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Anharmonic contribution to mode softening in V_3Si

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In order to assess the magnitude and significance of anharmonic effects in V_3Si the Landau theory of Bhatt and McMillan for the coupled-mode charge-density wave instability has been extended to higher order. The higher-order coupling parameters are determined empirically and are used to calculate nine second- through fourth-order elastic constants as a function of temperature. The nonlinear stress-strain curve calculated from these results is in good agreement with the experimental data of Patel and Batterman. The elastic-shear-mode softening has been investigated in the quasiharmonic anisotropic-elastic-continuum approximation, in which anharmonic effects enter through the third- and fourth-order elastic constants. A strong enhancement of the electronically driven instability by the anharmonic phonon-phonon interaction is found.

I. INTRODUCTION

The elastic-shear-mode softening and the associated low-temperature structural phase transformation in V_3Si and other A-15-type intermetallic compounds[1] have been explained previously on the basis of electronic effects. In the microscopic theories the mode softening is considered to arise either exclusively from a d-band Jahn-Teller effect at high-symmetry points of the Brillouin zone, resulting from the three orthogonal sets of transition-metal chains,[2-4] or in conjunction with the electron-phonon interaction giving rise to a Kohn anomaly[5-8] or a Peierls instability.[9-11] In the more recent phenomenological Landau theories the softening is attributed to a charge-density wave (CDW) instability.[12,13] On the other hand, the mode softening observed in ferroelectric and ferroelastic insulators has been accounted for in terms of anharmonic phonon-phonon interactions.[14,15] Since there is substantial experimental evidence for large anharmonic effects in A-15 compounds,[1] we have investigated the effect of the phonon-phonon interaction on the mode softening in V_3Si.

The most direct evidence for large anharmonicity consists of the strongly nonlinear stress-strain curve obtained by Patel and Batterman[16] by uniaxial compression of V_3Si at 25 °K, which shows a doubling of the soft shear modulus $c_s = \frac{1}{2}(c_{11} - c_{12})$ at a strain level as small as 5×10^{-4}. This result is corraborated by the effect of a radial compression on the ultrasonically measured shear modulus c_s observed by Testardi.[17] Although the dependence of the elastic constants on hydrostatic pressure[18-20] is normal, the temperature variation of their first pressure coefficients is unusual.[18-20] In V_3Ge the second pressure derivative of the shear modulus c_s is unusually large.[19] Other evidence of a more qualitative nature consists of a strong dependence of the low-temperature specific heat on nonhydrostatic stress[21] and the observation of acoustic second-harmonic generation.[22] Furthermore, the absolute magnitude of the Mössbauer recoil-free fraction in Nb_3Sn has been interpreted in terms of strongly anharmonic vibrations of the Sn atoms,[23] but this is not supported by x-ray measurements of the Debye-Waller factor.[24] Anharmonicity has also been invoked for explaining the temperature dependence of the specific heat of miscellaneous A-15 compounds[25] and of the thermal expansion of V_3Si (Ref. 26) and Nb_3Sn.[27] However, in the case of the specific heat, electronic effects cannot be ruled out as the exclusive cause, and the thermal-expansion data for V_3Si, which were obtained on polycrystals, are at variance with single-crystal data[28] and appear to be in conflict with the pressure derivatives of the single-crystal elastic constants.[18,20] The temperature dependence of the electrical conductivity at intermediate temperature has been attributed to anharmonic effects,[29] but the same data can also be explained in terms of intervalley electron scattering.[30] The potential importance of anharmonicity for understanding some of the unusual physical properties of A-15 compounds has been emphasized by Testardi.[17] In conclusion, it can be said that although much of the evidence is inferential and controversial, there are indisputable and quantitative experimental data, which make it compelling to include anharmonicity in the theory of A-15 compounds.

Therefore, it is the purpose of the present paper to evaluate for V_3Si the effect of the phonon-phonon interaction on the softening of the shear modulus c_s. The anharmonic effects are treated in the quasiharmonic anisotropic-continuum approximation and are characterized by the third- and fourth-order elastic (TOE and FOE) constants. Their magnitude and temperature dependence are evaluated empirically within the framework of a generalized Landau theory inspired by the coupled-mode CDW model of Bhatt and McMillan.[13]

II. THEORETICAL MODEL

An adequate microscopic theory of anharmonic effects in A-15 compounds would require consideration of the coupled electron-phonon system with electron-electron, electron-phonon, and phonon-phonon interactions treated on an equal footing. In order to circumvent the considerable difficulties arising from the complexities of these interactions and of the band structure, we choose a phenomenological approach based on the Landau theory of phase transitions.[31]

While in the original Landau theory the physical origin of the temperature dependence of the soft-mode frequency and of the order parameter are not specified in its more recent applications to A-15 compounds, the elastic-shear mode is considered to be driven soft by a CDW mode which acts as the primary order parameter. In the theory by Kragler and Thomas,[12] the shear-strain amplitudes are coupled directly to the fluctuation of the d-electron charge density in the three orthogonal chains of transition-metal atoms. The theory by Bhatt and McMillan[13] is more general in that optical modes are included in addition to the CDW amplitudes and the elastic strains, but the shear modes are coupled only to the optical-mode amplitudes, which, in turn, are coupled to the CDW amplitudes. In both theories the softening of the shear mode arises from the temperature dependence of the coefficient of the term quadratic in the order parameter. In the Kragler-Thomas theory this temperature dependence is determined empirically, whereas in the Bhatt-McMillan theory the usual linear temperature dependence is assumed. Both theories include dynamic effects through a Debye-type relaxation mechanism, and are able to explain the temperature dependence of the TA phonon branch[32,33] associated with the shear modulus c_s and the occurrence of a central peak observed in inelastic neutron scattering.[33]

In view of the strong evidence for anharmonic effects discussed above, it is surprising to note that these and other previous theories[3-13] are able to account for many of the anomalous properties of the A-15 compounds without explicitly including anharmonic effects.[34] In order to investigate the effect of anharmonicity on the temperature dependence and softening of the shear modulus c_s and the nonlinear stress-strain curve, we consider a modified Landau model for A-15 compounds in which the anharmonic contributions to the free energy are included in addition to the electronic effects arising from the CDW instability.

A. Quasiharmonic approximation

The simplest theory of anharmonic effects consists of the quasiharmonic approximation[35] (QHA). In this approximation the vibrations of the crystal lattice are described by harmonic oscillators representing $3sN$ normal modes with frequencies ω_i ($i=1,2,\ldots,3sN$; s is the number of atoms per unit cell; N is the number of unit cells in the crystal) which are explicitly strain dependent but which depend on temperature only indirectly through the temperature dependence of the thermal strain. Anharmonic effects arise through the strain dependence of the frequencies, and are described to any order n by the dimensionless nth strain derivatives (the microscopic nth Grüneisen parameters) defined by

$$\gamma^i_{\mu_1\cdots\mu_n}=(-1)^n\,\frac{1}{\omega_i}\,\frac{\partial^n\omega_i}{\partial\eta_{\mu_1}\cdots\partial\eta_{\mu_n}}\,, \tag{1}$$

where η_μ denotes the components of the Lagrangian strain tensor in Voigt notation.[36] The nth Grüneisen parameters depend on the anharmonic interatomic coupling parameters which give rise to phonon-phonon scattering processes of the order up to $n+2$.

Anharmonic properties that have been or which can be successfully tackled by the QHA are the temperature dependence of the linear thermal-expansion coefficient and the temperature dependence of the nth-order elastic constants.[35] In the QHA the molar free energy is given by[35]

$$F_{\mathrm{QH}}(T,\tilde{\eta}^{\mathrm{tot}})=\phi(\tilde{\eta}^{\mathrm{tot}})+\sum_i f^{\mathrm{th}}(T,\omega_i(\tilde{\eta}^{\mathrm{tot}}))\,. \tag{2}$$

Here $\phi(\tilde{\eta}^{\mathrm{tot}})$ denotes the strain energy of the static lattice, where $\tilde{\eta}^{\mathrm{tot}}$ is composed of the thermal strain and an additional homogeneous deformation strain. The sum in Eq. (2) is extended over all normal modes i with their vibrational contribution given by[35]

$$f^{\mathrm{th}}(T,\omega_i)=k_BT\ln[2\sinh(\hbar\omega_i/2k_BT)]\,. \tag{3}$$

Eliminating the thermal strain from the condition that the thermal stresses must vanish in the absence of a homogeneous strain, the free energy can be written as the sum of three contributions according to

$$F(T,\tilde{\eta})=F(T,0)+F^0(\tilde{\eta})+F^{\mathrm{anh}}(\tilde{\eta}) \tag{4}$$

