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Elastic Moduli and Magnetic Susceptibility of Monocrystalline Nb_3Sn

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The elastic moduli c_{11}, c_{12}, and c_{44} and the magnetic susceptibility χ of single-crystal Nb_3Sn have been measured as a function of temperature below 300 K. Detailed comparison is made between the experimental results and the predictions of simple one-dimensional band models. It is found that the behavior of the elastic moduli c_{11} and c_{12} above and below the cubic-tetragonal transformation at 45 K is well accounted for by the band model with an effective Fermi temperature of 80 K. Unlike the case of V_3Si, the modulus c_{44} is observed to undergo a considerable softening at low temperatures. This softening is not predicted by the theory. The susceptibility displays the predicted maximum near the lattice-transformation temperature. However, the decrease of χ in the tetragonal state, associated with a drop in the electronic density of states, is not nearly as large as expected. Furthermore, the cubic-state χ data indicate a much larger Fermi temperature (230 K) than is obtained from the c_{11} and c_{12} data. We review these anomalies in terms of available band-structure calculations. The implications of our experimental results for superconductivity in Nb_3Sn are discussed.

I. INTRODUCTION

The β-tungsten compounds Nb_3Sn and V_3Si show a crystallographic transformation[1,2] from a high-temperature-cubic to a low-temperature-tetragonal lattice state which causes a number of physical quantities to behave anomalously. Strong temperature variations have been observed for the magnetic susceptibility[3] and the Knight shift[4] in V_3Si and for the isomer shift in Mössbauer experiments[5] on

Nb_3Sn. The electrical resistivity[6] of Nb_3Sn as a function of temperature exhibits a behavior which deviates strongly from the commonly observed linear dependence at higher temperatures. The most drastic effect is found in the elastic moduli,[7-9] where the stiffness c_{11}-c_{12} against a tetragonal deformation becomes very small in the vicinity of the lattice-transformation temperature.

The compounds Nb_3Sn and V_3Si are superconductors[10,11] with high transition temperatures of 18 and 17.1 K, respectively. The work of Testardi *et al.*[12] suggested a connection between high-transition-temperature superconductivity and lattice instabilities. Thus, there is considerable interest, from the point of view of superconductivity, in the physical nature of the structural transition observed in Nb_3Sn and V_3Si.

An explanation of the observed anomalies has been sought in terms of rapid changes of the electronic density of states near the Fermi level.[3,9,13-17] Most of the investigations, both theoretical and experimental, however, have been devoted to the compound V_3Si, in which the crystallographic transformation occurs only approximately 4 deg above the transition to superconductivity. Niobium stannide is much better suited for studies of the effect of the lattice transformation on normal-state properties, since the range in which the crystal is crystallographically transformed, but not superconducting, covers more than 25 deg.[1]

In this paper we present experimental results of the magnetic susceptibility and sound velocities as a function of temperature obtained from a single crystal of Nb_3Sn which undergoes the lattice transformation. We have observed an anomalous behavior in all these quantities and have examined the extent to which this behavior may be described by a simple electronic band model. This model utilizes the idea of Labbé and Friedel[13] of a narrow d band caused by electronic overlap in the transition-metal chains of the β-tungsten structure. Instead of the tight-binding approach,[13] a simple model density-of-states function[16,17] is assumed and the effect of strain is described in a deformation-potential formalism. We find that while the model quantitatively describes the behavior of the elastic moduli c_{11} and c_{12} over the entire measured temperature range, we are unable to account for the temperature dependence of the elastic modulus c_{44} and the magnetic susceptibility.

II. SAMPLES AND EXPERIMENTAL TECHNIQUES

The Nb_3Sn crystal used for all of our measurements was grown by an HCl-gas-transport technique.[18] Previous ultrasonic experiments[6] were performed on the crystal, which did not undergo a lattice transformation. The crystal was subsequently annealed for about 50 h at 1000 °C in vacuum. By this treatment the lattice constant was slightly reduced[18] to 5.291 Å and the crystal clearly showed the spontaneous tetragonal deformation[1,19,20] below about 45 K. In preparation for the present ultrasonic measurements, a pair of parallel (110) faces was polished to optical quality. After measurement of the sound modes with direction of propagation along (110), a pair of (100) faces was also polished.

In the ultrasonic experiments three different sound modes were excited with the direction of propagation $\vec{n} \parallel [110]$. The direction of polarization for these modes was $\vec{e} \parallel [110]$, $[1\bar{1}0]$, and [001]. In addition, longitudinal waves in the [100] direction were excited. The corresponding phase velocities $V_s(n_1n_2n_3, e_1e_2e_3)$ were measured at 40 MHz by the pulse-echo method in a single-ended array, with quartz transducers bonded to one face with DC-200 silicon oil. The temperature was determined by a copper-constantan thermocouple, which was soldered to the sample-holder base plate. The accuracy in temperature is about 0.5 K.

