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## Phonon properties of *A*-15 superconductors obtained from heat-capacity measurements\*

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The heat capacities of Nb<sub>3</sub>Al, Nb<sub>3</sub>Sn, and Nb<sub>3</sub>Sb were measured between 2 and 400 K. Their superconducting transition temperatures  $T_c$  are 18.5, 17.9, and 0.2 K, respectively. The higher-temperature entropy was analyzed, and it was found that phonon-mode softening occurs on cooling for the two high- $T_c$  compounds, but not for Nb<sub>3</sub>Sb. Geometric mean phonon frequencies  $\omega_g$  are also evaluated for these compounds and for V<sub>3</sub>X, where X = Si, Ga, Ga<sub>0.5</sub>Sn<sub>0.5</sub>, and Sn. As is shown,  $\omega_g$  is an appropriate phonon average for evaluating McMillan's expression for the electron-phonon mass enhancement. Average phonon properties cannot reliably be used to calculate  $T_c$  values for these *A*-15 materials. It is suggested that, for the higher electronic density-of-states materials, select phonon modes strongly couple to the electronic system and influence the magnitude of  $T_c$  to a greater extent than average-phonon correlations would indicate. This view is supported by the observation that the higher-density-of-states materials exhibit the more pronounced phonon-mode softening on cooling.

### I. INTRODUCTION

Compounds that possess the *A*-15 crystal structure have the highest known superconducting transition temperatures. Accordingly, the *A*-15 superconductors have been the subject of extensive experimental and theoretical investigations.<sup>1</sup> Considerable evidence exists that soft phonons are associated with the *A*-15 high superconducting transition temperatures. Ultrasonic and inelastic neutron scattering experiments clearly indicate that, for the high- $T_c$  members V<sub>3</sub>Si and Nb<sub>3</sub>Sn, extensive acoustic-phonon softening occurs with decreasing temperature.<sup>1</sup> In an earlier paper devoted to vanadium-base *A*-15 superconductors, we used heat-capacity measurements to show that the extensive shifting of optical-phonon modes also appears to occur for the higher- $T_c$  *A*-15 compounds.<sup>2</sup> The purpose of the present study was to characterize certain average phonon properties for some niobium-base, as well as vanadium-base, *A*-15 superconductors, and to relate the phonon physics to the superconductivity of these interesting materials. To further elucidate the nature of the superconductivity of these well-studied *A*-15 compounds, we attempted to determine whether the variations in the magnitude of the superconducting transition temperatures were governed primarily by variations in phonon properties. In principle, the best experimental probes to investigate the problem under consideration, are superconductive tunneling and inelastic neutron spectroscopy. Unfortunately, practical limitations often preclude their use. Although the heat capacity is insensitive

to details of the phonon spectrum, certain averaged properties, or moments of the phonon spectrum, can be assessed by heat-capacity measurements. Closely related moments have been identified by McMillan as being the phonon properties relevant to superconductivity theory.<sup>3</sup>

It is particularly interesting to include the vanadium-base *A*-15 superconductors, which we reported earlier,<sup>2</sup> with the new results for the niobium-base compounds for the following reason. The superconducting transition temperature is known to increase strongly with *d*-electron density of states at the Fermi energy  $N_d(E_F)$  for the vanadium-base compounds, whereas only a weak correlation exists between  $T_c$  and  $N_d(E_F)$  for the niobium-base compounds. By a comparison of the properties of the vanadium- and niobium-base materials, insight can be gained in understanding the different roles the *d* electrons play in modifying the superconductive properties of these materials.

Concerning purely phononic properties, we find from the heat-capacity analysis that temperature-dependent phonon-mode softening does occur for the high- $T_c$  compounds Nb<sub>3</sub>Al and Nb<sub>3</sub>Sn, as was observed for the high- $T_c$  vanadium-base *A*-15 superconductors.<sup>2</sup> The magnitudes of the average phonon-mode shifts with temperature, for the high- $T_c$  niobium-base *A*-15 compounds, are smaller than those observed for the vanadium-base compounds. This observation is explicable within the framework we used previously in discussing the origin of the phonon-mode shifts in the V<sub>3</sub>X system. Using the idea that temperature-dependent electronic screen-

ing arising from peaked electronic densities of states in the vicinity of the Fermi energy causes temperature-dependent phonon-mode frequencies, we expect smaller frequency shifts for the niobium-base materials. This is because the niobium-base *A-15* compounds have electronic density of states that are less peaked in the vicinity of  $E_F$ , based on the temperature dependence of their magnetic susceptibilities and the magnitude of their normal-state electronic heat capacities at low temperatures.