The first term is the thermal free energy of the strain-free cyrstal. The second and third terms describe, respectively, the strain dependence of the static crystal (without zero-point and thermal motion) and the total anharmonic contribution resulting from zero-point and thermal motion. $F^0(\tilde{\eta})$ is approximated by a truncated Taylor expansion:

$$F_n^0(\tilde{\eta}) = V_0 \sum_{k=2}^{n} \sum_{\mu_1 \cdots \mu_k} \frac{1}{k!} c^0_{\mu_1 \cdots \mu_k} \eta_{\mu_1} \cdots \eta_{\mu_k} . \tag{5}$$

Here V_0 denotes the volume of the static crystal in the undeformed state, and $c^0_{\mu_1 \cdots \mu_k}$ denotes the kth-order elastic constants of the static crystal in the Voigt notation according to Brugger,[36] where the strain components are defined according to $\eta_\mu = \eta_{ij}$ for $\mu = 1, 2, 3$, and $\eta_\mu = 2\eta_{ij}$ for $\mu = 4, 5, 6$. A formally identical expression is obtained for $F_n^{\mathrm{anh}}(\tilde{\eta})$, where the corresponding expansion coefficients $c^{\mathrm{anh}}_{\mu_1 \cdots \mu_k}$ denote the total anharmonic contribution to the isothermal kth-order elastic constants arising from zero-point and thermal motion. The total isothermal kth-order elastic constants are then given by

$$c_{\mu_1 \cdots \mu_k} = c^0_{\mu_1 \cdots \mu_k} + c^{\mathrm{anh}}_{\mu_1 \cdots \mu_k} . \tag{6}$$

In the linear approximation in the thermal strain the total anharmonic contribution in the QHA is composed additively of the zero-point and thermal contributions:

$$c^{\mathrm{anh}}_{\mu_1 \cdots \mu_k} = c^{\mathrm{zp}}_{\mu_1 \cdots \mu_k} + c^{\mathrm{th}}_{\mu_1 \cdots \mu_k} . \tag{7}$$

For the second-order elastic constants the individual contributions in Eq. (7) are for cubic symmetry given by[35]

$$c^{\mathrm{zp}}_{\lambda\mu} = g^0_{\lambda\mu} E^{\mathrm{zp}} / V_0 , \tag{8}$$

$$c^{\mathrm{th}}_{\lambda\mu} = g_{\lambda\mu} \frac{E^{\mathrm{th}}}{V_0} + \left\langle \left(\sum_\mu \gamma^i_\mu \delta_\mu \right)^2 \right\rangle_c \frac{c_v T}{V_0} \delta_\lambda \delta_\mu , \tag{9}$$

where

$$g_{\lambda\mu} = \langle \gamma_{\lambda\mu} \rangle_\epsilon + \left[\left(c^0_{\lambda\mu} + \sum_\nu c^0_{\lambda\mu\nu} \delta_\nu \right) \Big/ B^0 \right] \sum_\rho \langle \gamma_\rho \rangle_\epsilon \delta_\rho , \tag{10}$$

and B^0 denotes the bulk modulus of the static crystal. E^{zp} and E^{th} denote the zero-point and thermal contributions to the internal energy, and $c_v = (\partial E^{\mathrm{th}} / \partial T)_v$, the molar specific heat. Equations (9) and (10) depend on weighted mode averages of the form

$$\langle A \rangle_w = \sum_{i=1}^{3sN} A_i w_i \Big/ \sum_{i=1}^{3sN} w_i , \tag{11}$$

where A denotes a Grüneisen parameter or a product of Grüneisen parameters, and w_i is the mean thermal energy ϵ_i of mode i (including zero-point energy), or the mode specific heat $c_i = (\partial \epsilon_i / \partial T)_v$. δ_μ denotes the Kronecker symbol in Voigt notation, i.e., $\delta_\mu = 1$ for $\mu = 1, 2, 3$, and $\delta_\mu = 0$ for $\mu = 4, 5, 6$. The superscript 0 in Eq. (8) refers to $T = 0$.

For the subsequent application to the A-15 structure the anharmonic contributions arising from coupling parameters up to and including fourth order will be considered. In addition, products involving three or more coupling parameters of any order, and two or more coupling parameters of fourth order are neglected. In this approximation the third- and higher-order elastic constants are independent of the zero-point and thermal contributions, and the free energy reduces to

$$F(T, \tilde{\eta}) = F(T, 0) + F_4^0(\tilde{\eta}) + F_2^{\mathrm{anh}}(T, \tilde{\eta}) . \tag{12}$$

Thus the static free energy $F_4^0(\tilde{\eta})$ depends on the static elastic constants of second through fourth order. The anharmonic contribution $F_2^{\mathrm{anh}}(T, \tilde{\eta})$ depends on the temperature-dependent contributions to the second-order elastic constants, which, in turn, depend on the coupling parameters of second through fourth order.

Equation (12) is the main result of this section. For subsequent construction of a Landau free energy, it is necessary to express this result in terms of the symmetry coordinates of the elastic strain. They are the eigenvectors of the 6×6 matrix of the second-order elastic constants. For cubic symmetry the symmetry coordinates are given by[37]

$$\begin{gathered} e_1 = (\eta_1 + \eta_2 + \eta_3)/\sqrt{3} , \quad e_2 = (\eta_1 - \eta_2)/\sqrt{2} , \\ e_3 = (\eta_1 + \eta_2 - 2\eta_3)/\sqrt{6} , \quad e_4 = \eta_4 , \\ e_5 = \eta_5 , \quad e_6 = \eta_6 . \end{gathered} \tag{13}$$

The two strain-dependent contributions to the free-energy density are given by

$$\frac{F_4(\tilde{e})}{V_0} = \frac{1}{2} \sum_\lambda \hat{c}^0_{\lambda\lambda} e^2_\lambda + \frac{1}{6} \sum_{\lambda\mu\nu} \hat{c}^0_{\lambda\mu\nu} e_\lambda e_\mu e_\nu + \frac{1}{24} \sum_{\lambda\mu\nu\rho} \hat{c}^0_{\lambda\mu\nu\rho} e_\lambda e_\mu e_\nu e_\rho \tag{14a}$$

and

$$\frac{F_2^{\mathrm{anh}}(\tilde{e})}{V_0} = \frac{1}{2} \sum_\lambda \hat{c}^{\mathrm{anh}}_{\lambda\lambda}(T) e^2_\lambda . \tag{14b}$$

Here and subsequently the second- through fourth-order elastic constants referred to symmetry coordinates are denoted by $\hat{c}_{\lambda\lambda}$, $\hat{c}_{\lambda\mu\nu}$, and $\hat{c}_{\lambda\mu\nu\rho}$. The second-order elastic constant matrix consists of the diagonal elements[37]

$$\begin{aligned} &\hat{c}_{11} = \hat{c}_{11} + 2\hat{c}_{12} , \\ &\hat{c}_{22} = \hat{c}_{33} = c_{11} - c_{12} , \\ &\hat{c}_{44} = \hat{c}_{55} = \hat{c}_{66} = c_{44} . \end{aligned} \tag{15}$$

$\frac{1}{3}\hat{c}_{11} = B$ is the bulk modulus and is associated with the totally symmetric mode e_1 which belongs to the irreducible representation Γ_1. The second eigenvalue corresponds to the shear modulus $\frac{1}{2}(c_{11}-c_{12})$, and is associated with the eigenvectors e_2 and e_3 which form basis vectors for the two-dimensional representation Γ_{12}. The third eigenvalue is equal to the shear modulus c_{44} and is associated with the three-dimensional representation Γ'_{25} with e_4, e_5, and e_6 as basis functions.

The TOE and FOE constants $\hat{c}_{\lambda\mu\nu}$ and $\hat{c}_{\lambda\mu\nu\rho}$ required here are related to the higher-order elastic constants in Voigt notation according to Brugger's definition[36] as follows:

$$\begin{aligned}\hat{c}_{111}&=(c_{111}+6c_{112}+2c_{123})/\sqrt{3}\,,\\ \hat{c}_{333}&=(-c_{111}+3c_{112}-2c_{123})/\sqrt{6}\,,\\ \hat{c}_{133}&=(c_{111}-c_{123})/\sqrt{3}\;;\end{aligned}\tag{16}$$

$$\begin{aligned}\hat{c}_{1111}&=\tfrac{1}{3}(c_{1111}+8c_{1112}+6c_{1122}+12c_{1123})\,,\\ \hat{c}_{3333}&=\tfrac{1}{2}(c_{1111}-4c_{1112}+3c_{1122})\,,\\ \hat{c}_{1133}&=\tfrac{1}{3}(c_{1111}+2c_{1112}-3c_{1123})\,,\\ \hat{c}_{1333}&=(-c_{1111}+c_{1112}-3c_{1123}+3c_{1122})/3\sqrt{2}\,.\end{aligned}\tag{17}$$

B. Quasiharmonic Landau free energy

The essential point of the Landau theory of phase transitions is an expansion of the free-energy difference between two homogeneous phases of different symmetry in terms of an order parameter η according to[31]

$$\Delta F=a\eta^2+b\eta^3+c\eta^4+\cdots\,.\tag{18}$$

The coefficient a is a function of temperature, and changes sign at a critical temperature T_c. Usually the high-temperature phase corresponds to the disordered state characterized by $\eta=0$. By expanding the coefficients $a, b, c\ldots$ in the vicinity of T_c with respect to $T-T_c$, the coefficient a is obtained in the linearly temperature-dependent form $a=a'(T-T_c)$, and the remaining coefficients are taken as constant. If the coefficient b of the third-order term is identically zero, or if it also vanishes at T_c, the transition is of second order, and T_c is identical to the transition temperature. For $b\neq 0$ the transition is of first order.