The magnetic susceptibility χ was determined by the Faraday-balance technique, suspending the crystal from an electrobalance[21] in an inhomogeneous magnetic field. The sample weight in zero field is 0.1646 g. The measurements were done at a field $H = 5.46$ kOe with constant-force pole faces such that $H|\vec{\nabla}H| = 5.45\times10^6$ Oe^2/cm. The magnetic force on the sample (typically 2×10^{-3} g) could be measured to a precision of ± 5 μg; the accuracy or reproducibility among experiments was about 2%. The experiment was calibrated against a crystal of pure niobium at 300 K.

Susceptibility-versus-temperature data were obtained by warming the sample slowly from liquid-neon to liquid-nitrogen temperature or from liquid-nitrogen to room temperature. Quasicontinuous data were obtained at various heating rates and the results were independent of rate to within the precision of the experiment. It was necessary to normalize the results of the neon-to-nitrogen experiment to the high-temperature data at 77 K because of the calibration changes in χ which occur among the various runs.

A chromel-alumel thermocouple was used to measure temperatures between 77 and 300 K. For measurements between 27 and 85 K, a chromel-versus-gold (with 0.07-at.% iron) thermocouple was used. Both thermocouples were placed in the 1.5-cm-diam quartz tube in which the sample hangs. Thermal contact was effected by an atmosphere of pure helium gas and both thermocouples were calibrated *in situ*. A possible source of systematic error in this method of temperature determination is a difference in the thermal response of the sample and that of the thermocouple due to the finite rate of temperature change. This error was estimated

by measuring χ versus T for another sample of Nb_3Sn both with the present experimental arrangement and in a vibrating-sample magnetometer with a temperature-controlled Dewar. Although the latter arrangement is less sensitive to changes in χ than the Faraday balance, the data were definitely obtained in thermal equilibrium. From these measurements it is estimated that the uncertainty in temperature in the Faraday balance experiments was ± 3 K.

III. EXPERIMENTAL RESULTS

Figure 1 shows the velocities of the four different acoustic modes as a function of temperature. The solid curves represent the smoothed experimental data. The limiting precision of the experiment, as represented by scatter of experimental points, is approximately $\pm\frac{3}{4}\%$. No corrections for thermal expansion and transducer effects have been made. Common to all four curves is a decrease with temperature in the range 50–300 K, which is strongest for the mode $(n_1n_2n_3,\ e_1e_2e_3) = (110,\ 1\bar{1}0)$. The lowest value obtained at 49.8 K for this type of wave is 0.5×10^5 cm/sec, which is 18% of the room-temperature value. Below this temperature no echoes could be detected due to high attenuation which sets in near the transformation temperature and is present throughout the tetragonal state. High attenuation also prevented measurements of the longitudinal mode (100, 100) below 46.2 K. The curve for $V_s(110, 001)$ shows a change in slope at about 49 K and continues to decrease as the temperature is lowered, whereas the longitudinal velocity $V_s(110, 110)$ reaches a minimum at the same temperature and is restored to its high-temperature values as $T\to 0$ K.

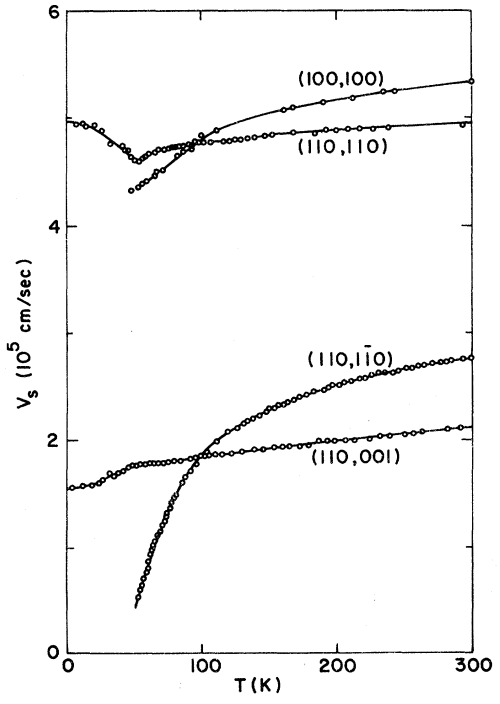

FIG. 1. Experimental sound velocities V_s versus temperature. In the notation $(n_1n_2n_3, e_1e_2e_3)$, the first triplet n_i denotes the direction of propagation, the second e_i indicates the direction of particle motion. The solid curves represent smoothed experimental data.

These results differ in three ways from those of previous measurements made by Keller and Hanak[8] on the same crystal before annealing: (i) The temperature at which the velocity of the "soft" shear mode (110, 1$\bar{1}$0) goes to very small values is considerably higher (49 K instead of 32 K); (ii) the velocity of the shear mode (110, 001) continues to decrease at temperatures below the collapse of the soft shear mode; and (iii) the longitudinal velocity (110, 110) exhibits a minimum.

