delta,\ T)\ . \tag{46}$$

The isothermal elastic constants[43] are obtained in the usual way from the second variation of the free energy in the presence of a static deformation with respect to this deformation. We obtain[44]

$$\begin{aligned} C_{11}&=C^0_{11}-[(G_{11}-G_{12})^2/K]\,K_{11}(K_{11}+K_{33})\ ,\\ C_{33}&=C^0_{11}-[2(G_{11}-G_{12})^2/K]\,K_{11}K_{33}\ ,\\ C_{12}&=C^0_{12}+[(G_{11}-G_{12})^2/K]\,K_{11}{}^2\ ,\\ C_{13}&=C^0_{12}+[(G_{11}-G_{12})^2/K]\,K_{11}K_{33}\ , \end{aligned} \tag{47}$$

where

$$K=2K_{11}+K_{33}\ . \tag{48}$$

The expressions for the isothermal elastic constants C_{44} and C_{66} are identical to those given by Eqs. (43). The expressions for $C_{11}-C_{12}$ are also equal, but in general the elastic constants obtained by the two approaches are different. It is interesting to note that if the dependence of the Fermi energy on the static deformation is neglected in the thermodynamic calculation, one obtains the result of the coupled-mode dispersion relation given by Eqs. (43).

In order to calculate the off-diagonal elements of K, an explicit model form for the wave-vector dependence of the d bands is required. The elastic constant C_{44} changes approximately 4% and 33% for V_3Si and Nb_3Sn, respectively, as the temperature is lowered from room temperature to $T=T_m$. This indicates that the coupling constant G_{44} is much larger for Nb_3Sn than for V_3Si.

For a sound wave propagating in the [110] direction with its polarization vector along $[1\bar{1}0]$, we obtain

$$\omega_q^2=\left((C^0_{11}-C^0_{12}/2M)-\frac{1}{2M}(G_{11}-G_{12})^2K_{11}\right)q^2\ . \tag{49}$$

If we make use of the definitions for the supercooling and superheating temperatures, this expression may be written

$$\omega_q^2=\frac{1}{2M}\,q^2(G_{11}-G_{12})^2\,\frac{1}{N}\sum_k[K_{11}(\Delta=0,\ T_0)-K_{11}(\Delta=0,\ T)] \tag{50}$$

and

$$\omega_q^2=\frac{1}{2M}\,q^2(G_{11}-G_{12})^2\times\frac{1}{N}\sum_k\left(\frac{3K_{11}(T_u)K_{33}(T_u)}{2K_{11}(T_u)+K_{33}(T_u)}-K_{11}(T)\right) \tag{51}$$

for the cubic and the tetragonal phase, respectively. In the cubic phase the frequency of this mode vanishes at the stability limit T_0, whereas in the distorted structure it remains finite at the stability limit $T=T_u$. For $T>T_u$ the frequency is complex and the mode is unstable.

For the constant-density-of-states model the temperature dependence of the elastic constants in the cubic phase is described by $n(0,\ T)$, and the scale of the temperature variation is determined by ϵ_F. In order to account for the strong temperature dependence of the elastic constant in this model, it is necessary to assume that $\epsilon_F(0)$ lies very close to the band edge, $T_F\sim 100$ °K. For $T\ll T_F$, $n(0,\ T)$ levels off, its slope being zero at $T=0$.

In the distorted structure the temperature dependence is determined by $n(\Delta,\ T)$ and $n(-2\Delta,\ T)$. Although Nb_3Sn and V_3Si show very similar behavior in the high-temperature phase, they behave very differently in the distorted structure. Whereas the elastic constants in Nb_3Sn stiffen in the low-temperature phase, in V_3Si they remain close to their value at $T=T_m$. For a positive deformation-potential coefficient $G_{11}-G_{12}$, it follows from Eq. (34) that $\rho_c>\rho_a$ if the c/a ratio is negative as in Nb_3Sn. The singlet band then has the lower energy and $\Delta>0$. From Eqs. (47) it then follows that at $T=0$,

$$C_{11}=C_{33}=C^0_{11},\quad C_{12}=C_{13}=C^0_{12}\ . \tag{52}$$

For V_3Si the c/a ratio is positive, which indicates either that the sign of $G_{11}-G_{12}$ or of Δ is opposite to that of Nb_3Sn. If $G_{11}-G_{12}<0$ and $\Delta>0$, the elastic constants remain close to zero only if $\Delta(0)<E_F(0)$, in which case both band edges lie below the Fermi level in the low-temperature limit. For $G_{11}-G_{12}>0$ and $\Delta<0$, one obtains for the domain-averaged elastic constants[45] in the low-temperature limit

$$\begin{aligned} (C_{11})_{\text{av}}-(C_{12})_{\text{av}}&\approx\tfrac{1}{2}(C^0_{11}-C^0_{12})\quad \text{for }-2\Delta(0)<\epsilon_F(0)\\ &\approx 0\quad \text{for }-2\Delta(0)>\epsilon_F(0)\ , \end{aligned} \tag{53}$$

which again suggests that both band edges might lie below the Fermi surface.