Concerning the relationship of the purely phononic properties to superconductivity, we find that average phonon properties cannot reliably be used to calculate superconductive properties for these *A-15* compounds. The reason, we believe, is that select phonon modes can be strongly coupled to the electronic system and influence the magnitude of  $T_c$  to a greater extent than average phonon correlations would indicate. Such a situation appears to occur most dramatically for  $V_3Si$ , and, in general, plays a larger role in the enhancement of the  $T_c$  values in the vanadium-base than in the niobium-base superconductors investigated.

## II. SAMPLES AND EXPERIMENTAL TECHNIQUE

The preparation and characterization of the  $V_3X$  compounds are described in Ref. 2. Each of the  $Nb_3X$  compounds were prepared differently because of metallurgical considerations unique to each system. The  $Nb_3Al$  was prepared by melting compacted powders of Nb and Al in a levitation furnace, and then heat treating at 1550 and 600°C for 5 min and 1 week, respectively. The  $Nb_3Sn$  sample was obtained by hot pressing appropriate amounts of Nb and Sn, in a graphite die ~1 cm in diameter, for 15 h at 1175°C and 2 kbar. The resultant pill was >90% of its theoretical density. The  $Nb_3Sb$  sample was prepared at La Jolla by an  $I_2$ -vapor-transport technique.<sup>4</sup> A stoichiometric mixture of 0.25-mm-Nb foil and 99.999% Sb were sealed with 40-mg  $I_2$  in a 10-cm-long, 1.5-cm-diam (out-gassed) quartz tube. After an overnight soak at 900°C, the tube was placed in an 800–900°C gradient for 2 weeks, with the charge at the cold end. To increase the transport rate, the charge temperature was lowered to 750°C and kept at that temperature for 1 week. All samples were studied by x-ray and metallographic analyses. The  $Nb_3Al$  and  $Nb_3Sn$  samples were at least 90% single phase, and the  $Nb_3Sb$  sample consisted of a collection of large single-phase grains.

The  $T_c$  values were determined from the heat-capacity data for all samples except  $Nb_3Sb$ , for which  $T_c$  was detected magnetically in a dilution refrigerator. The heat-capacity measurements on

the  $V_3X$  compounds were described previously.<sup>2</sup> The heat-capacity measurements on the  $Nb_3X$  compounds were made using the heat-pulse method, employing feedback to regulate the temperature of the radiation shields surrounding the sample.<sup>5</sup> The accuracy of the data above 20 K was of the order of 1%, based on measurements of American Calorimetry Conference Standard Cu.<sup>6</sup> Below 20 K, the accuracy of the data was of the order of 2% for  $Nb_3Sn$  and  $Nb_3Al$ . For  $Nb_3Sb$ , the accuracy was of the order of ±10% because only a small sample was available and the molar heat capacity of  $Nb_3Sb$  was small at low temperatures.

## III. ANALYSIS OF DATA AND RESULTS

The thermodynamics relevant to the analysis of the data will be introduced in the first portion of this section. We will not restrict ourselves to the harmonic approximation, since it is clear from our earlier work<sup>2</sup> that optic-phonon-mode shifting can be an important characteristic of the high  $T_c$  vanadium-base *A-15* superconductors. The lattice entropy  $S_L$  can be represented by using the results obtained from the harmonic approximation

$$S_L = k_B \sum_{s=1}^{3N} [\beta \hbar \omega_s n_s + \ln(n_s + 1)], \quad (1)$$

where  $\beta = (k_B T)^{-1}$ ,  $n_s = [\exp(\beta \hbar \omega_s) - 1]^{-1}$ , and allowing the  $\omega_s$  normal-mode frequencies of harmonic theory to be temperature dependent.<sup>7</sup> The above statement has long been known to be correct to lowest order in anharmonicity (phonon-phonon interactions) and is now also known to be correct to the lowest order when the phonon-frequency shifts with temperature are due to electron-phonon interactions.<sup>8</sup> (In our earlier paper,<sup>2</sup> we tacitly use the term anharmonicity to describe either of the above interactions. We will now use the term nonharmonicity to refer to either type.)