In A-15 compounds the cubic to tetragonal transition is weakly first order,[38] and the transformation strain is given by the symmetry coordinate e_3 according to Eq. (13). Writing the Landau free energy (LFE) with e_3 as the order parameter according to $\Delta F=F(T,e_3)-F(T,0)$, it is apparent from Eq. (14a) that a cube term in e_3 is present, and that the transformation must be of first order. This was pointed out first by Anderson and Blount.[39,40] These authors also suggested that a primary order parameter other than the elastic strain with no cube term present in the LFE is required to account for the essentially second-order nature of the phase transition. One of the two possibilities suggested by them, sublattice distortions associated with soft optical modes, has been ruled out because of the presence of cube terms for the Γ_{12} optical phonon modes[41] which couple linearly to the soft shear mode.[42] The second possibility would require a primary order parameter of electronic origin.[39] However, in most theories that consider electronic effects as the primary cause for the mode softening, the phase transition is of first order,[3-6,11,13] except in the quasi-one-dimensional model of Gor'kov,[10] where the weak first-order nature results from interchain coupling. It has recently been pointed out[43] that the essential results of the CDW model of Bhatt and McMillan are independent of a specific microscopic mechanism and would also follow from a Jahn-Teller-type instability.

In V_3Si both the bulk modulus and the shear modulus c_{44} are practically independent of temperature.[44] This suggests that the total anharmonic contributions to both quantities are very small. Hence we shall set $B^{\text{anh}}=c_{44}^{\text{anh}}=0$. Since the phase transformation does not involve the shear strains e_4, e_5, and e_6, they may be set equal to zero in Eq. (14a). In the resulting expression for the elastic free energy the orthorhombic strain component e_2 must be retained because it belongs to the same irreducible representation Γ_{12} as the tetragonal strain e_3, and the component e_1 will be retained as a parameter because of its pertinence for the volume dependence of the transformation temperature.

With these simplifications the quasiharmonic free-energy difference per unit volume becomes

$$\begin{aligned}\Delta F/V_0=&\tfrac{1}{2}\hat{c}_{11}e_1^2+\tfrac{1}{2}\hat{c}_{33}(e_2^2+e_3^2)+\tfrac{1}{6}\hat{c}_{111}e_1^3+\tfrac{1}{2}\hat{c}_{133}e_1(e_2^2+e_3^2)+\tfrac{1}{6}\hat{c}_{333}e_3(e_3^2-3e_2^2)+\tfrac{1}{24}\hat{c}_{1111}e_1^4\\ &+\tfrac{1}{4}\hat{c}_{1133}e_1^2(e_2^2+e_3^2)+\tfrac{1}{6}\hat{c}_{1333}e_1e_3(e_3^2-3e_2^2)+\tfrac{1}{24}\hat{c}_{3333}(e_2^2+e_3^2)^2\,.\end{aligned}\tag{19}$$

Except for $\hat{c}_{33}$, all elastic constants refer to the static lattice without zero-point and thermal motion. However, because of the coupling to the CDW amplitudes they depend now on temperature.

The soft shear modulus is given by

$$\hat{c}_{33}=\hat{c}_{33}^{\,\text{el}}+\hat{c}_{33}^{\,\text{anh}}\,.\tag{20}$$

The first term represents the contribution of the "static" lattice; because of its temperature dependence arising from electronic effects it has been so labeled. The second term represents the total anharmonic contribution from zero-point and thermal motion, as given by Eqs. (8)–(11).

C. Charge-density wave contribution to Landau free energy

The CDW model of Bhatt and McMillan[13] was inspired by Gor'kov's theory[9] of the shear-mode softening in A-15 compounds as the result of a Peierls instability of the three orthogonal one-dimensional (1-D) chains of transition-metal atoms in the A-15 structure. Since at the X point of the Brillouin zone of the A-15 structure, all electron bands are twofold degenerate, if the Fermi level lies close to the X point according to Gor'kov, a Peierls gap may open up from a displacement of nearest-neighbor transition-metal atoms along the chain in opposite directions. The irreducible representations Γ_2 and Γ_{12} of the optical modes containing these pairing motions have the basis functions

$$\begin{aligned} Q_1 &= (Q_x + Q_y + Q_z)/\sqrt{3}\,, \\ Q_2 &= (Q_x - Q_y)/\sqrt{2}\,, \qquad (21) \\ Q_3 &= (Q_x + Q_y - 2Q_z)/\sqrt{6}\,, \end{aligned}$$

where Q_1 belongs to Γ_2 and Q_2 and Q_3 belong to Γ_{12}. The subscripts x, y, and z refer to the directions of the three chains of transition-metal atoms in the A-15 structure that run parallel to the coordinate axes. The vibrational amplitudes of adjacent transition-metal atoms in the x chain are given by $\pm Q_x$, etc. The Γ_{12} optical modes are coupled linearly to the soft shear modulus c_s.[6] The changes in the d-electron charge density induced by the pairing motion of the transition-metal atoms represent an alternating increase and decrease of bond charges between adjacent atoms, and are denoted by ϕ_x, ϕ_y, and ϕ_z. Since the Peierls gap is proportional to the CDW amplitudes, the ϕ's may be treated as order parameters.[11,13] The associated symmetry coordinates are

$$\begin{aligned} \phi_1 &= (\phi_x + \phi_y + \phi_z)/\sqrt{3}\,, \\ \phi_2 &= (\phi_x - \phi_y)/\sqrt{2}\,, \qquad (22) \\ \phi_3 &= (\phi_x + \phi_y - 2\phi_z)/\sqrt{6}\,. \end{aligned}$$

In the model of Bhatt and McMillan[13] the shear-mode instability is caused by the CDW instability through the coupling of the CDW amplitudes to the Γ_{12} optical modes, which, in turn, are coupled to the elastic strains.

Following Bhatt and McMillan[13] we consider a static LFE ΔF_L in the approximation of a homogeneous phase as a function of the symmetry coordinates for three CDW amplitudes ϕ_x, ϕ_y, and ϕ_z, for the three optical-mode amplitudes Q_x, Q_y, and Q_z, and for the three diagonal components of the Lagrangian strain tensor η_{xx}, η_{yy}, and η_{zz} [cf. Eq. (13)]. Considering ΔF_L as a function of the seven variables ϕ_2, ϕ_3, Q_2, Q_3, e_1, e_2, and e_3, the truncated Taylor expansion up to fourth order exhibiting the proper symmetry of space group $O_h^3(Pm3n)$ is given by

$$\begin{aligned} \Delta F_L/V_0 = {} & \tfrac{1}{2}A_{33}(\phi_2^2+\phi_3^2) + \tfrac{1}{6}A_{333}\,\phi_2(\phi_2^2-3\phi_3^2) + \tfrac{1}{24}A_{3333}(\phi_2^2+\phi_3^2)^2 + \tfrac{1}{2}B_{33}(Q_2^2+Q_3^2) + \tfrac{1}{6}B_{333}\,Q_2(Q_2^2-3Q_3^2) \\ & + \tfrac{1}{24}B_{3333}(Q_2^2+Q_3^2)^2 + \tfrac{1}{2}C_{11}\,e_1^2 + \tfrac{1}{2}C_{33}(e_2^2+e_3^2) + \tfrac{1}{6}C_{111}\,e_1^3 + \tfrac{1}{2}C_{133}\,e_1(e_2^2+e_3^2) + \tfrac{1}{6}C_{333}\,e_3(e_3^2-3e_2^2) \\ & + \tfrac{1}{24}C_{1111}\,e_1^4 + \tfrac{1}{4}C_{1133}\,e_1^2(e_2^2+e_3^2) + \tfrac{1}{6}C_{1333}\,e_1e_3(e_3^2-3e_2^2) + \tfrac{1}{24}C_{3333}(e_2^2+e_3^2)^2 + F_{33}(\phi_2Q_2+\phi_3Q_3) \\ & + F_{222}[(\phi_2^2-\phi_3^2)Q_2 - 2\phi_2\phi_3Q_3] + F'_{222}[(Q_2^2-Q_3^2)\phi_2 - 2Q_2Q_3\phi_3] + G_{23}(\phi_2e_3-\phi_3e_2) \\ & + G_{222}[\phi_2(e_2^2-e_3^2) - 2\phi_3e_2e_3] + G_{231}(\phi_2e_3-\phi_3e_2)e_1 + G'_{223}[(\phi_2^2-\phi_3^2)e_3 + 2\phi_2\phi_3e_2] + G'_{221}(\phi_2^2+\phi_3^2)e_1 \\ & + H_{23}(Q_2e_3-Q_3e_2) + H_{222}[Q_2(e_2^2-e_3^2) - 2Q_3e_2e_3] + H_{231}(Q_2e_3-Q_3e_2)e_1 \\ & + H'_{223}[(Q_2^2-Q_3^2)e_3 + 2Q_2Q_3e_2] + H'_{221}(Q_2^2+Q_3^2)e_1\,. \qquad (23) \end{aligned}$$