Using the formulas for a cubic crystal and a density of 8.87 g/cm^3, all three elastic moduli can be calculated above 49 K from these data. Since the velocities of four modes were measured, the three c_{jk} are overdetermined. Thus, the elastic modulus c_{11} may be determined directly from $V_s(100, 100)$ or deduced from the other three measured velocities. Below 49 K, the missing information due to the observed high attenuation in the (110, 1$\bar{1}$0) and (100, 100) modes is replaced by the assumption that the bulk modulus $B = \frac{1}{3}(c_{11} + 2c_{12})$ remains constant at its 49 K value. This extrapolation is suggested by the very slow variation of B above 49 K in the "normal" sense (i.e., slight stiffening at lower temperatures), and as will be shown in Sec. IV, is also justified on a theoretical basis. In Fig. 2 these derived elastic moduli are plotted as a function of temperature. The solid curves are the smoothed results of the computations of the $c_{jk}(T)$. In the tetragonal phase the values correspond to averages over the various orientations of microscopic domains. The values for c_{11}, derived directly from $V_s(100, 100)$, coincide well with those inferred from the other three velocities only for temperatures above approximately 62 K. Below 62 K there is a discrepancy [dotted curve in Fig. 2(b)] which increases with decreasing temperature, the directly measured values being higher than the deduced values. This discrepancy is discussed in Sec. IV A.

Figure 3 shows the mass susceptibility χ of Nb_3Sn as a function of temperature from 27 to 300 K. Four runs in the high-temperature range (77–300 K) and three in the low-temperature range (27–85 K) gave the temperature dependence shown to within the precision of the experiment (0.5%). The maximum in χ occurs at $T_{max} = 56 \pm 3$ K; the fractional change $[\chi(56) - \chi(300)]/\chi(300) = 0.29$. Earlier measurements[16,17] of $\chi(T)$ for a powdered sample of Nb_3Sn gave $T_{max} \cong 60$ K, in agreement with the

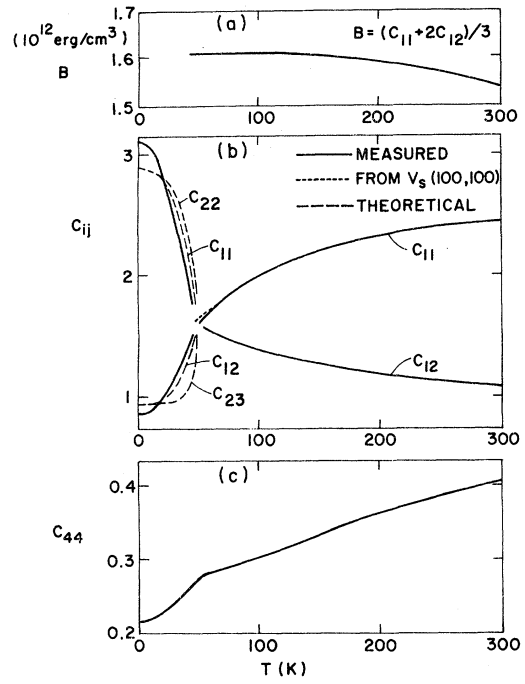

FIG. 2. Elastic moduli versus temperature, calculated from measured sound velocities in the (110) and (100) direction. Panel (a) gives the behavior of the bulk modulus B; panel (b) gives c_{11} and c_{12}; and panel (c) shows c_{44}. The solid lines represent the smoothed results of the computations of the c_{jk} from the two measured shear velocities and the (110) longitudinal velocity. The dotted curve in Fig. 2(b) indicates the behavior of c_{11} below 62 K as inferred from $V_s(100,100)$. Below the lattice transformation, comparison is made to the theoretical c_{ij} [dashed curve in Fig. 2(b)] obtained from the band model with $T_0 = 80$ K.

present work. The value for the powdered sample,[16,17] $\chi(300) \cong 1.9\times10^{-6}$ emu/g, agrees with the present results $\chi(300) = 2.03\times10^{-6}$ emu/g, to well within the 10% accuracy of the early work, but the precision was not sufficiently high to permit the detailed quantitative analysis given in Sec. IV. Further measurements from 77 to 300 K on a powdered sample of Nb_3Sn show that the temperature dependence of χ is independent of whether the sample is a powder or a single crystal.

IV. THEORY AND DISCUSSION

Clearly, the observed anomalies in the elastic and magnetic behavior are closely related to the cubic-to-tetragonal lattice transformation near 45 K, which has been studied in detail by x-ray[1,19,20] and neutron diffraction.[22,23] Following Labbé and Friedel,[13] the lattice transformation in Nb_3Sn and in the isomorphous compound V_3Si is a direct consequence of the A-15 (β-tungsten) lattice structure and the special electronic band structure resulting from it. The transition-metal atoms Nb or V, being arranged in chains within the body-centered-cubic lattice of the partner metal Sn or Si, form narrow threefold-degenerate d bands. If the number of conduction electrons has such a value that the Fermi level lies close (~10 meV) to one edge of the d bands, the application of elastic deformations or a magnetic field lifts the degeneracy of the d bands and gives rise to contribution to the c_{jk} and χ which are temperature dependent in the common experimental temperature range $1\ \mathrm{K} \lesssim T \lesssim 10^3$ K.