From Eq. (1), it can be shown that  $S_L$  approaches its high-temperature limiting form

$$S_L = 3Nk_B \left[ 1 - \ln \frac{\hbar \omega_g}{k_B T} - \sum_{n=1}^{\infty} (-1)^n \binom{2n-1}{2n(2n)!} B_{2n} \left( \frac{\hbar}{k_B T} \right)^{2n} \langle \omega^{2n} \rangle \right], \quad (2)$$

where, if  $N$  is Avogadro's number, the entropy is expressed on a per gram-atom basis, the  $B_n$  are Bernoulli numbers ( $B_2 = \frac{1}{6}, B_4 = \frac{1}{30}, B_6 = \frac{1}{42}$ , etc.),  $\langle \omega^n \rangle$  is the  $n$ th moment of the phonon spectrum defined for all  $n > -3, \neq 0$  as

$$\langle \omega^n \rangle = \frac{1}{3N} \sum_{s=1}^{3N} \omega_s^n, \quad (3)$$

TABLE I. Table of smoothed constant-pressure heat-capacity data for the indicated niobium-base A-15 superconductors. The units are J/°K atom.

T (°K)	Nb <sub>3</sub> Al	Nb <sub>3</sub> Sn	Nb <sub>3</sub> Sb
20	0.77	1.26	0.35
25	1.44	2.10	0.77
30	2.27	3.15	1.39
35	3.25	4.40	2.16
40	4.36	5.71	3.22
45	5.46	6.95	4.29
50	6.50	8.17	5.46
60	8.47	10.45	7.65
70	10.37	12.39	9.90
80	11.96	14.07	11.75
90	13.45	15.34	13.35
100	14.68	16.42	14.73
120	16.66	18.31	17.04
140	18.41	19.74	18.98
160	19.71	21.06	20.33
180	20.71	21.90	21.45
200	21.52	22.51	22.35
220	22.13	22.98	22.99
240	22.63	23.27	23.46
260	23.04	23.64	23.85
280	23.39	23.87	24.19
300	23.72	24.18	24.45
320	24.02	24.36	24.67
340	24.30	24.55	24.85
360	24.56	24.72	25.00
380	24.70	24.85	25.13
400	25.02	24.95	25.21

and  $\omega_g$  is the geometric mean frequency

$$\omega_g = \left( \prod_{s=1}^{3N} \omega_s \right)^{1/3N}. \quad (4)$$

We will show in Sec. IV that  $\omega_g$  is closely related to the average over the phonon spectrum that Mc-Millan<sup>3</sup> indicated to be important for superconductivity. It is also useful to assign  $n$  different Debye temperatures  $\Theta_D(n)$ , each of which corresponds to a Debye phonon spectrum that has the same  $n$ th moment as the actual spectrum

$$\Theta_D(n) = \frac{\hbar}{k_B} \left( \frac{n+3}{3} \langle \omega^n \rangle \right)^{1/n}, \quad n > -3, \neq 0. \quad (5)$$

Within this formalism,  $\Theta_D(-3)$  is defined as the Debye temperature obtained from the elastic constants. For  $n=0$ ,

$$\Theta_D(0) = e^{1/3} \hbar \omega_g / k_B, \quad (6)$$

i.e., the expressions for  $\langle \omega^n \rangle$  and  $\Theta_D(n)$  are well behaved in the limit as  $n \rightarrow 0$ . Representing the moments by their associated Debye temperatures facilitates comparisons in that the  $\Theta_D(n)$  all have the same dimensionality, whereas the  $\langle \omega^n \rangle$  do not. The  $\Theta_D(n)$  are expected to vary smoothly with  $n$ , and, in general, vary slowly for  $n$  greater than

approximately  $-1$ , especially for solids that are metallically bonded.<sup>9</sup>

The high-temperature limiting form of the lattice heat capacity  $C_L$  can be obtained from Eq. (2), since  $C_p = T(\partial S/\partial T)_p$ ,

$$C_L = 3Nk_B \left[ 1 + \frac{1}{12} \frac{\hbar^2 \langle \omega^2 \rangle}{k_B^2 T^2} - \dots \right] + AT, \quad (7)$$

where only the first term in the power series of Eq. (2) was retained, and

$$\frac{A}{3Nk_B} = -\frac{d \ln \omega_g}{dT} = -\frac{1}{3N} \sum_{s=1}^{3N} \frac{1}{\omega_s} \frac{d\omega_s}{dT}. \quad (8)$$

In harmonic theory, the  $\omega_s$  are independent of  $T$  and  $A=0$ , hence  $AT$  can be identified as an explicit nonharmonic contribution to the heat capacity in the high-temperature limit.