As specified below, certain fourth-order terms allowed by the O_h^3 symmetry have been neglected. There are a total of 28 expansion coefficients in Eq. (23). They are assumed to be independent of temperature, except A_{33}, for which the usual linear temperature dependence pertaining to the Landau theory is assumed, i.e.,

$$A_{33} = A'(T-T_c)\,. \qquad (24)$$

Consequently, ϕ_2 and ϕ_3 are the primary order parameters, and are coupled through bilinear and higher-order terms to Q_2, Q_3, e_2, and e_3. The symmetry coordinates ϕ_1 and Q_1 have been omitted from ΔF_L because they belong to the Γ_2 representation and there are no bilinear coupling terms with any of the other seven variables. Thus these modes are inconsequential for the softening of the shear modulus c_s. Although e_1 does not couple bilinearly to any other symmetry coordinate, it has been retained in Eq. (23) because it is related to the volume dependence of all second- and higher-order elastic constants and of the transition temperature. In order to reduce the number of independent parameters, fourth-order coupling terms among the three different species ϕ, Q, and e of symmetry coordinates have been omitted.

The static model considered implies the adiabatic approximation, so that the internal variables, ϕ_α, Q_α ($\alpha = 2, 3$) may be eliminated through minimization, $\partial \Delta F_L / \partial \phi_\alpha = \partial \Delta F_L / \partial Q_\alpha = 0$. Substituting the solutions $\phi_\alpha(e_1, e_2, e_3)$ and $Q_\alpha(e_1, e_2, e_3)$ into Eq. (23) results in Eq. (19) for the elastic free-energy difference, where because of the mode coupling and the temperature dependence of A_{33} all nine "static" elastic constants $\hat{c}_{\lambda\mu}$, $\hat{c}_{\lambda\mu\nu}$, and $\hat{c}_{\lambda\mu\nu\sigma}$ are now functions of T. As outlined at the end of Sec. II B, in the present model these "static" constants, except $\hat{c}_{33}$, are equal to the total elastic constants in the free-energy difference, Eq. (19). However, according to Eq. (20), the anharmonic contribution $\hat{c}_{33}^{\text{anh}}$ must be added to the static constant $\hat{c}_{33}^{\text{el}}$ obtained here. In order to obtain the leading terms in the T dependence, we use the solutions in the linear approximation according to

$$\begin{aligned} \phi_2 &= \Delta_1 e_3, \quad \phi_3 = -\Delta_1 e_2, \\ Q_2 &= \Delta_2 e_3, \quad Q_3 = -\Delta_2 e_2, \end{aligned} \tag{25}$$

with

$$\Delta_1 = \frac{B_{33} G_{23} - F_{33} H_{23}}{A_{33} B_{33} - (F_{33})^2}, \quad \Delta_2 = \frac{A_{33} H_{23} - F_{33} G_{23}}{A_{33} B_{33} - (F_{33})^2}. \tag{26}$$

In this approximation the temperature dependence becomes

$$\hat{c}_{33}^{\text{el}} = \hat{c}_{33}^{*}(1 + \alpha_{33}\Theta), \tag{27a}$$

$$\hat{c}_{133} = \hat{c}_{133}^{*}(1 + \alpha_{133}\Theta + \beta_{133}\Theta^2), \tag{27b}$$

$$\hat{c}_{333} = \hat{c}_{333}^{*}(1 + \alpha_{333}\Theta + \beta_{333}\Theta^2 + \gamma_{333}\Theta^3), \tag{27c}$$

$$\hat{c}_{3333} = \hat{c}_{3333}^{*}(1 + \alpha_{3333}\Theta + \beta_{3333}\Theta^2 + \gamma_{3333}\Theta^3 + \delta_{3333}\Theta^4), \tag{27d}$$

where

$$\Theta = [1 + \Lambda(T - T_c^*)/T_c^*]^{-1} \tag{28}$$

is related to the renormalized critical temperature T_c^* defined by

$$T_c^* = T_c + \frac{C_{33}(F_{33})^2 - 2F_{33}G_{23} + B_{33}(G_{23})^2}{A'[B_{33}C_{33} - (H_{23})^2]}. \tag{29}$$

The coefficient Λ is given by

$$\Lambda = A'[B_{33}C_{33} - (H_{23})^2] B_{33} / (F_{33}H_{23} - B_{33}G_{23})^2. \tag{30}$$

The constants $\hat{c}_{33}^{*}$, $\hat{c}_{133}^{*}$, α_{33}, α_{133}, β_{133}, etc., in Eq. (27) depend on the 28 expansion coefficients in Eq. (23). For example, $\hat{c}_{33}$ and α_{33} are given by

$$c_{33}^{*} = [B_{33}C_{33} - (H_{23})^2]/B_{33}, \tag{31a}$$

$$\alpha_{33} = -(F_{33}H_{33} + B_{33}G_{23})^2/(F_{33}H_{23} - B_{33}G_{23})^2. \tag{31b}$$

The remaining five elastic constants $\hat{c}_{11}$, $\hat{c}_{111}$, $\hat{c}_{1111}$, $\hat{c}_{1133}$, and $\hat{c}_{1333}$ are independent of temperature.

The three coefficients α_{3333}, β_{3333}, and γ_{3333} are interrelated through the relation

$$3\alpha_{3333}\gamma_{3333} = 4(\beta_{3333})^2. \tag{32}$$

Thus the second- and higher-order elastic constants and their T dependence according to Eqs. (27) and (28) involve a total of 20 independent parameters, which in turn depend on the 28 expansion coefficients in Eq. (23). It is apparent that in the linear approximation of Eq. (25) nine of the expansion terms in Eq. (23) do not affect the form of the resulting Eqs. (27), although they are allowed by symmetry. For example, either one of the two third-order terms in Eq. (23) involving the coefficients A_{333} or B_{333} may be omitted without affecting the result. Also, the five terms in Eq. (23) resulting from the direct coupling of the CDW amplitudes to the strains are not essential in this sense.

In fact, results formally identical to Eqs. (19) and (27a)–(27c) can be obtained by omitting in Eq. (23) all terms involving the optical-mode amplitudes. This would be equivalent to a generalization of the model of Kragler and Thomas,[12] in which the charge-density fluctuations are coupled directly to the elastic strains, without the intermediate role of the optical modes. The only difference is that in this case the T dependence of the FOE constant $\hat{c}_{3333}$ would consist only of the Θ^4 term in (27d), and that in order to obtain the terms of lower order in Θ all fourth-order coupling terms between the CDW amplitude and the strain must be included in Eq. (23). Thus the essential result obtained from the generalized CDW model of Bhatt and McMillan,[13] consisting of the LFE as given by Eq. (19) and the T dependence of the elastic constants according to Eqs. (27) and (28), is largely independent of the particular model used. We have chosen to derive Eqs. (19) and (27) from the CDW model of Bhatt and McMillan[13] because the underlying physical mechanism of the optical-mode-driven Peierls instability provides an intuitively convincing reason for the T dependence of the coefficient A_{33} of the term quadratic in the charge-density amplitude. On the other hand, in the interchain charge-transfer model of Kragler and Thomas[12] this T dependence is postulated in terms of a T-dependent effective d-electron density of states which is determined empirically from the T dependence of the shear modulus.

It has been shown recently that the primary softening mechanism in A-15 compounds may also be a Jahn-Teller effect occurring at the R point,[4] or at the M point and at two saddle points located along the ΓX directions[11] of the Brillouin zone. In these cases the symmetry coordinates and their transformation properties under O_h^3 would be different from those given in Eq. (22), but it is not to be expected that this would lead to drastically different results for the T dependence of the second- and higher-order elastic constants.