A. Elastic Moduli

The quantitative description of the behavior of the elastic moduli may be derived from an expression of the free energy G of the lattice, consisting of atomic cores and the system of d electrons, as a function of temperature T and uniaxial elastic strains ϵ_i:

$$G(T,\epsilon) = \tfrac{1}{2}A_{11}(\epsilon_1^2+\epsilon_2^2+\epsilon_3^2) + A_{12}(\epsilon_1\epsilon_2+\epsilon_2\epsilon_3+\epsilon_3\epsilon_1) + \tfrac{1}{2}A_{44}(\epsilon_4^2+\epsilon_5^2+\epsilon_6^2) + NE_F - \sum_{i=1}^{3}\int_{E_i}^{\infty}\ln(1+e^{(E_F-E)/kT})N(E-E_i)\,dE. \quad (1)$$

The coefficients A_{jk} represent the elastic moduli

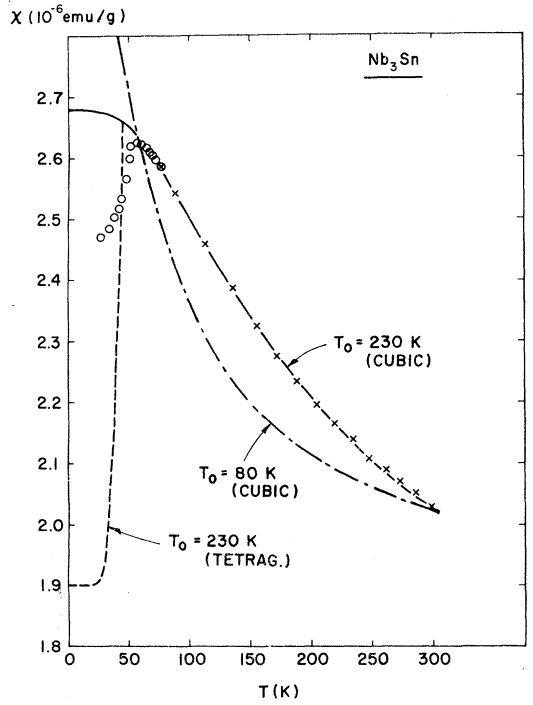

FIG. 3. Magnetic susceptibility χ versus temperature. The ×'s represent points obtained from warming runs from liquid nitrogen, while the ○'s represent points obtained during runs from liquid neon. The various curves represent calculations of $\chi(T)$ for the indicated values of T_0.

arising from electrons other than those in the d band. The Fermi energy is denoted by E_F, the density of d electrons by N, and the density of states of both spins by $N(E)$. The interaction of the d electrons with the strain field ϵ is expressed in terms of the shifts E_i in the band-edge energies:

$$E_i = U[\epsilon_i - \tfrac{1}{2}(\epsilon_1+\epsilon_2+\epsilon_3)], \quad i=1, 2, 3. \tag{2}$$

The strain effect is described by a single deformation-potential constant U, characterizing a uniaxial deformation along one cube axis. The elastic moduli c_{jk} are defined as second derivatives of the free energy with constant electron number N in the d bands:

$$c_{jk} = \left(\frac{\partial^2 G}{\partial \epsilon_j \partial_k}\right)_N . \tag{3}$$

It has been shown previously[16,17] that a good fit to experimental data can be obtained by a constant density-of-states model:

$$N(E) = \begin{cases} \tfrac{1}{3}N_0, & E \geq 0 \\ 0, & E < 0. \end{cases} \tag{4}$$

Under this assumption, the condition for the conservation of d-band electrons is written[24]

$$N = \tfrac{1}{3}N_0 kT \sum_{i=1}^{3} \ln(1+e^{(E_F - E_i)/kT}) = \text{const} = N_0 kT_0. \tag{5}$$

The quantity T_0 is a measure of the Fermi energy $E_F(0) = kT_0$ of a hypothetical nontransforming material at 0 K.