Table I contains smoothed constant-pressure heat-capacity data  $C_p$  above 20 K. The  $C_p$  was not converted to constant volume  $C_v$ . The dilation contribution to the heat capacity  $C_p - C_v$  (typically  $\sim 1\%$  of  $C_p$  for these materials at room temperatures) is an anharmonic contribution, and it is absorbed in the  $A$  coefficient at high temperatures. Also, to facilitate a comparison of our results with inelastic neutron scattering studies, when they become available, the total frequency shifts are the relevant quantities of interest.

To analyze our data for phonon properties, we first need to characterize the electronic contributions to  $C$  and  $S$ . To lowest order, the normal-state electronic heat capacity  $C_E$  and entropy  $S_E$  are linear in temperature. In the low-temperature limit,  $C_E = S_E = \gamma_0 T$ . Table II contains  $\gamma_0$  values obtained in the usual manner.<sup>2</sup> To improve upon the linear approximation, we have used the results of model calculations to describe the additional temperature dependences to  $C_E$  and  $S_E$  caused by both electron-phonon renormalization<sup>10</sup> and band-structure effects.<sup>2</sup> For the latter effect, the temperature dependences of additional electronic properties (i.e., the magnetic susceptibility or <sup>51</sup>V nuclear spin-lattice relaxation time  $T_1$ ) were utilized as constraints.<sup>2</sup> For the Nb<sub>3</sub>X compounds,  $C_E$  and  $S_E$  tend to be smaller in magnitude and have smaller temperature-dependent band-structure contributions than in the V<sub>3</sub>X compounds. Hence, although  $T_1$  measurements are currently lacking for the Nb<sub>3</sub>X system, both systems can be adequately characterized electronically. Using the procedure described in detail in Ref. 2, room-temperature  $\gamma$  values of  $3.0 \pm 0.3$ ,  $3.6 \pm 0.4$ , and  $0.6 \pm 0.1$  mJ/°K<sup>2</sup>-g-atom are estimated for Nb<sub>3</sub>Al, Nb<sub>3</sub>Sn, and Nb<sub>3</sub>Sb, respectively.

Thus, we can now proceed with the thermodynamic evaluation of the phonon properties. Equation (7), as written, is convergent in the vicinity

TABLE II. Calorimetrically determined properties of A-15 compounds.

Compounds	$T_c$ ( $^{\circ}\text{K}$ )	$\gamma_0$ ( $mJ/^{\circ}\text{K}^2 \text{g atom}$ )	$\Theta_D(2)$ ( $^{\circ}\text{K}$ )	$\hbar\omega_g/k_B$ ( $^{\circ}\text{K}$ )
$\text{V}_3\text{Si}$	16.5	16.7	498	326
$\text{V}_3\text{Ga}$	14.3	21.6	399	254
$\text{V}_3\text{Ga}_{0.5}\text{Sn}_{0.5}$	5.6	10.2	371	257
$\text{V}_3\text{Sn}$	3.8	7.22	364	259
$\text{Nb}_3\text{Al}$	18.5	7.62	370	239
$\text{Nb}_3\text{Sn}$	17.9	12.2	308	201
$\text{Nb}_3\text{Sb}$	0.2	1.1	335	246

