

Heat capacity of V_3X compounds and the relationship between T_c and anharmonicity*

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The heat capacities of V_3Si , V_3Ga , V_3Sn , and $V_3Sn_{0.5}Ga_{0.5}$ were measured between 2 and 400°K. The high- T_c compounds V_3Ga and V_3Si have smaller high-temperature heat capacities than the two lower- T_c materials. Given the magnitudes of the measured low-temperature heat capacities, this observation can only result from unusually large anharmonicity of the higher- T_c compounds. A phenomenological model is proposed that semiquantitatively relates the electron-phonon mass enhancement, and hence T_c , to the high-temperature anharmonic heat capacity observed in these materials. The model assumes a temperature-dependent screening caused by sharp structure in the electronic density of states, which renormalizes the bare phonon-mode frequencies.

I. INTRODUCTION

Considerable evidence exists that soft phonons are associated with the high superconducting transition temperatures observed in some $A-15$ compounds.^{1,2} Elastic-constant measurements on the high- T_c compounds V_3Si and Nb_3Sn reveal extensive softening, with decreasing temperature, of some acoustic phonon modes, followed by martensitic phase transitions from cubic to tetragonal symmetry.¹ Neutron inelastic-scattering measurements on V_3Si and Nb_3Sn reveal that the acoustic phonon softening, observed ultrasonically, persists throughout a substantial portion of the Brillouin zone.³⁻⁶ The well-studied acoustic modes, however, are only one-eighth of the total phonon modes. Little experimental information exists concerning the higher-energy optical modes. It is well known that phonon-mode shifting with temperature results in deviations from the harmonic-lattice contribution to the heat capacity.⁷ The purpose of the present study was to probe the average shifting of all phonon modes using heat-capacity measurements and to relate the phonon physics to the superconductivity of some $A-15$ materials.

The heat capacities of V_3Si ($T_c \sim 17^\circ K$), V_3Ga ($T_c \sim 15^\circ K$), V_3Sn ($T_c \sim 4^\circ K$), and $V_3Sn_{0.5}Ga_{0.5}$ ($T_c \sim 6^\circ K$) were measured between 2 and 400°K. The magnitudes of the measured high-temperature heat capacities of the high- T_c materials V_3Ga and V_3Si are significantly smaller than those for the two lower- T_c materials. It will be shown that this depression could only be caused by large negative anharmonic heat-capacity contributions in the higher- T_c materials at elevated temperatures. Thus extensive shifting of optical, as well as acoustical, phonon modes does indeed appear to occur for the higher- T_c vanadium-base $A-15$ superconductors, as has been predicted for Nb_3Sn .^{5,8} A detailed analysis of the high-temperature data, combined with that of recent NMR (nuclear-magnetic-resonance) studies of these compounds,^{9,10} yields the

magnitudes of the anharmonic heat-capacity contributions at high temperatures.

The results of the present study are, in general, consistent with a model in which the soft phonon modes and thus the high- T_c values are caused by sharp structure in the d -band density of states near the Fermi energy ϵ_F , which causes strong temperature-dependent renormalization of the bare phonon frequencies. The existence of unusual structure in the electronic density of states has been inferred from the anomalous behavior of numerous physical properties.^{1,2} For the high- T_c vanadium-base $A-15$ superconductors, the magnetic susceptibility and the low-temperature electronic heat-capacity coefficient are unusually large. Also, the strong temperature dependencies of these quantities, the NMR Knight shift, and T_1T (where T_1 is the nuclear spin-lattice relaxation time) readily lend themselves to a peaked-density-of-states interpretation. Band-structure calculations are, in general, consistent with the proposed peak in the vicinity of ϵ_F for these materials.²

McMillan¹¹ recognized that "high-density-of-states materials are elastically softer." In the present study, the link between the high electronic density of states at ϵ_F and the phonon-mode softening is taken to be electronic screening that renormalizes the bare phonon-mode frequencies. We have calculated shifts in the electron-phonon mass enhancement λ from the magnitudes of the anharmonicity, using a phenomenological relationship that is derived by means of the theory of Allen and Cohen.¹² Semiquantitative agreement is found between the λ values thus calculated and the λ values obtained from McMillan's equation¹¹ for T_c .