Under the spontaneous tetragonal deformation[1,19,20] ϵ_s, the d band is split into subbands with the density of states $\frac{1}{3}N_0$ and $\frac{2}{3}N_0$. Their band edges are displaced[16,25] from $E_i = 0$ to $E_1 = -U\epsilon_s$ and $E_{2,3} = +\frac{1}{2}U\epsilon_s$. Using these values and introducing the Fermi distribution function at the band edge E_i by

$$f(E_i) = (1+e^{(E_i - E_F)/kT})^{-1} \equiv f_i , \tag{6}$$

we get, for the elastic moduli,[25]

$$c_{11} = A_{11} - 2N_0U^2 f_1 f_2/3(f_1+2f_2), \tag{7}$$

$$c_{22} = c_{33} = A_{11} - N_0U^2 f_2(f_1+f_2)/3(f_1+2f_2), \tag{8}$$

$$c_{12} = c_{13} = A_{12} + N_0U^2 f_1 f_2/3(f_1+2f_2), \tag{9}$$

$$c_{23} = A_{12} + N_0U^2 f_2^2/3(f_1+2f_2), \tag{10}$$

$$c_{44} = c_{55} = c_{66} = A_{44} . \tag{11}$$

In the cubic state the mean positions of the band edges coincide,

$$f_1 \to f_0 = f(0) = (1+e^{-E_F/kT})^{-1} , \tag{12}$$

and the following expressions for the elastic moduli are obtained:

$$c_{11} = A_{11} - \tfrac{2}{9}N_0U^2 f_0, \tag{13}$$

$$(c_{11} - c_{12}) = (A_{11} - A_{12}) - \tfrac{1}{3}N_0U^2 f_0 . \tag{14}$$

Upon cooling to the transformation temperature, the Fermi occupation number f_0 at the band edge attains higher and higher values, so that the negative electron term in (14) more nearly compensates the lattice contribution $A_{11} - A_{12}$. At the point of lattice instability this cancellation is nearly total. Detailed studies[19] have shown that the first-order lattice transformation to a spontaneous tetragonal distortion $\epsilon_s(T_c)$ occurs at a temperature T_c where the compensation is about 98%:

$$\tfrac{1}{3}N_0U^2 f_0 \Big|_{T_c} = 0.984(A_{11} - A_{12}). \tag{15}$$

The transformation is believed to be complicated by material inhomogeneities.[19,20] For temperatures $T_c = 45.5\,\text{K} < T \lesssim 52\,\text{K}$, a small precursor strain is observed[19,20] in x-ray investigations. This precursor is believed to arise from small regions of the crystal which become unstable with respect to tetragonal distortions above T_c. Because these regions are clamped by the neighboring stable material, the full value of the spontaneous strain is not achieved. After the bulk of the crystal has softened according to Eq. (15), domains[19,20] appear showing the full value of $\epsilon_s(T_c)$.

In the limit of very low temperatures only one of the three subbands is occupied, so that the Fermi occupation numbers f_1 and f_2 reach the values 1 and 0, respectively. Thus, the electronic contributions to the elastic moduli vanish, and the elastic moduli are restored[9,17] to their stiff lattice values A_{jk}. In the high-temperature limit the Fermi level E_F moves out of the d band and lies in an overlapping low-density s band. The electronic part of the elastic moduli approaches a constant which is determined by the value of the s-band density of states.[16,24]

From Eq. (11), it is seen that the elastic modulus c_{44} is predicted to be temperature independent. This result is a direct consequence of the assumed "one dimensionality" of the model, since a simple shear does not alter the distance between adjacent atoms on a transition-metal chain to first order in the applied strain.

In the cubic region $T > T_c$ the temperature variation of c_{11} and c_{12} is governed by the Fermi occupation number f_0. We find that the best fit of the experimental data [Fig. 2(b)] for c_{11} and c_{12} to Eqs. (12)–(14) is obtained for $T_0 = 80$ K. With this value of T_0, the experimental curves of c_{11} and c_{12} can be fit to within 2% over the temperature range $49\,\text{K} \leq T \leq 300$ K. Including the effects[26] of d-electron screening of the acoustic mode and the renormalization of c_{11}-c_{12} due to coupling to an optic mode gives small corrections to Eqs. (12)–(14) which do not appreciably alter the value[26] of T_0.

Using the value $T_0 = 80$ K, we find the fit to the experimental c_{11} and c_{12} yields the following values of the coefficients A_{11}, A_{12}, and N_0U^2:

$A_{11} = 2.94 \times 10^{12}$ erg/cm^3,

$A_{12} = 0.84 \times 10^{12}$ erg/cm^3,

$N_0U^2 = 7.47 \times 10^{12}$ erg/cm^3 from Eq. (13) and c_{11}

$= 7.86 \times 10^{12}$ erg/cm^3

from Eq. (14) and $c_{11} - c_{12}$.

The 5% difference between the values of N_0U^2 obtained from the analyses of the c_{11} and the $c_{11} - c_{12}$ data arises from a slight temperature dependence of the bulk modulus $B = \frac{1}{3}(c_{11} + 2c_{12})$. In the approximation of our theory $B = \frac{1}{3}(A_{11} + 2A_{12})$, independent of electronic effects in both the cubic and tetragonal state. Experimentally, as can be seen in Fig. 2(a), there is a gradual decrease in B at high temperatures presumably due to ordinary thermal expansion. The experimental fits implicitly contain this variation, as can be seen by computing B from Eqs. (13) and (14) with the parameters given above: $B = (1.54 + 0.08 f_0) \times 10^{12}$ erg/cm^3. Upon cooling from 300 K to the lattice transformation, f_0 increases from about 0.3 to 0.8, thereby giving rise to the observed temperature dependence of B.