of  $\sim 0.7 > \Theta_D(2)/T > 1.3$ . Since  $C_E$  and the nonharmonic contribution to  $C_L$  are approximately linear in temperature, the slope of a  $(C - 3R)/T$  vs  $T^{-3}$  plot yields a  $\langle\omega^2\rangle$  value, and hence a  $\Theta_D(2)$  value, for each material.<sup>11</sup> The values of  $\Theta_D(2)$  appear in Table II. The experimental entropy for each material as a function of temperature was obtained by evaluating the area under appropriate  $C/T$  vs  $T$  plots. The high-temperature values of  $\omega_g$ , or the equivalent  $\Theta_D(0)$ , for each material, could be obtained from Eq. (2). To follow the temperature dependence of  $\Theta_D(0)$  for temperatures above  $\frac{1}{3}\Theta_D$ , the lowest temperature for which Eq. (2) is rapidly convergent, the terms in Eq. (2) through order  $\langle\omega^6\rangle$  were retained and two assumptions were made. First, we assumed  $\Theta_D(6) = \Theta_D(4) = \Theta_D(2)$ . For a Debye spectrum, the  $\langle\omega^4\rangle$  and  $\langle\omega^6\rangle$  terms in Eq. (2) are small compared with the total lattice entropy above  $\sim \frac{1}{3}\Theta_D$ , and, for any spectrum with a reasonably well-defined cutoff frequency, the  $\Theta_D(n)$  values vary slowly and smoothly for  $n > 2$ . Hence, this assumption is not unreasonable and cannot cause significant errors in the determination of  $\Theta_D(0)$ . The second assumption is that the temperature dependence of  $\Theta_D(2)$  is one-half that of  $\Theta_D(0)$ . This required that Eq. (2) be iterated to obtain consistent  $\Theta_D(0)$  vs  $T$  plots. The precise value of one-half was chosen somewhat arbitrarily. However, if the one-half value is varied by  $\pm 100\%$ ,  $\Theta_D(0)$  values shift a maximum of only a few percent and only below a temperature of  $\sim \frac{1}{2}\Theta_D(0)$ . It is expected that  $\Theta_D(2)$  is less temperature sensitive than  $\Theta_D(0)$ , since the present work taken together with  $\text{V}_3\text{Si}$  and  $\text{Nb}_3\text{Sn}$  ultrasonic and inelastic neutron scattering studies indicate that the lowest moments exhibit the largest shifts with temperature. In Fig. 1, the temperature dependence of  $\Theta_D(0)$  (and hence  $\omega_g$ ) is displayed for the materials of interest. Phonon-mode softening with decreasing temperature occurs most dramatically for  $\text{V}_3\text{Si}$  and  $\text{V}_3\text{Ga}$ . Only the slope of  $\Theta_D(0)$  vs  $T$  plot for  $\text{Nb}_3\text{Sb}$  has the expected sign, if dilation governs

the phonon-mode shifts (i.e., since  $C_p - C_v > 0$ ,  $d\omega_g/dT < 0$ , and mode softening occurs as the melting temperature is approached).

From the slopes of the straight lines drawn through the data in Fig. 1, the values of the frequency-shift parameters  $A/3R$  are obtained [Eqs. (6) and (8)]. These  $-A/3R$  values are listed in the second column of Table III. It should be emphasized that ambiguity exists in interpreting the magnitudes of these  $A/3R$  values. For example, for  $\text{V}_3\text{Si}$  at room temperature, a value of  $-0.07$  is found for  $A/3R$  times temperature, but is not

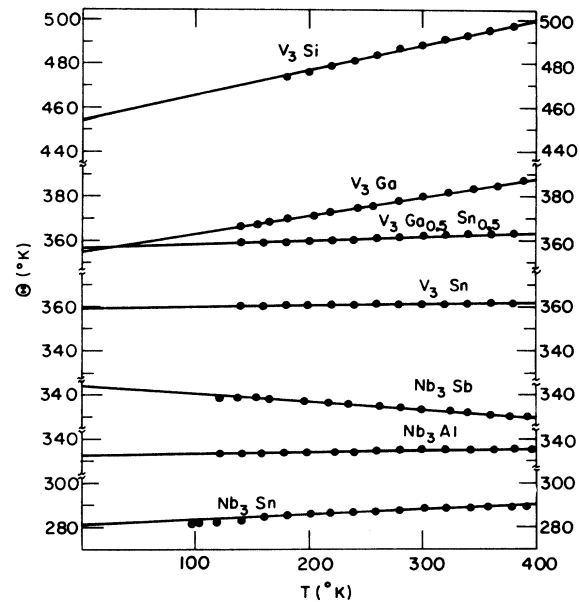


FIG. 1. Temperature dependence of the Debye temperature associated with the  $n$ th moment of the phonon spectrum in the limit  $n \rightarrow 0$ . This Debye temperature is proportional to the geometric-mean frequency of the phonon spectrum and is closely related to the appropriate phonon properties for calculating  $\lambda$ . Note the trend of phonon softening with decreasing temperature, which is most pronounced for the high- $T_c$  compounds  $\text{V}_3\text{Si}$ ,  $\text{V}_3\text{Ga}$ , and  $\text{Nb}_3\text{Sn}$ .

