Solution of (9) for large A yields $\sigma_m=\frac{1}{2}A^{1/3}$, while $\sigma_c=A^{1/2}$. A plot of σ_m, σ_c, and the numerical results for case II, given in Fig. 3, shows that σ_m slightly underestimates the observed conductivity, by a greater amount than in case I. The data points for large A fall roughly on a straight line in this log-log plot, with a slope closer to $\frac{1}{3}$ than to $\frac{1}{2}$.

The logarithmic distribution of case II arises in a description of ionic transport by thermal activation across barriers whose heights are distributed uniformly over a range $\pm\Delta E$ about some average E_0. In this case, we can factor out the average conductance, $\sigma_0(T)\propto\exp(-E_0/kT)$, and identify $\ln A=\Delta E/kT$, $\sigma_m/\sigma_0(T)=\frac{1}{2}\exp(+\Delta E/3kT)$, and $\sigma_c/\sigma_0(T)\propto\exp(+\Delta E/2kT)$ for low T. The effective activation energy $\Delta E/3$, given by the effective-medium theory, is in agreement with the calculated results of Fig. 3, while the prefactor $\frac{1}{2}$ is too low by about 25%. The critical-path analysis gives too large an effective activation energy, and no information about the prefactor. We conclude that the changes with T in the composition of the critical paths and the varying importance of currents along noncritical paths are sufficiently great that $\sigma_c(T)$ alone does not provide a quantitative description of the conductivity, at least for this simple example.

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Lattice Dynamics of Nb_3Sn-Type Compounds*

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It is shown that, in the cubic phase, the doubly degenerate Γ_{12} mode is the only long-wavelength optical mode which is temperature dependent in the harmonic approximation. However, it does not become unstable on cooling because it would drive a shear acoustic mode unstable first. The elastic constants are calculated by the method of long waves. Only $C_{11}-C_{12}$ is temperature dependent. Its calculated values for Nb_3Sn are in fair agreement with experiment.

I have developed a method for the first-principles calculation of phonon frequencies in the intermetallic compounds of β-W structure in the harmonic approximation. I have examined the temperature dependence, in the cubic phase, of the long-wavelength optical modes and of the elastic constants, from which can be deduced some knowledge of the existence and the nature of the martensitic transformation in these compounds.

To calculate the electronic polarization which modifies the ion-ion interaction,[1] we start with a model of the band structure of an unperturbed crystal A_3B, where the s and p electrons from elements A and B are treated as nearly free and where the d electrons from the transition element A are treated in the tight-binding approximation.[2] The width of a d band is entirely due to the overlap of nearest neighbors in the same chain of A atoms. The Fermi level is near the top or bottom of one set of these d bands. The resultant high density of states has been used to interpret the unusual temperature dependence of the electronic and related properties. For simplicity, we neglect the other d bands. The d-electron wave function is taken to be the $m=0$ component with the radial part given in Slater form.

The electronic polarization is calculated in the random-phase approximation. We improve it a little by removing from the polarization the term which corresponds to two d electrons of the same spin residing on the same atom. The polarization due to d electrons is of separable form, and the inversion of the dielectric function, including also the s-electron screening, is easily carried out.[3] By the method of Ref. 1 we obtain the dynamical matrix. Further details will be given in a separate article.

We examine the phonon modes at $\vec{q}=0$ in the adiabatic approximation here. The d-electron contribution to the dynamical matrix covers only the elements $\Phi_{xx}(1, 2)$, $\Phi_{xy}(1, 3)$, $\Phi_{xx}(1, 1)$, and others which can be obtained from these by symmetry operations. The atoms are numbered as shown in Fig. 1. The nonzero force constant between A atoms of the same chain, e.g., (1, 2), is an obvious consequence of the tight-binding model. We also have a nonvanishing d-electron contribution to the force constant between A atoms in different chains, e.g., (1, 3), because we have included the electric forces of all electrons and ions.

It follows that of all the optical modes at $\vec{q}=0$, only the twofold degenerate branch[4] Γ_{12} depends on the d bands. Hence, Γ_{12} is the only mode which is temperature dependent in the harmonic approximation. We conclude that the low-temperature structural transition in these compounds A_3B is *not* of the ferroelectric type.[4,5] Klein and Birman[6] have found that the Γ_{15} and Γ_{25} modes can go soft. We believe that their use of the diagonal dielectric tensor gives incorrect d-electron contributions. Γ_{15} and Γ_{25} modes involve rigid displacements of the A-atom chains, which cannot excite d-electrons in the tight-binding model used here. Γ_{12} modes involve atoms in the same chain moving against each other (see Fig. 1), which can excite d electrons.

