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THEORY OF SOFT OPTIC MODES AND PHASE TRANSITIONS IN β-W STRUCTURE TRANSITION-METAL ALLOYS*

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A calculation of the phonon frequencies of the β-W structure crystals shows that long-wavelength optic-mode instabilities occur. These are associated with a high density of electronic states in the transition-metal d bands. The $\Gamma_{15}^{(-)}$ and $\Gamma_{25}^{(-)}$ optic modes soften: these are consistent with a second-order structural phase transition.

Soft optic modes have been proposed[1,2] as underlying the structural phase transition,[3,4] and other anomalous properties[5] of the β-W compounds V_3Si and Nb_3Sn, including possibly their transition to the superconducting state.

In this Letter we report on a theoretical mechanism for such optic-mode softening. We find that when the Fermi level falls in a region of large electronic density of states, the long-range bare-ion Coulomb potentials are overscreened and two $\vec{q}=0$ optic modes are destabilized. These are two of the three modes which the Landau theory permits to be order parameters in a second-order structural phase transition.[2] The remaining optic modes are stable.

The calculation of the phonon spectrum makes use of the adiabatic harmonic approximation, and is for zero temperature ($T=0$). Results for $T>0$ will be published elsewhere. We have used the linear chain model[6,7] for the d-band states, and we have assumed that the Fermi level falls within the d bands, and that transitions to other bands (s, p, etc.) can be neglected or can be included in an effective charge for the ions.[8]

The long-range-force contributions to the dynamical matrix[9] have been accounted for by using bare-ion Coulomb potentials screened by the wave-number-dependent, zero frequency, self-consistent-field dielectric function, computed for scattering within the d bands in the diagonal screening tensor approximation.[8-10] The details of the calculation are given in Ref. 8. In computing the dielectric function, matrix elements involving the d-band Bloch functions are required.[10] We have constructed these Bloch functions from atomic d functions of the form

$$\Phi_m^d = R(\lambda) Y_{2m}(\theta, \varphi), \tag{1}$$

where

$$R(\lambda) = \tfrac{2}{3}(2\lambda^7/5)^{1/2} r^2 e^{-\lambda r} \tag{2}$$

with λ a free parameter determining the range of the d-state Bloch functions, and $Y_{2m}(\theta, \varphi)$ a spherical harmonic.

In Fig. 1 we illustrate the linear chain or nearest-neighbor tight-binding model d-band energies.[6] The ξ_m are related to atomic overlap integrals, k is one of the three Cartesian components of the wave vector, and a is the lattice constant. There are three degenerate sets of one-dimensional-like d bands corresponding to the three coordinate (chain) directions.

The adjustable parameters in the theory are ξ_0, ξ_1, ξ_2, Z_A, Z_B, E_F, and $\lambda a = \sigma$. Here the Z's are the bare ionic charges, and E_F is the position of the $T=0$ Fermi energy within the d bands.

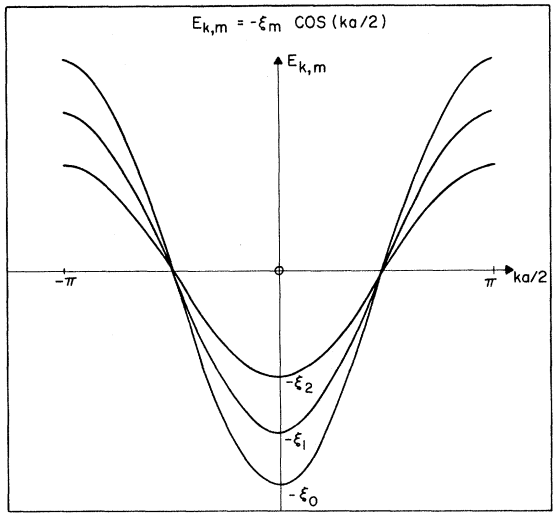

FIG. 1. Linear-chain model d-band structure for V_3Si or Nb_3Sn. The ξ_m are the absolute value of atomic overlap integrals.

For given values of these parameters, the dynamical matrix at phonon wave vector $\vec{q}$ was computed and the phonon frequencies and polarization vectors were determined. We were particularly interested in the modes at long wavelengths, as the structural phase transitions in V_3Si and Nb_3Sn occur without any change in the unit cell volume,[3,4] so that any optic modes which act as order parameters in a second-order phase transition must be those at $\vec{q}=0$ (Γ). Also, as we discuss more fully below, we found that the overscreening of the long-range Coulomb forces, which is the mechanism for the optic-mode instabilities, is maximal at long wavelengths.