TABLE III. Additional properties of A-15 superconductors.

Compounds	$-A/3R = d \ln \omega_g / dT$ ( $10^{-4} \text{ }^\circ\text{K}^{-1}$ )	$N(E_F)$ (states/eV atom)	$\lambda$	$M\omega_g^2$ (eV/Å <sup>2</sup> )	$\lambda M\omega_g^2$ (eV/Å <sup>2</sup> )
V <sub>3</sub> Si	2.4	3.8	0.86	8.61	7.4
V <sub>3</sub> Ga	2.3	4.8	0.91	6.43	5.9
V <sub>3</sub> Ga <sub>0.5</sub> Sn <sub>0.5</sub>	0.4	2.7	0.62	7.30	4.5
V <sub>3</sub> Sn	0.1	2.0	0.56	8.14	4.6
Nb <sub>3</sub> Al	0.2	1.6	1.07	7.82	8.4
Nb <sub>3</sub> Sn	0.8	2.4	1.17	7.18	8.4
Nb <sub>3</sub> Sb	-1.0	0.4	0.3	10.85	3.3

known whether, for instance, *all* the modes shift 7% on cooling from room temperature, or *half* the modes shift 14% on cooling, etc. We will again refer to this important point in Sec. IV. The errors associated with the  $A/3R$  values are  $\pm 4 \times 10^{-5} \text{ }^\circ\text{K}^{-1}$ . For the V<sub>3</sub>X compounds,  $A$  values were obtained earlier<sup>2</sup> from a high-temperature heat-capacity analysis, which are the same as those listed in Table III, to within the stated error limits.

#### IV. DISCUSSION

In Sec. III, certain phononic properties, such as the geometric-mean frequency  $\omega_g$  and its temperature coefficient,  $-d \ln \omega_g / dT = A/3R$ , were obtained from the heat-capacity measurements. In this section, we will first discuss these purely phononic properties and then their relationship to superconductivity.

Referring again to Fig. 1, it is clear that, except for Nb<sub>3</sub>Sb (for which dilation effects play a dominant role), phonon-mode softening with decreasing temperature is a characteristic of all the A-15 compounds investigated. Although the effect is not pronounced for V<sub>3</sub>Sn and Nb<sub>3</sub>Al, it should be noted that even in these cases the mode softening with decreasing temperature is sufficiently strong to totally mask the usual dilation effect. In our earlier paper, we argued that the phonon-mode softening was due to conduction-electronic screening of the bare-ion potentials.<sup>2</sup> Temperature-dependent softening occurs because the sharp structure in the  $d$ -band density of states in the vicinity of the Fermi energy, which causes electronic properties such as the magnetic susceptibility to be temperature dependent, produces temperature-dependent electronic screening of the phonon-mode frequencies. The present study supports that viewpoint. Nb<sub>3</sub>Sb does not soften on cooling because  $d$  character at  $E_F$  is barely present, based on the magnitude of its low-temperature electronic heat-capacity coefficient in the normal state  $\gamma_0$  (Table II). The compounds V<sub>3</sub>Sn and Nb<sub>3</sub>Al exhibit less

softening on cooling than the remainder of the compounds under consideration (except Nb<sub>3</sub>Sb) because less peaking of their  $d$ -band density of states occurs at  $E_F$ . Again, this is based on the magnitudes and temperature dependences of their electronic properties, such as  $\gamma_0$  and  $\chi$ .