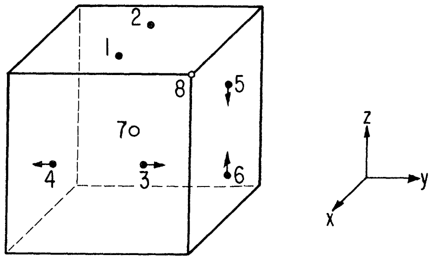

FIG. 1. Arrangements of the atoms of Nb_3Sn in a unit cell. Closed circles, Nb atoms; open circles, Sn atoms. The arrows indicate the motion of the atoms in one of the two optical modes of symmetry Γ_{12}.

The elastic constants are obtained by the method of long waves.[7] One of the shear moduli is given by

$$\tfrac{1}{2}(C_{11}-C_{12}) = Y+\theta W/(1-\theta U) - 3[t+\theta X/(1-\theta U)]^2\omega^{-2}(\Gamma_{12}). \quad (1)$$

To obtain the frequency for small q, one expands the dynamical matrix in powers of q. The term of the order q^2 gives the first two terms on the right. Y denotes the contribution from the ion-ion interaction screened by s electrons. The second term comes from d electrons. θ is a polarization term at zero wave vector and frequency. W measures the d-electron–ion interaction (screened by the s electrons). U is the d-d screening of the shear mode. The term of order q in the dynamical matrix when included to second order gives the last term on the right of Eq. (1).

A long-wavelength shear wave produces a movement of some sublattices against the others. By symmetry, it turns out that the $C_{11}-C_{12}$ shear is coupled to the sublattice motion corresponding to the Γ_{12} optical mode. The contribution of this motion to the shear modulus is the last term on the right of Eq. (1). In their calculation of the elastic constants of V_3Si from the free energy, Barisić and Labbé[8] did not include this term (nor U). This term shows that even the only temperature-dependent optical mode Γ_{12} cannot become unstable because the shear modulus will vanish when $\omega^2(\Gamma_{12})$ is sufficiently small. We conclude that *no* optical modes become unstable in the martensitic transformation of Nb_3Sn-type compounds. This was confirmed recently by the neutron-scattering experiments of Shirane and Axe[9] on Nb_3Sn.

The other shear modulus C_{44} is given by a formula similar to Eq. (1). The optical mode coupled to it is Γ_{25}'. It follows from the dynamical matrix described above that there is no d-electron contribution to C_{44} which is, therefore, temperature independent. The bulk modulus is not coupled to any long-wave optical mode. Its d-electron contribution is small because of the large density of states at the Fermi level. Thus, the bulk modulus is very weakly temperature dependent.

We give a rough evaluation of Eq. (1) for the shear modulus of Nb_3Sn. The constant-density-of-states model of Cohen and co-workers[10] is used to evaluate the polarization θ,

$$\theta = -(8/\Omega_0)N_0F_0(T)$$

with

$$F_0(T) = 1 - \exp(-T_F/T).$$

Ω_0 is the unit cell volume, N_0 the density of states, and T_F the Fermi temperature. All other quantities are evaluated assuming that all interactions are Coulombic, screened by s electrons in the Thomas-Fermi approximation, with the screening vector given in terms of the s-electron density of states, αN_0, with $\alpha = 0.04$. We have chosen two values[10,11] for N_0, 5.6 and 3 states per eV atom. The Slater coefficient of the d-electron wave function is taken to be 0.74 $Å^{-1}$, roughly the atomic value. We have found that the value of 0.27 $Å^{-1}$ which Barisić and Labbé used for V_3Si gives negligible d-electron contribution in our theory.

The calculated frequency $\omega(\Gamma_{12})$ and elastic constant $C_{11} - C_{12}$ for $T_F = 70$ and 85°K are plotted in Figs. 2 and 3, respectively. The values of the Fermi temperature were chosen by Rehwald.[11] In view of the rather crude Yukawa potential we used for the electron-electron and electron-ion interaction, we regard the fair agreement of the temperature dependence for $N_0 = 3$ states per eV atom as encouraging. A more careful evaluation of the phonon spectrum for these compounds is planned.