The above parameters, obtained from the cubic-state data, allow us to calculate[27] the elastic moduli c_{11}, c_{12}, c_{22}, and c_{23} in the tetragonal state. Using Eqs. (7)–(10) and the experimental[1] $\epsilon_s(T)$, we obtain the calculated c_{jk} shown in Fig. 2(b). As can be seen from the figure, the agreement between theory and the experimental domain-averaged elastic moduli is very good; the predicted restoration[9,17] of the lattice moduli A_{jk} at low temperatures is observed, although not quite as rapidly as is predicted by the theory.

The discrepancy between the moduli c_{11}, calculated from velocities measured in the (110) and (100) directions requires explanation. This discrepancy is believed to arise from material inhomogeneities[19,20] which result in spatial variations of the sound velocities. In an inhomogeneous crystal, the pulse-echo method measures the average of the reciprocal velocity $\langle v_s^{-1} \rangle$. From the relation $(\langle v_s^{-1} \rangle)^{-1} \leq \langle v_s \rangle$, it follows that those regions of the crystal which have undergone the most severe elastic softening give rise to a velocity, determined from the transit time, which is always less than the average velocity throughout the crystal. Since the most drastic softening occurs for the $c_{11} - c_{12}$ mode, a calculation of c_{11} using $V_s(110, 1\bar{1}0)$ results in values of c_{11} which are lower than the crystal average. The c_{11} values determined from $V_s(100, 100)$ are less affected by crystal inhomogeneities, and the lowest temperature (46.2 K) at which the longitudinal mode (100, 100) could be observed lies closer to the transformation temperature (45.5 K) determined from x-ray studies.[19,20] It follows, therefore, that the values of the parameters A_{11}, A_{12}, N_0U^2, and T_0 given above should be viewed as characteristic of the softer parts of the specimen. Small variations of these parameters may be expected throughout the sample.

As shown in Fig. 2(c), the elastic modulus c_{44} softens considerably at low temperatures, while the theory predicts [Eq. (11)] a temperature independent c_{44}. This behavior is much different than that observed[7] in V_3Si, where c_{44} decreases by only a few percent upon cooling from 300 to 21 K. Furthermore, unlike the other elastic moduli of Nb_3Sn, the decrease of c_{44} is not reversed below the lattice transformation. Neutron-diffraction experiments[23] indicate, surprisingly, that the softening of this mode extends to the edge of the Brillouin zone. None of this behavior is understood in terms of the present theory.

B. Magnetic Susceptibility

We shall discuss the magnetic susceptibility results in terms of a theory which treats Coulomb-exchange interactions in the random-phase approximation. The result of Clogston[28] may be easily generalized to include the possibility of three nondegenerate subbands. We assume, in the spirit of the one-dimensional model, that interactions between electrons in different subbands can be neglected. One then finds for the susceptibility

$$\chi(T) = \chi_{\text{orb}} + \chi_s + \chi_d(T), \tag{16}$$

where χ_{orb} and χ_s are temperature-independent orbital and s-band contributions, respectively, and $\chi_d(T)$ is a temperature-dependent d-electron contribution given by

$$\chi_d(T) = \mu_B^2 \sum_{i=1}^{3} \int_{E_i}^{\infty} N(E - E_i) \left(-\frac{\partial f(E)}{\partial E} \right) dE \Big/ \left[1 - \frac{3J}{2} \int_{E_i}^{\infty} N(E - E_i) \left(-\frac{\partial f(E)}{\partial E} \right) dE \right]. \tag{17}$$

Here μ_B is the Bohr magneton, $f(E)$ is the Fermi function, and J is a Coulomb-interaction energy.[28] For the case of the simple model density of states (4), Eq. (17) yields

$$\chi_d(T) = \tfrac{1}{3} N_0 \mu_B^2 \sum_{i=1}^{3} f_i/(1 - \mu f_i), \tag{18}$$

where $\mu = \frac{1}{2} N_0 J$ is a dimensionless interaction term. Equation (18) differs from previous results[16,17] in that interaction effects are included here explicitly by the denominator in Eq. (18).