In Figs. 2(a), 2(b), and 2(c) we exhibit numerical results for cubic V_3Si for $\vec{q}=0$ and $T=0$. Ionic charges of $Z_V=0.5$ and $Z_{Si}=0.4$ have been used, $\xi_0=4.0$, $\xi_1=3.5$, $\xi_3=3.0$ eV, and $\sigma=4.5$. Actually, the relative positions of the optic modes depends on the ratio Z_A/Z_B which we have chosen to be 5/4; the actual numerical values of the frequencies are determined by the specific values chosen for the ionic charges (scaling as Z^2). We have plotted $\omega_{optic}{}^2$ vs $n(E_F)$, the total d-band density of states at E_F.[11] In the linear-chain model, $n(E_F)\to\infty$ when $E_F\to\pm\xi_m$. It is seen that in the regions where the $\Gamma_{15}{}^{(-)}$ and $\Gamma_{25}{}^{(-)}$ optic modes are unstable ($\omega^2<0$), all of the other optic modes are stable ($\omega^2>0$). For much larger values of $n(E_F)$ the other optic modes destabilize, but the $\Gamma_{15}{}^{(-)}$ and $\Gamma_{25}{}^{(-)}$ optic modes are the most unstable by far. The numerical results for Nb_3Sn are qualitatively the same, with the instabilities in the $\Gamma_{15}{}^{(-)}$ and $\Gamma_{25}{}^{(-)}$ optic modes being shifted to a slightly higher density of states than in V_3Si for the same values of the parameters (with the nuclear masses and a lattice constant appropriate to Nb_3Sn). In the regions of the instabilities, the values of $\omega_{optic}{}^2$ vary approximately linearly with the density of states, but they deviate from linearity and approach constant values for much smaller or much larger densities of states. Similar results are obtained for different band widths. The effect of increasing (decreasing) σ is to shift the instabilities to lower (higher) densities of states.

The instabilities are caused by overscreening due to intraband scattering within the d band which has the Fermi level near $\pm\xi_m$. This is because at $\vec{q}=0$ the effective polarizability part of the dielectric function has terms proportional to

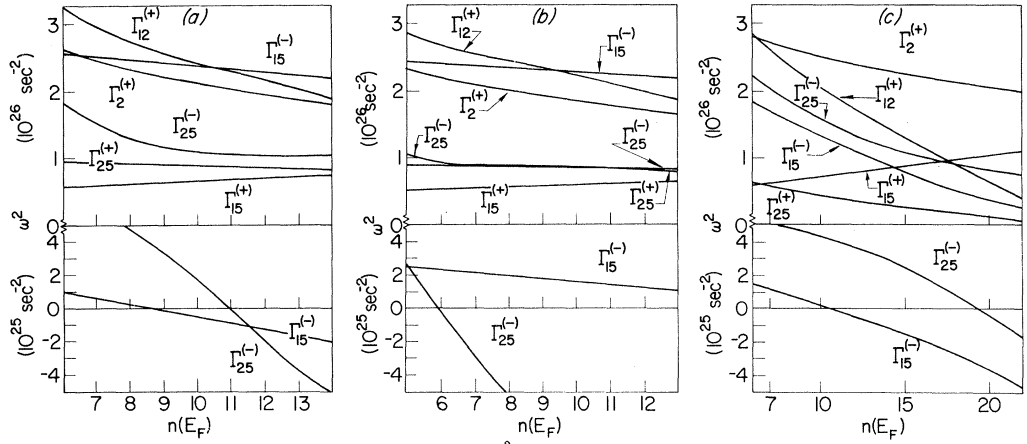

FIG. 2. The square of the optic-mode frequencies ω^2 vs $n(E_F)$, the total d-band density of electronic states at the Fermi level. $n(E_F)$ is in units of states per eV per vanadium atom for both spin directions. (a) $3.5<|E_F|<4.0$ eV; (b) $3.0<|E_F|<3.5$ eV; and (c) $0<|E_F|<3.0$ eV.

the various intraband densities of states, and a large density of states overscreens the bare-ion potentials.

Labbé has shown that for the linear chain model with the Fermi level falling near $\pm\xi_m$, the effective (T dependent) density of electronic states, $n(E_F, T)$, is an increasing function as the temperature is lowered from above the structural phase-transition temperature.[12] From our results shown in Fig. 2, this corresponds to the soft mode frequency decreasing with decreasing T, as required for the phase transition. Our numerical results for the acoustic modes and elastic constants also shows a softening with decreasing temperature as is observed experimentally.

Although our theory allows either the $\Gamma_{15}^{(-)}$ or $\Gamma_{25}^{(-)}$ optic modes to be soft, we are unable to determine which one of these two modes is soft for a specific β-W compound. This is due to the fact that in our calculations the soft mode is determined by the position of the Fermi level within the d bands, and we use this position as a parameter. Because of this, V_3Si and Nb_3Sn may have different soft optic modes. Their resulting lower symmetry tetragonal space groups (as yet experimentally undetermined) would then differ also.[13] By contrast, the $\Gamma_{15}^{(+)}$ optic mode which is also group-theoretically permissible as an order parameter is found to be stable in our calculations.

Our results may transcend the limitations of the simple linear-chain d-band model. Detailed study of the dynamical matrix shows that the reason that the $\Gamma_{15}^{(-)}$ and $\Gamma_{25}^{(-)}$ optic modes are the most unstable is a combination of the β-W structure itself (which to a large extent determines the allowed normal-mode displacement patterns independent of the forces), the high density of electronic states at the Fermi level, and the localized nature of the d-electron Bloch functions. These conditions cause those normal modes having nearest-neighbor transition-metal atoms moving parallel to each other to be the most highly renormalized from the bare-ion frequencies. The $\Gamma_{15}^{(-)}$ and $\Gamma_{25}^{(-)}$ optic modes have displacement patterns satisfying this condition. It seems likely that these features will persist in a more complicated model. We also note that the overscreening decreases away from Γ, so that the instability mechanism we have described is truly a long-wavelength phenomenon.

Experimental results determining which of the two long-wavelength optic modes are soft for a given β-W compound are needed. This would enable us to determine the parameters in our theory, and would also facilitate an investigation of the relationship between any soft optic modes and the superconducting properties of these compounds.

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