We now attempt to relate the phonon properties to the magnitudes of the observed  $T_c$  values. McMillan's strong-coupling formulation of the BCS theory is used, whereby  $T_c$  is related to the electron-phonon mass enhancement  $\lambda$  via the semi-empirical expression<sup>3</sup>

$$T_c = \frac{\Theta}{1.45} \exp\left(\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right), \quad (9)$$

where  $\mu^*$  is a Coulomb repulsion parameter, which is approximately equal to 0.13 for transition metals, and  $\Theta$  is a characteristic phonon parameter. We use  $\Theta_D(0)$  extrapolated to its value at  $T_c$  for the  $\Theta$  in Eq. (9). McMillan indicated that

$$\lambda \approx \frac{N(E_F)\langle I^2 \rangle}{M(\langle \omega \rangle / \langle \omega^{-1} \rangle)}, \quad (10)$$

where  $I$  is the electronic matrix element of the change in crystal potential when one atom is moved, and for  $M$  we use the gram-atomic weight. Using Eqs. (5) and (6) and since  $\Theta_D(n)$  varies slowly and smoothly as a function of  $n$  for  $n > -1$ , one finds

$$\langle \omega \rangle / \langle \omega^{-1} \rangle = \frac{1}{2} (k_B / \hbar)^2 [\Theta_D(+1)] [\Theta_D(-1)] \approx \omega_g^2, \quad (11)$$

hence,  $\lambda \approx N(E_F)\langle I^2 \rangle / M\omega_g^2$ .

McMillan noted that, for a number of bcc transition metals, the numerator in Eq. (10) is empirically found to be approximately constant.<sup>3</sup> Hopfield<sup>12</sup> has since provided a theoretical basis for understanding McMillan's empirical observation. However, Hopfield's arguments might not be valid in the presence of gross lattice instabilities. He suggested that both the product  $N(E_F)\langle I^2 \rangle$  is independent of  $N(E_F)$  for metals with large  $d$  electron contributions to  $N(E_F)$ , and the magnitude of

$N(E_F)\langle I^2 \rangle$  is largely determined by the identity of the transition-metal element for binary alloys composed of transition and nontransition metals such as  $Nb_3X$  and  $V_3X$ . An important consequence of this finding is that  $\lambda$  should be inversely proportional to average force-constant values such as  $M\omega_g^2$  within the  $V_3X$  and  $Nb_3X$  systems. The  $\lambda$  values obtained from Eq. (9) are shown in column 4 of Table III. In columns 5 and 6, the  $M\omega_g^2$  and  $\lambda M\omega_g^2$  values, respectively, are listed. The nonconstancy of the  $\lambda M\omega_g^2$  values in column 6 and the lack of any simple trend in their values indicate that A-15 superconductors under consideration are exceptions to the McMillan-Hopfield expectations. [This statement remains true even if  $Nb_3Sb$  is excluded from consideration on the basis that it does not meet Hopfield's criterion of substantial  $d$ -electron contributions to  $N(E_F)$ .] For instance, we note first that  $V_3Ga$  and  $V_3Si$  have  $\lambda$  values that differ by only  $\sim 6\%$ , but their  $M\omega_g^2$  values differ by  $30\%$ . Second,  $V_3Sn$  and  $V_3Si$  have  $\lambda$  values that differ by  $\sim 40\%$ , but their  $M\omega_g^2$  values are quite similar—the lower- $T_c$  compound  $V_3Sn$  is actually  $\sim 6\%$  softer on the average. Hence, *average phonon properties cannot be reliably used to calculate superconductive properties, such as  $T_c$  or  $\lambda$ , for these interesting A-15 compounds.*

We now attempt to explain our observation that variations in  $M\omega_g^2$  do not quantitatively correlate with variations in the  $T_c$  values of the A-15 superconductors of interest. We focus primarily on the  $V_3X$  compounds because our observation above is most firmly established for the vanadium-base compounds. We recall that an important correlation has been found between  $T_c$  and density of states at  $E_F$  for the  $V_3X$  compounds. NMR studies indicate that, for the pseudobinaries  $V_3Ga_{1-x}Sn_x$  and  $V_3Ga_{1-x}Si_x$ ,  $T_c$  (normalized by a Debye temperature) increases strongly and monotonically with the bare or "band-structure"  $N(E_F)$  value.<sup>13</sup> This is a particularly striking observation since the  $T_c$  vs  $x$  curves are different for the two pseudobinary systems and nonmonotonic for  $V_3Ga_{1-x}Si$ . We recall also that a strong correlation between the bare electronic density of states at  $E_F$  and the frequency-shift parameter  $A$  has been found (Table III). Hence,  $N(E_F)$ , an electronic property, strongly correlates with both  $T_c$ , a superconductive property, and  $A$ , a phonon property. To understand the lack of quantitative correlation between  $T_c$  and the phonon property  $M\omega_g^2$ , we return to the ambiguity in the interpretation of the magnitude of the  $A$  parameter. For a given  $A$  value, for instance, it is not clear whether essentially all the phonon modes are uniformly shifting a certain percentage with temperature, or whether a small number of modes are shifting much more dramatically with