II. EXPERIMENTAL

The polycrystalline samples were prepared by arc melting, followed by anneals for one week at 1000 and 700°K. Samples were checked by x-ray and metallographic analysis and were found to be

at least 90% single phase. The superconducting transitions were detected in fields below 20 Oe, using a Faraday susceptibility apparatus. The magnetic susceptibility, coefficient of thermal expansion, and bulk modulus K were also measured. The magnetic susceptibility was measured between 77 and 320 °K by means of Faraday technique. The coefficient of thermal expansion (α) was measured between 90 and 350 °K with a Theta Industries differential dilatometer. The bulk modulus was determined only at room temperature from measurements of the longitudinal (v_L) and transverse (v_T) velocities of sound, where

$$K = \rho(v_L^2 - \frac{4}{3}v_T^2).$$

A standard heat-pulse technique¹³ was used to obtain heat-capacity measurements between 2 and 20 °K, and a differential technique¹⁴ was used for measurements between 50 and 400 °K. Absolute accuracies were better than 1% in both cases.

III. ANALYSIS OF DATA AND RESULTS

Some high-temperature heat-capacity data for V_3Sn are shown in Fig. 1. Table I lists smoothed C_p data for the four samples, where C_p is the measured constant-pressure heat capacity. The curve labeled C_p was used to obtain the smoothed representation of the data contained in Table I. The heat capacity can be represented as the sum

$$C_p = C_D + C_v = C_D + C_E + C_L, \quad (1)$$

where C_D is the dilation contribution, C_v is the con-

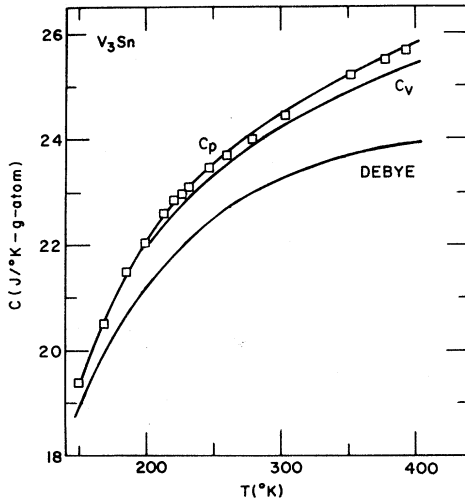


FIG. 1. Heat capacity of V_3Sn . The squares indicate the measured C_p data points. The curve labeled C_p was used to obtain the smoothed representation of the data contained in Table I. The curve labeled C_v is the constant-volume heat capacity. The curve labeled Debye is a Debye heat capacity using the characteristic temperature $\Theta_\infty = 364^\circ K$.

TABLE I. Table of smoothed constant-pressure heat-capacity data for the indicated vanadium-base A-15 superconductors. The units are $J/^\circ K g$ atom.

T (°K)	V_3Sn	$V_3Sn_{0.5}Ga_{0.5}$	V_3Ga	V_3Si
60	7.15	7.28	7.35	4.45
70	9.05	9.49	9.50	6.30
80	11.05	11.62	10.92	7.96
90	12.54	13.38	12.37	9.45
100	14.06	14.64	13.65	10.83
120	16.80	15.02	15.75	13.15
140	18.50	18.95	17.40	15.10
160	19.95	20.23	18.78	16.60
180	21.15	21.20	19.95	17.70
200	22.05	22.05	20.85	18.75
220	22.75	22.64	21.60	19.95
240	23.27	23.18	22.21	20.24
260	23.70	23.69	22.71	20.85
280	24.07	24.15	23.10	21.33
300	24.40	22.55	23.42	21.82
320	24.72	24.90	23.75	22.27
340	25.01	25.23	24.05	22.65
360	25.27	25.52	24.85	23.02
380	25.55	25.75	24.51	23.25
400	25.70	25.94	24.70	23.45

stant-volume heat capacity, C_E is the conduction-electronic contribution that includes electron-phonon renormalization effects, and C_L is the lattice contribution that can be calculated if the phonon density of states is known. The dilation contribution is $C_D = \alpha^2 KVT$, where V is the molar volume. Since the bulk modulus K was only measured at room temperature, it was necessary to approximate C_D as a function of temperature by $C_D = \alpha C_p^2 T$, where α is 1.3, 1.9, 1.7, and 1.6 g atom/MJ for V_3Sn , $V_3Ga_{0.5}Sn_{0.5}$, V_3Ga , and V_3Si , respectively. This approximation is adequate since the dilation correction is always small, i. e., <2% of C_p at room temperature.