Equations (23) and (19) are generalized forms of Bhatt and McMillan's[13] Eqs. (31) and (32). Equation (31) of Ref. 13 involves seven independent parameters,[45] which are (in the notation of the present paper) A_{33}, A_{3333}, B_{33}, C_{33}, F_{33}, H_{23}, and G'_{223}. However, Eq. (32) of Ref. 13 involves only four parameters, which are (in our notation) T_c^*, $(c_{33}^*\Lambda)$, c_{333}^*, and c_{3333}^*, in conjunction with $\alpha_{33}=-1$. The reduction of the number of parameters from seven to four results from Landau's approximation of a linear temperature dependence of the soft shear modulus $\hat{c}_{33}$, and of taking the third and fourth-order coefficients $\hat{c}_{333}$ and $\hat{c}_{3333}$ as constants. If this approximation is not made, the resulting equation would involve the additional parameters β_{333} and δ_{3333}, and $\hat{c}_{33}^*$ and Λ would enter individually.

In the present model 13 additional parameters enter. They are α_{33}, α_{133}, β_{133}, α_{333}, γ_{333}, α_{3333}, and β_{3333}, which according to Eq. (27) describe the temperature dependence of the four temperature-dependent second- through fourth-order elastic constants, and c_{11}, c_{111}, c_{1111}, c_{1133}, c_{1333}, and c_{133}^*, which are required to describe volume-dependent effects.

Inclusion of the temperature dependence of the higher-order elastic constants is demanded by the available experimental data for $\hat{c}_{133}$ calculated from the first pressure derivative of the soft shear modulus[18] (see Fig. 1 below). Since the remaining two T-dependent elastic constants $\hat{c}_{333}$ and $\hat{c}_{3333}$ represent the first and second derivatives of the soft shear modulus $\hat{c}_{33}$ with respect to the tetragonal strain e_3, Eq. (13), they may also be expected to be temperature dependent, but no experimental data are yet available.

The extension of the CDW model of Bhatt and McMillan[13] described in this section is necessary in order to obtain all nine second- through fourth-order elastic constants which are in the approximation of the present paper required to characterize and calculate the anharmonic contribution to the soft shear modulus according to Eqs. (7)–(10).

D. Thermodynamic equilibrium conditions

As will be described in Sec. III A, the independent parameters of the present model are determined from the available experimental data of the elastic constants and of the transformation strain, in conjunction with several thermodynamic conditions. For this purpose pressure effects are included, and instead of the LFE [Eq. (19)] the Landau-Gibbs free energy (LGFE) $\Delta G=\Delta F+p\Delta V$ must be introduced in accordance with the nonlinear theory of elasticity.[46] The term

$$\Delta V=V(p;e_1,e_2,e_3)-V(p;0,0,0)$$

represents the additional volume change associated with a strain (e_1,e_2,e_3) superimposed on a hydrostatic compression. The total strain composed of the strain caused by the hydrostatic pressure p and the additional strain (e_1,e_2,e_3) is in symmetry coordinates given by

$$e_1^{\text{tot}}=(\tfrac{1}{2}\sqrt{3})(\lambda^2-1)+\lambda^2 e_1\,, \tag{33a}$$

$$e_2^{\text{tot}}=\lambda^2 e_2\,, \tag{33b}$$

$$e_3^{\text{tot}}=\lambda^2 e_3\,, \tag{33c}$$

where $\lambda^3=V(p)/V_0$ denotes the volume ratio associated with the hydrostatic compression. Taking the strain in Eq. (19) to be the total strain according to Eqs. (33a)–(33c), and expanding ΔF and ΔV with respect to the additional strain components e_1, e_2, e_3, one obtains the LGFE for V_3Si after setting[47] $e_1=e_2=0$ in the form

$$\Delta G/V=Ae^2+Be^3+Ce^4\,. \tag{34}$$

Here $e=e_3$ is the order parameter, and A, B, and C are the pressure-dependent second-, third-, and fourth-order effective elastic constants. V denotes the volume at pressure p for $e=0$. In the approximation of the present paper anharmonic effects are considered up to fourth order only, and the pressure dependence of these coefficients is then explicitly given by

$$2A=\hat{c}_{33}(p)=\hat{c}_{33}+\hat{c}'_{33}p+\tfrac{1}{2}\hat{c}''_{33}p^2\,, \tag{35a}$$

$$6B=\hat{c}_{333}(p)=\hat{c}_{333}+\hat{c}'_{333}p\,, \tag{35b}$$

$$24C=\hat{c}_{3333}\,. \tag{35c}$$

The pressure derivatives denoted by primed quantities are expressed in terms of the elastic constants of second through fourth order according to[46]

$$\hat{c}'_{33}=-(\hat{c}_{33}+\sqrt{3}\,\hat{c}_{133})/\hat{c}_{11}-2\,, \tag{36a}$$

$$\hat{c}''_{33}=[(1+\hat{c}'_{11})\,\hat{c}_{33}+(4+\hat{c}'_{11})\sqrt{3}\,\hat{c}_{133}+3\hat{c}_{1133}]/(\hat{c}_{11})^2\,, \tag{36b}$$

$$\hat{c}'_{333}=-(3\hat{c}_{333}+\sqrt{3}\,\hat{c}_{1333})/6\hat{c}_{11}+1/3\sqrt{6}\,. \tag{36c}$$

The quantities

$$\hat{c}'_{11}=-\sqrt{3}\,\hat{c}_{111}/\hat{c}_{11}\,, \tag{36d}$$

$$\hat{c}''_{11}=[(1-3\hat{c}'_{11}-(\hat{c}'_{11})^2)\hat{c}_{11}+3\hat{c}_{1111}]/\hat{c}_{11}^2 \tag{36e}$$

correspond to the first and second pressure derivatives of the bulk modulus $B=\frac{1}{3}\hat{c}_{11}$.

The substance of the Landau theory is contained in the two equations

$$\Delta G = 0\,, \tag{37a}$$

$$\frac{\partial \Delta G}{\partial e} = 0\,, \tag{37b}$$

which express thermodynamic and mechanical equilibrium between the cubic and the tetragonal phase, respectively. From Eq. (37b) the strain in the tetragonal phase satisfying the stability condition $\partial^2 \Delta G/\partial e^2 \geqslant 0$ is obtained as a function of T and p in the form

$$e_{\text{tet}}(T,p) = -(3B/8C)\left[1+(1-32AC/9B^2)^{1/2}\right]\,, \tag{38}$$

where in the present model the coefficients A, B, and C depend on T and p according to Eqs. (27) and (35), respectively. The transformation temperature $T_m(p)$ is determined by the condition

$$4AC = B^2\,, \tag{39}$$

obtained by substituting (38) into (37a).

The coefficients A, B, and C are now functions of pressure only, $A=A(T_m(p),p)$, etc., and Eq. (39) is valid at any pressure p.

E. Anisotropic-continuum approximation

In the anisotropic-continuum model[49-51] (ACM) the phonon dispersion relations are approximated by the acoustic branches in the long-wavelength limit, and the third- and fourth-order coupling parameters reduce to the TOE and FOE constants.

For O_h symmetry there are 6 TOE and 11 FOE constants. For lack of information the Cauchy relations for these higher-order elastic constants have been assumed,[52] whereby the number of independent higher-order elastic constants is reduced to three and four, respectively.[51,53] Thus in view of Eqs. (8)–(11) c_{33}^{anh} is given by a functional of the form

$$\hat{c}_{33}^{\text{anh}}(T) = \hat{c}_{33}^{\text{anh}}(\hat{c}_{11}, \hat{c}_{33}^{\text{el}}(T), \hat{c}_{111}, \hat{c}_{133}(T), \hat{c}_{333}(T), \hat{c}_{1111}, \hat{c}_{1133}, \hat{c}_{1333}, \hat{c}_{3333}(T); T)\,, \tag{40}$$

and depends on temperature both through the T dependence of some of the elastic constants according to Eqs. (27) and through the temperature dependence of the weight factors w_i in the mode average defined in Eq. (11).

The relations for the anharmonic contributions to the elastic constants in terms of the second- through fourth-order elastic constants have been given[50,51] for cubic symmetry (O, O_h, and T_d) in the limiting cases $T=0$ and $T > \Theta_D$ (= Debye temperature). Numerical application to alkali halides, noble metals, and β-brass has demonstrated that in these limiting cases the ACM is capable of accounting for the temperature dependence of the elastic constants on the basis of experimental values for the TOE and adjusted values for the FOE constants.[50,51] It has further been shown that for a variety of materials the T dependence of the thermal first Grüneisen parameter $\gamma = \beta B^s/\rho C_p$ can be accounted for semiquantitatively in the entire temperature range on the basis of the ACM.[49]

Encouraged by this success, we have calculated in this paper the temperature dependence of the anharmonic contribution $\hat{c}_{33}^{\text{anh}}$ on the basis of the ACM over the entire temperature range. In the intermediate temperature range the standard expansions of the Debye function for the two ranges $\hbar\omega_i > k_B T$ and $< k_B T$ were used. In the ACM the integration over the first Brillouin zone reduces to a directional average over the unit sphere which has been evaluated by Gaussian quadrature by using a total of 64 integration points per octant. Increasing the number of integration points by a factor of 4 did not alter the results significantly.