temperature. Ultrasonic and inelastic neutron scattering experiments on  $V_3Si$  and  $Nb_3Sn$ , which have probed acoustic modes to approximately one-half the Brillouin-zone boundary—a small fraction of the total number of phonon modes—indicate that anomalous softening only occurs for certain branches and over certain ranges of wave numbers.<sup>1</sup> Adopting the viewpoint that the calorimetrically determined frequency-shift parameter is being influenced by a small fraction of the total number of modes, which are selectively softening, we can understand the lack of quantitative correlation between  $M\omega_g^2$  and  $\lambda$ . *Select phonon modes couple strongly to the electronic system and influence the magnitude of  $T_c$  to a greater extent than average phonon property correlations would indicate.* Extensive theoretical work has provided a basis for the above statement.<sup>14</sup>

The recent work of Sinha and Harmon is particularly relevant to our discussion in that it presents a clear theoretical basis for selective electronically driven phonon softening that enhances  $T_c$  in high-density-of-states materials.<sup>15</sup> Sinha and Harmon address their work to the phonon anomalies in Nb and NbC. The anomalies were detected by neutron inelastic scattering measurements, and consist of dips in the frequency versus wave-number curves for certain acoustic-phonon branches near the zone boundary. According to Sinha, the  $I$  values [cf. Eq. (10)] for these select branches and wave numbers will be enhanced by roughly  $(1 + V_q\chi_q)^{-1}$ , where  $V_q$  is a  $q$ -dependent potential-energy term, which is negative at high- $q$  values, and  $\chi_q$  is the generalized susceptibility, which is approximately equal to the  $d$ -band density of states at  $E_F$ .<sup>16</sup> Therefore, if  $V_q\chi_q \leq 1$  over certain ranges of  $q$ , these modes will dominate over the other electron-phonon couplings and strongly enhance  $\lambda$ . These same soft modes, because they are relatively few in number, will have a much smaller effect on  $\omega_g$  and on the frequency-shift parameter obtained from heat-capacity measurements.

Based on the rather erratic magnitudes of the  $M\omega_g^2$  values in column 6 of Table III, we believe that the extremely strong coupling of select phonon modes to the conduction electrons, which, for example is addressed by the Sinha-Harmon theory,<sup>15</sup> occurs most dramatically for  $V_3Si$ . The high- $T_c$  compounds  $Nb_3Al$  and  $Nb_3Sn$  have considerably smaller values of  $N(E_F)$  than the high- $T_c$  compounds  $V_3Ga$  and  $V_3Si$ . The frequency-shift parameters of these niobium-base A-15 compounds are accordingly smaller than those of the high- $T_c$  vanadium-base compounds. Also, although a correlation between  $T_c/\Theta$  (or  $\lambda$ ) and  $N(E_F)$  is not well established for the niobium-base A-15 superconductors, it is safe to conclude that  $\lambda$  is a weaker function of

$N(E_F)$  for the niobium-base than for the vanadium-base A-15 superconductors of interest. The large values of  $\lambda$  for  $Nb_3Al$  and  $Nb_3Sn$  appear to be largely associated with inherently strong electron-phonon coupling at the niobium sites, as suggested, for instance, by Hopfield.<sup>12</sup> The  $V_3X$  compounds appear to have an inherently weaker electron-phonon coupling at the vanadium sites compared with that at the niobium sites in the  $Nb_3X$  compounds. High- $T_c$  values occur for some  $V_3X$  compounds because  $\lambda$  can be significantly enhanced by selective electron-phonon couplings in the higher- $d$  electronic density-of-state  $V_3X$  compounds. In general, since selective coupling seems to play a

larger role in producing high- $T_c$  values in the vanadium-base than in the niobium-base A-15 superconductors investigated, we predict that neutron inelastic scattering experiments should reveal that the phonon anomalies of the type observed in NbC will be much more pronounced in  $V_3Si$  than in  $Nb_3Sn$ .

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