In the cubic state $T > T_c = 45.5$ K, we have, as noted in Sec. IVA, all $E_i = 0$ and $f_i = f_0$. The susceptibility is then

$$\chi(T) = \chi_{\text{orb}} + \chi_s + N_0 \mu_B^2 f_0/(1 - \mu f_0). \tag{19}$$

Thus, the cubic state $\chi(T)$ is expected to increase with decreasing temperature in a manner governed

by the same characteristic temperature T_0 which determines the temperature dependence of the cubic-state elastic moduli. Upon cooling below the lattice-transformation temperature T_c, χ is predicted to decrease rapidly. At $T=0$ K, we recall that $f_1=1$ and $f_2=f_3=0$, so that the low temperature limit of χ is

$$\chi(0)=\chi_{\rm orb}+\chi_s+\tfrac{1}{3}N_0\mu_B^2/(1-\mu). \tag{20}$$

The factor $\frac{1}{3}$ in Eq. (20) reflects the fact that the low-temperature d-electron density of states at the Fermi energy in the tetragonal lattice state is predicted to be only $\frac{1}{3}$ of the (hypothetical) cubic-state value.

From Fig. 3 it is seen that the cubic-state data for $\chi(T)$ are very well reproduced by Eq. (19) with the values $N_0=2.36$ states/eV atom, $(\chi_{\rm orb}+\chi_s)=1.52\times10^{-6}$ emu/g, $\mu=\frac{1}{3}$, and $T_0=230$ K. This value of T_0 is far larger than that deduced from the elastic moduli data. As can be seen from Fig. 3, an attempt to fit the data with $T_0=80$ K gives much greater curvature in $\chi(T)$ than is observed experimentally. The value of T_0 required to reproduce the experimental $\chi(T)$ is relatively insensitive to the value chosen for μ. For example, if we take $\mu=0$, the required value of T_0 decreases only to 200 K, while the derived value of N_0 rises to 4.01 states/eV atom. Increasing μ beyond the value $\frac{1}{3}$ raises the required T_0 above 230 K, thereby increasing the discrepancy between the results of the susceptibility and the elastic moduli analyses. The value $\mu=\frac{1}{3}$ for Nb_3Sn is regarded as reasonable because the value $N_0=2.36$ states/eV atom so obtained from the χ data analysis is in good agreement with that estimated from the specific-heat density of states[29] and the McMillan electron-phonon interaction.[30,31]

The inability of the theory to reproduce the susceptibility and elastic constant data with the same effective Fermi temperature cannot be ascribed to the particular choice Eq. (4) for the density of states $N(E)$. Equations (13) and (14) for the cubic state c_{jk} and Eq. (19) for χ hold for any $N(E)$ provided that N_0f_0 is replaced by

$$g_0=\int_0^\infty N(E)\left(-\frac{\partial f(E)}{\partial E}\right)dE. \tag{21}$$

Aside from the small effect of the interaction term μ in Eq. (19), the temperature-dependent part of the c_{jk} and χ is predicted to be proportional to $g_0(T)$. Thus, a single choice of $N(E)$ and the density of electrons N should reproduce the temperature dependence of both experimental quantities. The difference in the functions $g_0(T)$ required to explain the results of the two experiments, as represented by the difference in the derived values of T_0, is far beyond experimental error and cannot be accounted for by reasonable corrections for interactions.[26]

Figure 3 shows that the peak in χ occurs 10 ± 3 K above the measured lattice-transformation temperature $T_c=45.5$ K. This discrepancy is believed to arise from the precursor tetragonal strain observed[19,20] above T_c.

As can be seen from Fig. 3, although the measured $\chi(T)$ decreases in the tetragonal state as predicted by the theory,[27] the magnitude of the decrease is only about 25% of the predicted drop. We find that this discrepancy is increased if, instead of Eq. (4), one takes $N(E)\propto E^{-1/2}$ as in the one-dimensional model.[13,14] Assuming a three-dimensional effective-mass model $N(E)\propto E^{1/2}$ improves the agreement somewhat, but the predicted drop in $\chi(T)$ below the lattice transformation is still three times larger than is observed experimentally. Thus, we conclude that the actual drop in the electronic density of states, as measured by the susceptibility, is far less than is predicted by the theory.

V. CONCLUSIONS

We have shown that although certain qualitative features of the elastic constant and susceptibility data for Nb_3Sn are correctly predicted by the theory, several important discrepancies are present. In particular, while the band structure accounts for the observed temperature dependence of the elastic moduli c_{11} and c_{12}, it cannot explain the large monotonic softening of c_{44}. The prediction of a maximum in the susceptibility χ near the lattice-transformation temperature is verified, but the temperature dependence of χ in both the cubic- and tetragonal-lattice states is not in quantitative agreement with theory.