III. RESULTS AND DISCUSSION

A. Determination of parameters for V_3Si

As outlined in Sec. II C, the model involves 21 parameters; three of these are interrelated through one constraint according to Eq. (32). Since it was found that a better fit to the diverse experimental data was obtained without this constraint, it was decided to omit this condition.

The parameters of the model have been determined for transforming V_3Si in conjunction with the thermodynamic conditions of Sec. II D from the following experimental data: (i) The soft shear modulus $\hat{c}_{33}(T)$ from 37 to 300 °K (Ref. 18); (ii) the first pressure derivative $\hat{c}_{33}'(T)$ from 37 to 300 °K (Ref. 18); (iii) the bulk modulus $B=\frac{1}{3}\hat{c}_{11}$ and its linear pressure dependence from 0 to 10 kbar, independent of temperature (Ref. 18); (iv) the lattice parameters in the tetragonal phase as a function of temperature from 17 to about 21 °K (Ref. 48); and (v) the linear pressure dependence of the transformation temperature from 0 to 18 kbar (Ref. 54).

While all parameters in the theory refer to the isothermal second- and higher-order elastic constants, most experimental input data are either adiabatic ($\hat{c}_{11}$) or mixed isothermal-adiabatic ($\hat{c}_{111}$, $\hat{c}_{1111}$, and $\hat{c}_{133}$). For $\hat{c}_{33}$ the adiabatic and isothermal constants are identical, and for the remaining data the difference will be neglected in the subsequent numerical applications.

A constant value of the pressure coefficient of the bulk modulus ($B' = 4.6$) has been inferred from only two data points at 77 and 300 °K. However, the extrapolation to lower temperature is ambiguous and could lead to a weak temperature dependence of B'. We have verified that the numerical results of the present paper are not affected by this.

The three parameters $\hat{c}_{11}$, $\hat{c}_{111}$, and $\hat{c}_{1111}$ are directly given by the experimental data according to (iii), in conjunction with Eqs. (36d) and (36e).

The 14 parameters occurring in Eqs. (27b)–(27d) and (28) are fitted to the data (i), (ii), and (iv), with extrapolated values of $\hat{c}_{33}(T)$ used below 37 °K. Since the elastic data (i) and (ii), and the x-ray data (iv) were obtained from two different samples with different transformation temperatures, the temperature scale of the x-ray data was shifted. The magnitude of the shift was determined through minimization so as to give the best overall fix for both sets of data.

The two FOE constants $\hat{c}_{1133}$ and $\hat{c}_{1333}$ are obtained from the first and second pressure derivatives of the thermodynamic condition Eq. (39), evaluated at zero pressure, with the pressure dependence of the transformation temperature involved taken from the data according to (v). Condition (39) was relaxed to $|4AC/B^2 - 1| < 10^{-5}$, instead of zero.

Finally, the two remaining parameters c^*_{33} and α_{33}, which determine the T dependence of the electronic contribution c^{el}_{33} as given in Eq. (27a), are obtained in the following manner. According to Eq. (20) the soft shear modulus $\hat{c}_{33}(T)$ is additively composed of the electronic part $\hat{c}^{el}_{33}(T)$ and the anharmonic part $\hat{c}^{anh}_{33}(T)$, which according to Eq. (41) also depends on $\hat{c}^{el}_{33}(T)$ and, in addition, on all previously determined second- and higher-order elastic constants. For each of a sequence of nine selected temperatures from 37 to 300 °K, $\hat{c}^{el}_{33}$ was determined iteratively from Eqs. (20) and (40), with the experimental data according to (i) used for the total value $\hat{c}_{33}$ in Eq. (20). The self-consistent electronic part $\hat{c}^{el}_{33}(T)$ so obtained was then least-squares fitted to Eq. (27a), thus completing the determination of the parameters.

TABLE I. Temperature-independent second-, third-, and fourth-order elastic constants (in 10^{12} dyn/cm^2).

$\hat{c}_{11}$	$\hat{c}_{111}$	$\hat{c}_{1111}$	$\hat{c}_{1133}$	$\hat{c}_{1333}$
5.355	−41.78	403.2	11,392	−33,457

The complete set of parameters so determined is listed in Tables I and II. The results obtained with these parameters are presented and will be discussed in Sec. III B.

B. Third- and fourth-order elastic constants

All seven TOE and FOE constants were determined from experimental data within the framework of the anharmonic CDW model only, and are not affected by the assumptions underlying the quasiharmonic anisotropic-continuum approximation. The four constants $\hat{c}_{111}$, $\hat{c}_{1111}$, $\hat{c}_{1133}$, and $\hat{c}_{1333}$ are independent of temperature, and their numerical values are listed in Table I. As a result of the CDW instability the remaining three constants $\hat{c}_{133}$, $\hat{c}_{333}$, and $\hat{c}_{3333}$ depend, according to Eqs. (27b)–(27d), on temperature, and are shown in Fig. 1. All three curves are very similar. At low temperature they exhibit a steep rise with increasing T, and after passing through a maximum near 60 °K they decrease more gradually with T.

The transformation temperature T_m defined by Eq. (39) as calculated with the parameters from Tables I and II is found to be 21.95 °K. It is apparent from Fig. 1 that both $\hat{c}_{333}$ and $\hat{c}_{3333}$ assume small but finite values at T_m.

The TOE and FOE constants $c_{\lambda\mu\nu}$ and $c_{\lambda\mu\nu\sigma}$, respectively, in the conventional Voigt notation are obtained from the quantities $\hat{c}_{\lambda\mu\nu}$ and $\hat{c}_{\lambda\mu\nu\rho}$ referred to symmetry coordinates according to Eqs. (16) and (17), and are plotted in Fig. 2 as a function of T.

TABLE II. Parameters describing the temperature dependence of the electronic parts of the second-, third-, and fourth-order elastic constants according to Eqs. (27) and (28). $\Lambda = 0.3169(°K)^{-1}$; $T^*_c = 7.4287$ °K.

$\mu\nu\cdots$	$c^*_{\mu\nu\cdots}$ (10^{12} dyn/cm^3)	$\alpha_{\mu\nu\cdots}$	$\beta_{\mu\nu\cdots}$	$\gamma_{\mu\nu\cdots}$	$\delta_{\mu\nu\cdots}$
33	1.807	1.257			
133	−16.457	−4.187	7.056		
333	−4.426	−333.769	88.669	710.776	
3333	37.798	84.997	−109.783	−84.981	75.507

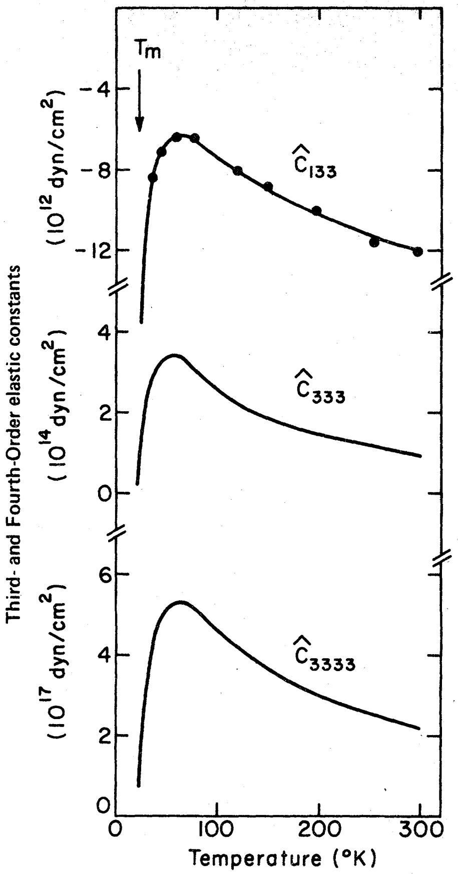

FIG. 1. Temperature dependence of third-order constants $\hat{c}_{133}$ and $\hat{c}_{333}$ and of fourth-order elastic constant $\hat{c}_{3333}$. Solid line, calculated; ●, selected experimental data calculated from Carcia and Barsch (Ref. 18) with Eq. (36a).

With the exception of c_{1123}, all quantities $c_{\lambda\mu\nu}$ and $c_{\lambda\mu\nu\rho}$ are temperature dependent. The type of dependence is the same as for $\hat{c}_{\lambda\mu\nu}$ and $\hat{c}_{\lambda\mu\nu\rho}$, but there are differences in the magnitude of the temperature variation, which is largest for c_{123} and c_{1111} and smallest for c_{112}, c_{1112}, and c_{1122}. The absolute magnitude of these TOE and FOE constants is unusually large. Typically, TOE constants are about one, and FOE constants about two order of magnitudes larger than the second-order elastic constants.[55-57] According to Fig. 1 for V_3Si, the TOE constants at 300 °K are about one to two, and at 50 °K about two to three orders of magnitude larger than the soft shear modulus c_s. The FOE constants at 300 °K are about four to five, and at 50 °K up to six orders of magnitude larger than c_s. This, of course, implies unusually large anharmonic effects, especially at lower temperatures.