It should be noted, however, that when $\Delta(0) < \epsilon_F(0)$, the model containing only a linear coupling between the strain and the electron density does not give a stable low-temperature structure. This is most easily seen by considering the static relationship Eq. (28) in the limit $T=0$. For $\Delta(0) < \epsilon_F(0)$, this equation takes the form

$$C_{11}^0 - C_{12}^0 = \tfrac{1}{3} N_0 (G_{11} - G_{12})^2 , \tag{54}$$

which is inconsistent with the definition of T_0 [Eq. (36)] because $n(0, T_0) < 1$ for $T_0 > 0$. In order to stabilize the lattice, higher-order strain interactions or higher-order couplings of the strain with the electron density,[6] analogous to higher-order Jahn-Teller interactions, must be taken into account.

The coupled-mode dispersion relation yields strongly temperature-dependent elastic constants in the $q=0$ limit. For a bandwidth[6] of 1–2 eV and $\epsilon_F \sim 100\,^\circ\mathrm{K}$, $k_F \ll q_D$, where q_D is the Debye wave vector. Equation (23) then predicts that the renormalization of sound frequencies with $q \sim q_D$ will be small and only weakly temperature dependent. Recent neutron scattering data for V_3Si[36] show that the softening of the elastic constants extends about halfway to the zone boundary.

VI. CONCLUSION

A Hamiltonian describing the interaction of the strain and the acoustic phonons with electrons in a triply degenerate *d* band has been considered. A linear coupling of the strain with the electron density is sufficient to describe the transition for Nb_3Sn. For V_3Si, higher-order interactions must be taken into account.

From the Hamiltonian a description of the phase transition has been obtained, making very simple approximations. Setting the static parts of the equations of motion equal to zero yields expressions for the strain distortion and the repopulation of the electron bands. These may be derived alternatively from an approximate free-energy expression. Fluctuations about the average values are described by linearized equations of coupled acoustic-phonon–electron density fluctuations. The model yields low-frequency elastic constants which are strongly temperature dependent in agreement with the ultrasonic experiments, whereas for $q \sim q_D$ they are nearly temperature independent.

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[42] In Ref. 15 the special case $G_{12} = -\frac{1}{2} G_{11}$ was considered.

[43] Low-frequency ultrasonic experiments measure the adiabatic elastic constants. In the cubic phase the isothermal and the adiabatic elastic constants are equal. They are also equal at $T = 0$. For intermediate temperatures the two sets of elastic constants are somewhat different.

[44] Compare Ref. 29.

[45] $(C_{11})_{av} = \frac{1}{3}(2C_{11} + C_{33})$, $(C_{12})_{av} = \frac{1}{3}(2C_{13} + C_{12})$.

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Generalized Susceptibility Function for Rare Earths and Thorium and Their Alloys*

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The results of calculations of the generalized susceptibility function $\chi(\vec{q})$ for the rare-earth metals and thorium and its alloys with rare earths are presented. For the heavy rare earths Gd, Tb, Dy, Er, and Lu, the calculation was confined to the ΓA direction, and a mesh of 450 000 points in the Brillouin zone was used. For the double-hexagonal close-packed crystals Nd and Pr, a mesh of 400 000 points in the Brillouin zone was chosen, while for thorium and its fcc alloys with rare earths, a mesh of 2 048 000 points in the Brillouin zone was used. The results of calculations on Sc and Y have also been included for the sake of comparison with the heavy rare earths. The matrix elements, which couple the f electron and the conduction electron, appearing in the expression for the generalized susceptibility function, were taken to be constant. Our calculations show that the $\chi(\vec{q})$ curves obtained in this way are reasonably smooth and the scatter of points along the curves is less than 3%. The results have been compared with the experimental data on turn angles, spin-wave dispersion curves, and phonon spectra where available.

I. INTRODUCTION

The rare earths form a class of metals which exhibit fascinating magnetic structures below characteristic transition temperatures. In general, most heavy rare earths, with which we shall be chiefly concerned in this paper, have been found to exist in antiferromagnetic phases with a sinusoidal, a spiral, or a more complex arrangement of magnetic moments which are periodic with the periodicity along the c axis.[1] The electronic configuration of these metals is described by a set of closed shells containing 54 electrons corresponding to xenon, a partially filled $4f$ shell, and three electrons in the $5d$ and $6s$ states. The $4f$ electrons are highly localized and retain their orbital moment, as indicated by the data on entropy and magnetic properties. The $5d$ and $6s$ electrons are itinerant, as expected. Because of the high degree of localization of $4f$ electrons, there is practically no overlap between the neighboring ion cores, the nearest-neighbor distance being on the average 10 times the ionic radius. The principal mechanism responsible for magnetic ordering is believed to be the indirect exchange in which the conduction electrons play a key role to help neighboring ions interact with each other. The idea is that each $4f$ shell moment polarizes the spins of the conduction electrons in the neighborhood of the ion through an exchange interaction. The conduction electrons respond with an oscillatory and long-range polarization, and this in turn aligns a number of other f moments within the range.

The theory of indirect exchange interaction was first developed by Ruderman and Kittel[2] for the case of nuclei interacting via the hyperfine interaction with the conduction electrons. Kasuya[3] and Yosida[4] extended these ideas and obtained the so-called Ruderman-Kittel-Kasuya-Yosida (RKKY) exchange interaction for magnetic materials such as rare earths where there is almost no direct overlap between the magnetic ions.[5–8] It is assumed in this theory that the interaction of the Heisenberg $\vec{S}\cdot\vec{s}$ type between the f spin $\vec{S}$ and the conduction electron spin $\vec{s}$ is valid. This con-