We conclude that the electronic band model provides a useful framework for discussion of the many complicated phenomena observed in Nb_3Sn. However, not surprisingly, it appears to be too oversimplified to account for all the experimental observations. Recently, Goldberg and Weger[32] have performed a band-structure calculation for V_3Ga and V_3Si using the tight-binding method including interchain coupling and interactions between transition-metal and nontransition-metal atoms as well as nearest-neighbor intrachain coupling.[13,14] Sharp density-of-states structure near the Fermi level is obtained. This structure is found to arise from a superposition of contributions from several van Hove singularities and appears to be a characteristic[32] of the β-W lattice. Since interactions beyond those between nearest-neighbor transition-metal atoms are included, a temperature dependent c_{44} can be obtained, unlike the case of the strictly one-dimensional model. Furthermore, since the density-of-states structure results from a combination of van Hove singularities, one would not expect to be able to represent the re-

sponse of the entire band structure to a strain by a single-energy independent-deformation-potential U. In fact the observation of only a slight drop in χ below the transformation temperature indicates that only a small part of the electronic density of states near the Fermi level distorts in a manner dictated by the band model. On the other hand, the response of the band structure to a magnetic field may be reasonably expected to be described by the single "deformation potential" μ_B. Thus, unlike the simple model presented in Sec. IV, the temperature dependence of the cubic state c_{11} and c_{12} is, in general, substantially different than that of the cubic state χ. It is noteworthy that the electron-phonon part of the electrical resistivity is described very well by a characteristic temperature[6,16] $T_0 \approx 100$ K, similar to the value obtained from the elastic moduli. This is to be expected because the deformation potential enters the calculation[33] of the resistivity in a manner similar to that for the elastic moduli.

Our experimental results have an important bearing on superconductivity in Nb_3Sn. In contrast to a previous prediction,[34] the observation of the slight decrease in the electronic density of states in the tetragonal state, as determined by the χ measurements, indicates that the lattice transformation should have only a small effect on the superconducting transition temperature. However, the considerable softening observed in c_{44} at low temperatures, which is found[23] to extend to the edge of the Brillouin zone, should appreciably increase the McMillan[30] electron-phonon interaction through a lowering of the average phonon frequency.[30] This effect may contribute substantially to the high-superconducting transition temperature of Nb_3Sn.

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PHYSICAL REVIEW B VOLUME 6, NUMBER 2 15 JULY 1972

Electron-Phonon Umklapp-Scattering Processes in the Low-Temperature Thermal Resistivity of Potassium*

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Using the variational method, the *electronic* contribution to the low-temperature thermal conductivity of potassium is calculated for a number of different pseudopotentials and a realistic phonon spectrum. A detailed evaluation of electron-phonon umklapp-scattering effects is presented. In particular, umklapp processes have a negligible effect on the thermal resistivity and Wiedemann-Franz ratio below ~2 °K, but significantly enhance both at temperatures above this. Higher-order corrections to the variational calculation are evaluated and it is found that these are significantly larger for the umklapp component of the thermal resistivity than for the normal component. The *lattice* contribution to the low-temperature thermal conductivity is calculated and compared with the results for the electronic component.

I. INTRODUCTION

In an earlier paper[1] we reported calculations of the ultrasonic attenuation and electrical resistivity of potassium which included a detailed evaluation of the role of electron-phonon umklapp-scattering processes at low temperatures. In this paper, a similar treatment has been extended to the thermal resistivity of potassium.

In Secs. II and III, the electronic contribution to the thermal conductivity is calculated, including an explicit evaluation of umklapp-scattering effects. It is found that above ~2 °K umklapp processes significantly enhance both the thermal resistivity and the Wiedemann-Franz ratio. The results for the total thermal resistivity (umklapp plus normal components) are in reasonable agreement with experimental observation,[2] although a detailed comparison must await more precise experimental study. In Sec. IV, higher-order corrections to the variational calculation are evaluated. The umklapp component is affected by such corrections to a much greater extent than the normal component. In Sec. V, the lattice conductivity is calculated in order to quantitatively evaluate the relative importance of heat conduction by the lattice compared to that by the electronic system.

II. THEORY

Taking the phonon system to be in equilibrium, the variational expression for the thermal resistivity W of a metal due to electron-phonon scattering (i.e., in the absence of electron-impurity scattering) is given by[3]

$$W = \frac{(1/k_B)\int\int\int [\phi(\vec{k}') - \phi(\vec{k})]^2 P\, d\vec{q}\, d\vec{k}\, d\vec{k}'}{|\vec{v}(E-\mu)\phi(\vec{k})(\partial f_0/\partial E)\, d\vec{k}|^2}\,, \tag{1}$$

where P is the probability for an electron in a state of wave vector $\vec{k}$ to be scattered to a state of wave vector $\vec{k}'$ through the absorption (or creation) of a phonon of wave vector $\vec{q}$ ($\vec{k}' - \vec{k} = \vec{q} + \vec{G}$, with $\vec{G}$ a reciprocal-lattice vector). Here $\vec{v}$ is the electron group velocity, E is the electron energy, k_B is Boltzmann's constant, and μ is the chemical potential. The trial function ϕ represents the deviation of the true electron distribution f from the equilibrium Fermi distribution f_0:

$$f - f_0 \equiv \left(-\frac{\partial f_0}{\partial E}\right)\phi\,; \tag{2}$$

it is chosen to minimize the right-hand side of Eq. (1). As a first approximation, we shall use the standard trial function appropriate to the solution