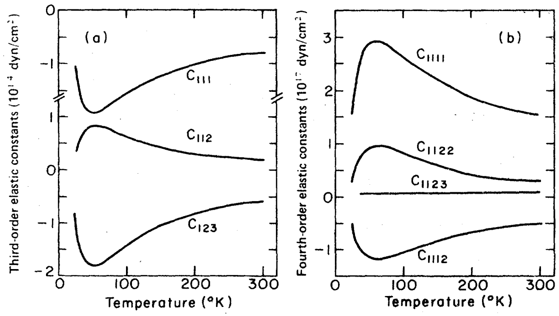

FIG. 2. Calculated temperature dependence of higher-order elastic constants in Voigt notation: (a) third-order elastic constants, (b) fourth-order elastic constants.

It is noteworthy that for V_3Si the kind of temperature dependence of the higher-order elastic constants displayed in Fig. 1 has been obtained for the Grüneisen parameter referred to the tetragonal strain in Eq. (13) (which is equivalent to $\hat{c}_{333}$) on the basis of a microscopic linear chain model with a step-function-like density of states.[58]

No experimental data of the individual TOE and FOE elastic constants are available for comparison with the results in Fig. 1. However, these results will be used in Sec. III C to calculate the nonlinear stress-strain relation for comparison with the measurements of Patel and Batterman[16] at 25 °K. Finally, in Sec. III D the temperature-dependent anharmonic contributions to c_s calculated from the TOE and FOE constants of Fig. 2 will be presented and discussed.

C. Nonlinear stress-strain relation

Patel and Batterman[16] have directly studied the elastic softening at low temperatures of V_3Si by measuring with x-rays the temperature dependence of the transverse strain η_{22} for a series of constant static stresses σ_{33}. From these data a stress-strain relation has been obtained that shows strongly nonlinear behavior.[16] In a previous paper this stress-strain relation has been calculated on the basis of nonlinear elasticity theory from a truncated series expansion of the form

$$-\sigma = \alpha\eta + \beta\eta^2 + \gamma\eta^3 , \qquad (41)$$

where the coefficients α, β, and γ have been given in terms of the second- through fourth-order elastic constants.[59,60] In Eq. (41), $-\sigma = \sigma_{33}$ is the component of the Cauchy stress tensor for uniaxial compression along x_3, and $\eta = \eta_{22}$ the component of the Lagrangian strain tensor corresponding to the transverse strain. Numerical application to V_3Si based on estimates of the TOE and FOE constants resulted in a nonlinear stress-strain curve in rough semiquantitative agreement[61] with the results of Patel and Batterman.

We have recalculated the stress-strain curve according to Eq. (41) by using as input the TOE and FOE elastic constants of Fig. 2 and the second-order elastic constants from Carcia and Barsch.[18] Because of the temperature dependence of all elastic constants involved, the results are also strongly temperature dependent. In Fig. 3 the calculated results are shown for 26, 27, and 28 °K together with the data of Patel and Batterman[16] at 25 °K. It is apparent that, except for the data point at the highest stress level, the calculated curves for 27 and 28 °K agree within experimental error with the experimental curve at 25 °K. The discrepancy in temperature may be attributed in part to the different transformation temperatures of the V_3Si crystals used in the x-ray determination of the stress-strain curve[16] (20.5 °K) and in the ultrasonic measurements[18] (about 22 °K) on which the higher-order elastic constants in Fig. 2 are based. Since the transformation temperature depends on the concentration of such defects as determine the residual resistance ratio,[48,62,63] it is also conceivable that the difference between the static and the dynamic elastic behavior arises from a defect relaxation mechanism.[64] Finally, the discrepancy in Fig. 3 at the highest stress level could perhaps be attributed to the truncation error implied in the cubic approximation of Eq. (41).

On the whole, the agreement between the calculated and the experimental data in Fig. 3 obtained without adjustable parameters suggests that the TOE and FOE constants of Fig. 2 possess the correct order of magnitude and temperature variation.[65] Therefore, the results of Fig. 2 will be used in the following Sec. III D to assess the magnitude and temperature dependence of the anharmonic contribution to the softening of the shear modulus.

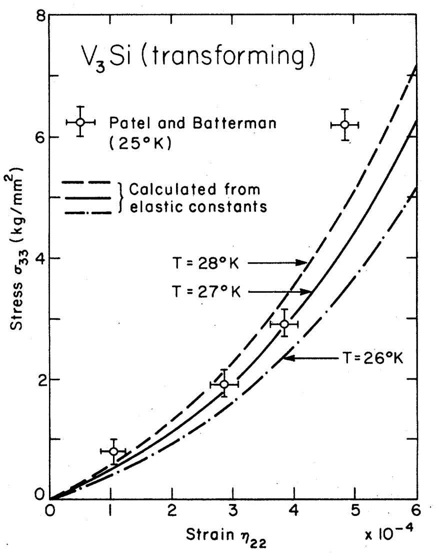

FIG. 3. Comparison of theoretical stress-strain relation calculated from Eq. (41) and higher-order elastic constant data of Fig. 2 with experimental results of Patel and Batterman (Ref. 16).

D. Anharmonic contribution to shear modulus

Figure 4(a) shows the decomposition of the soft shear modulus $c_s(T)$ into the electronic and anharmonic contributions according to Eq. (20), and Fig. 4(b) shows the decomposition of the anharmonic contribution into the two separate contributions from zero-point and thermal motion[66] according to Eq. (7). In Fig. 4(a) the experimental data for the shear modulus are included in addition to the calculated total shear modulus which was fitted to these data by iteratively determining the individual electronic and anharmonic contributions from Eqs. (20) and (40) on the basis of the ACM. Also included in Fig. 4(a) is the fit of the so-determined electronic contribution to the functional form of the CDW model as given by Eq. (27a).

It is apparent that with decreasing temperature both the electronic and the anharmonic contributions decrease by comparable amounts, and thus

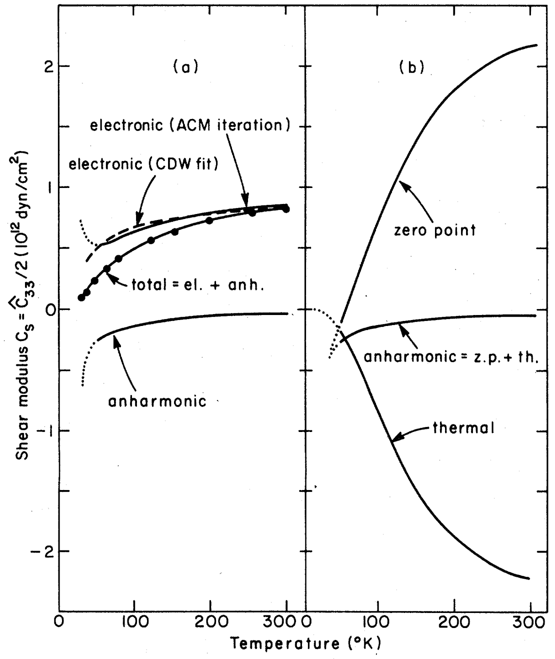

FIG. 4. Temperature dependence of the shear modulus $c_s = \frac{1}{2}\hat{c}_{33}$ and of its individual contributions. (a) Calculated total shear modulus with selected experimental data from Carcia and Barsch (Ref. 18) (●); calculated electronic and anharmonic contributions from ACM iteration according to Eq. (20) and (40); further shown is the fit of the electronic contribution to Eq. (27a) of the CDW model. (b) Calculated zero-point, thermal, and anharmonic contributions according to Eq. (7).

both are responsible for the shear mode softening. The zero-point and the thermal contributions that make up the anharmonic part are at high temperature considerably larger than either the anharmonic or the electronic contributions, or than the total shear modulus. With decreasing temperature the thermal contribution has a stabilizing effect, and zero-point motion as well as the total anharmonic contribution has a destabilizing effect.[66] The zero-point contribution to the shear modulus is temperature dependent because in the present model the corresponding second strain derivative of the zero-point energy depends on the temperature-dependent electronic parts of the second- through fourth-order elastic constants. The negative sign and the trend of the temperature dependence of the thermal contribution are the same as typically found in the temperature dependence of weakly anharmonic solids,[35] but the relative magnitude with respect to the total elastic constants is considerably larger than normal. Although the total anharmonic contribution arises as the sum of two large contributions of opposite sign, it constitutes at low temperature a much larger function of the total shear modulus than, and exhibits a temperature dependence opposite to that which is typical for, weakly anharmonic solids.[35] As a result, the electronically driven weak softening is enhanced by the anharmonic phonon-phonon interaction, in contrast to all previous models of A-15 compounds, which attribute the shear mode softening entirely to electronic effects.