The d-electron screening U turns out to be quite small ($-\theta U \simeq 0.21$ at $T = 0$°K and $N_0 = 3$ states per eV atom). The softening of the shear constant $C_{11} - C_{12}$ is due in a large part to the second term on the right-hand side of Eq. (1). The coupling to the Γ_{12} mode is small but not negligible. The temperature dependence of the rather high-frequency Γ_{12} mode is weak. Thus, the Γ_{12} optical mode does not go soft, nor is it wholly responsible for driving the acoustic mode unstable. However, the coupling of the shear mode to the Γ_{12} optical mode causes a tetragonal distortion of the Γ_{12} type when the shear mode goes unstable. This is experimentally confirmed.[9] Thus, we conclude that the structural phase transition is of first order.[4,12]

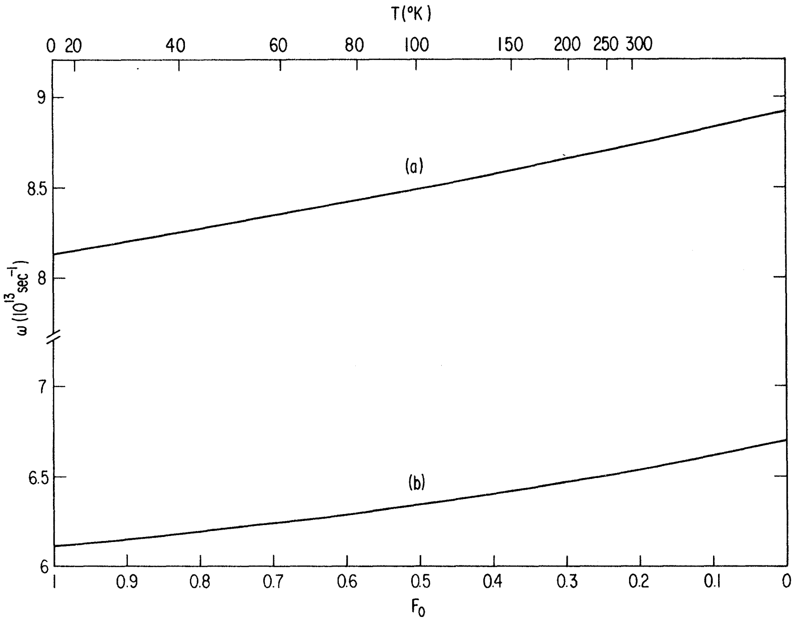

FIG. 2. The calculated frequency of the optical mode Γ_{12} versus $F_0(T)$. Curve a, $N_0=3$ states per eV atom; curve b, $N_0=5.6$ states per eV atom. The temperature scale on top corresponds to $T_F=70$°K.

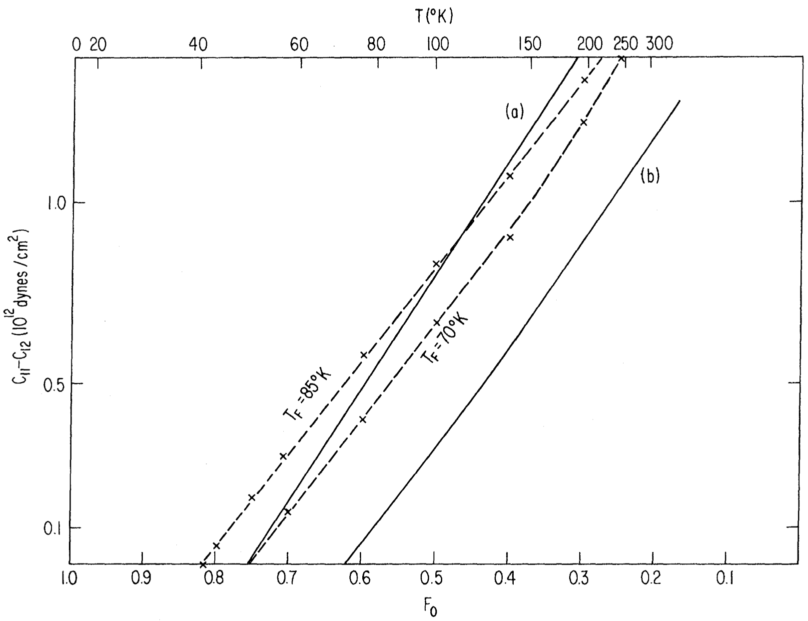

FIG. 3. Dashed curves, measured shear modulus $C_{11}-C_{12}$ versus $F_0(T)$ with T_F indicated. Solid curves, calculated shear modulus: curve a, $N_0=3$ states per eV atom; curve b, $N_0=5.6$ states eV atom. The temperature scale shown on top corresponds to $T_F=70°K$.

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