No direct experimental verification of the decomposition of the shear modulus into the electronic and anharmonic parts, and of the anharmonic part into the zero-point and the thermal contributions in Figs. 4(a) and 4(b), appears possible.

The decomposition of the shear modulus c_s^{tot} into c_s^{el} and c_s^{anh} results from the iterative solution of the equation $c_s^{\text{el}}(T)=c_s^{\text{tot}}(T)-c_s^{\text{anh}}(c_s^{\text{el}}(T),T)$ for c_s. Here the explicit temperature dependence of c_s^{anh} arises according to Eq. (40) from the temperature dependence of the higher-order elastic constants, with all required parameters already independently determined. Therefore the solution for c_s^{el} involves no additional adjustable parameters. This is all the more remarkable since according to Eq. (40) c_s^{anh} is a very complicated function of T and depends sensitively on c_s^{el}. Depending on the initial trial value of c_s^{el}, several other solutions for c_s^{el} were obtained and discarded because the electronic and anharmonic contributions involved were unreasonably large.

It is gratifying to observe that above 50 °K the electronic contribution so obtained shows the positive temperature dependence characteristic of the CDW model. This dependence is a purely harmonic effect described by Eq. (27a), and involves the two additional parameters $\hat{c}_{33}^*$ and α_{33} in Table II. On the other hand, the negative temperature coefficient of c_s^{el} below the minimum at 50 °K is in conflict with the CDW instability, and could be attributed to the approximations made in order to incorporate anharmonic effects into the CDW model. Specifically, the rather abrupt change of the temperature coefficient of c_s^{anh} near 50 °K and the greatly enhanced negative values of c_s^{anh} shown as the dotted line in Fig. 4(a) seem to suggest that below 50 °K the anharmonic contributions to the higher-order elastic constants should also have been included. Because of the other approximations summarized in Sec. III E, the specific numerical values of c_s^{el}, c_s^{anh}, c_s^{zp}, and c_s^{th} should be regarded only as first estimates, even above 50 °K.

Since the quasiharmonic approximation does not give the imaginary part of the phonon self-energy, investigation of phonon lifetime effects, for which there appears to be some evidence,[12] would require extension of the theory by using field-theoretic techniques.

E. Order of the transition

The LGFE, according to Eq. (34), used in the present work with the cubic term present describes a first-order phase transition. However, as is apparent from Figs. 1 and 4(a) in connection with Eq. (35) for zero pressure all three expansion coefficients A, B, and C become zero near 21 °K. The extrapolated shear modulus $\hat{c}_{33}=2A$ used in the present work becomes zero at 21.74 °K. At this temperature the third-order coefficient B has decreased to 2% of its maximum value, thereby rendering the transition almost second order. On the other hand, at this temperature, the fourth-order coefficient C has decreased only to 10% of its maximum value, so that the LGFE expansion, Eq. (34), presumably is still valid.

The phenomenon that the second- and third-order expansion coefficients vanish almost simultaneously seems to arise from the presence of the two distinct but interrelated softening mechanisms of electronic and anharmonic origin.

From the numerical data of Table I and Eq. (36c), one obtains for the pressure coefficient of the third-order expansion coefficient B a value of +300. This implies that the first-order character of the transition becomes more pronounced with increasing pressure.

F. Limitations of model

The main objective of the present paper has been the assessment of the anharmonic contribution to the shear mode softening. For this purpose the TOE and FOE constants were determined within the framework of a generalized Landau theory from experimental data, and were subsequently used to evaluate the temperature dependence of both the anharmonic and the electronic contributions to the soft shear modulus c_s on the basis of the quasiharmonic ACM. Consequently, the TOE and FOE constants are subject to the limitations of the specific Landau model, but the individual contributions to the soft shear modulus are, in addition, affected by the limitations of the quasiharmonic ACM.

The basic presuppositions of the Landau theory, namely, the analytic behavior of the free-energy function with respect to the variables ϕ, Q, and e and with respect to temperature in the vicinity of T_c are postulates that are usually justified *a posteriori* by the success of this approach. In the present work it has been possible to describe the temperature variation of the lattice parameters in the tetragonal phase and of the elastic constants $\hat{c}_{33}$ and $\hat{c}_{133}$ in the cubic phase up to 300 °K, and to account, without adjustable parameters, for the nonlinear stress-strain relation in V_3Si. Because of the additional assumption of homogeneity and restriction to static mean-field theory, fluctuations of the order parameters are ignored, except for the long-wavelength acoustic-phonon mode, for which fluctuations are included without dissipation effects in the quasiharmonic approximation. Since the instability appears to be confined to one shear mode propagating in the vicinity of the [110] directions, critical fluctuations are unimportant.[67,68]

The specific properties of V_3Si enter through the free-energy expression, Eq. (23). The particular form of this expression is determined by the coupling of the quantities ϕ, Q, and e at the Γ point in accordance with the O_h^3 symmetry. The Peierls-Gor'kov-type instability provides the mechanism for the softening of the primary order parameter ϕ_3 via the linear temperature dependence of the coefficient A_{33} in Eq. (23). As discussed in Sec. II C, other mechanisms for the instability, or other locations of the associated wave vector in the Brillouin zone, would lead to a different functional form for the free energy [Eq. (23)] but the temperature dependence of the second- and higher-order elastic constants obtained through elimination of ϕ and Q might not be significantly different.

In addition, the following assumptions were made: The free energy [Eq. (23)] was truncated beyond the fourth-order terms, and certain coupling terms of lower order were also neglected. The elimination of the variables ϕ and Q was based on the linear approximation (25), and in the temperature dependence of $\hat{c}_{3333}$ the constraint given by Eq. (32) was neglected. Anharmonic effects were not included in any of the elastic constants, except c_{33}, and in the evaluation of c_{33}^{anh} the Cauchy relations for the higher-order elastic constants were assumed. Furthermore, any interaction between the mode softening and the onset of superconductivity was neglected.

The numerical application of the general theory to V_3Si is further subject to the simplifying assumptions made in the data reduction as enumerated in Sec. III A.

IV. SUMMARY AND CONCLUSIONS

Based on an extended version of the Landau theory of Bhatt and McMillan[13] for A-15 compounds, numerical values for the TOE and FOE constants c_{111}, c_{112}, c_{123}, c_{1111}, c_{1112}, c_{1122}, and c_{1123} (in Voigt notation) and their dependence on temperature have been determined for V_3Si from experimental data in conjunction with thermodynamic equilibrium conditions. The experimental input data used are the lattice parameters versus temperature in the tetragonal phases, the elastic constants and their pressure coefficients as a function of temperature in the cubic phase, and the pressure coefficient of the structural transition temperature. Most of the higher-order elastic constants are found to be exceptionally large and rather strongly temperature dependent. Although no experimental data on the individual higher-order elastic constants are available for comparison, these data are consistent with and reproduce the measured nonlinear stress-strain curve.[16]

The higher-order elastic constants so obtained were used to calculate the zero-point and phonon contributions to the soft shear modulus in the quasiharmonic ACM. Above 100 °K, these two contributions are of opposite sign and comparable to the electronic contribution. The total anharmonic contribution is negative, and with decreasing temperature it has a destabilizing effect. Only a fraction of the total softening arises from the electronic contribution, with the remaining softening resulting from the balance between the zero-point and the phonon contributions.

The origin of the large anharmonicity cannot be explained on the basis of the present phenomenological theory. Equally plausible microscopic causes are electronic band-structure effects,[58] or defect-induced local structural instabilities.[69,70]

Previously A-15 intermetallic compounds and ferroelectric materials were believed to be qualitatively different, in that the mode softening in the former was attributed exclusively to electronic band-structure effects, and in the latter to anharmonic phonon-phonon interactions. However, it has recently been suggested that the optical-mode softening in oxide perovskites is caused by the nonlinear anisotropic electronic polarizability of the oxygen ion via strong phonon-phonon interactions.[71] Therefore, the essential difference between the two classes of materials now disappears, since both electronic and phonon mechanisms contribute to the mode softening in both classes of materials.

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[61] Because of an error in Eq. (2b) in Ref. 59 the numerical values obtained for the TOE are too large. If Eqs. (2b) of Ref. 59 is corrected by replacing the coefficient of c_{111} by -1, the values obtained for the TOE constants are (in Mbar) $c_{111} = -199$, $c_{112} = 86$, and $c_{123} = -180$. With these values the agreement between the calculated stress-strain curve and the results of Patel and Batterman (Ref. 16) is considerably improved. It is noted that these corrected values (obtained from rather crude assumptions) correspond to the values of the extrema at 45 °K of the curves in Fig. 1(a) of the present paper. In Eq. (2c) of Ref. 59 the coefficient of c_{1112} should be replaced by -3; however, for the numerical application this is inconsequential, since it was assumed that $c_{1112} = 0$.

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