In the low-temperature limit, C_v in the normal state can be represented by an odd power of T series. The linear term is electronic in nature and is related to the band-structure density of states at the Fermi level $N(\epsilon_F)$ and to the electron-phonon mass enhancement, λ ,

$$\lim_{T \rightarrow 0} (C_E/T) = \frac{2}{3} \pi^2 k_B^2 N(\epsilon_F) (1 + \lambda) \equiv \gamma_0 \equiv \gamma_b (1 + \lambda). \quad (2)$$

The higher terms in the expansion characterize the lattice

$$C_L = \frac{234R}{\Theta_0^3} T^3 + DT^5 + \dots, \quad (3)$$

where R is the gas constant, Θ_0 is the low-temperature Debye temperature, and D is a constant that is dependent on the phonon density of states.

To obtain γ_0 , Θ_0 , and D , the data were fitted to the three-term expansion of Eqs. (2) and (3), utiliz-

TABLE II. Superconducting transition temperature T_c , the low-temperature electronic heat-capacity coefficient γ_0 , the band-structure electronic heat-capacity coefficient $\gamma_b = \gamma_0 (1 + \lambda)^{-1}$, and the low-temperature Debye temperature Θ_0 for vanadium-base compounds.

Compounds	T_c (°K)	γ_0 (mJ/°K ² g atom)	γ_b (mJ/°K ² g atom)	Θ_0 (°K)
V_3Si	16.5	16.7	9.18	442 ± 40
V_3Ga	14.3	20.3	11.0	343 ± 30
$V_3Ga_{0.5}Sn_{0.5}$	5.6	10.2	6.30	321 ± 10
V_3Sn	3.8	7.22	4.63	318 ± 10

ing the additional constraint that normal-state and superconducting-state entropies are equal at T_c . The entropy constraint helps ensure that the electronic contribution is properly characterized, since for V_3Ga and V_3Si the electronic entropy is ~80% of the total at T_c . Although the γ_0 terms can be accurately characterized for these materials, the determinations of Θ_0 are quite uncertain because the T^3 contribution to the heat capacity (a) is small compared with the linear term in the temperature range of interest, (b) may be influenced by the temperature dependence of C_E/T (Fig. 5), and (c) may also be small with respect to higher terms in the lattice heat-capacity expansion. Testardi and Mattheiss,^{1,15} using a model acoustic phonon density of states, found that an apparent linear term in the lattice heat capacity develops in a region $T \gtrsim T_c$ for V_3Si . Since this apparent linear term will not persist to $T = 0$ °K, the entropy constraint and the inclusion of the T^5 term in the lattice heat-capacity expansion are quite necessary for a meaningful separation of terms. The low-temperature normal-state parameters γ_0 and Θ_0 are collected in Table II. Note that neither the Θ_0 nor the D values will be used in the analysis that follows. In general, the γ_0 values agree within 10% with other published determinations.¹ However, the γ_0 value for V_3Ga is somewhat low, indicating a slight Ga deficiency.¹⁶ (It has been shown that T_c and γ_0 for V_3Ga are strongly dependent on stoichiometry.¹⁶)

The constant-volume lattice entropy is given, to lowest order in the anharmonicity, by the usual harmonic expression^{7,17}

$$S_L = k_B \sum_{s=1}^{3N} [\beta \hbar \omega_s n_s + \ln(n_s + 1)], \quad (4)$$

where the phonon frequencies ω_s are now temperature dependent, $\beta = (k_B T)^{-1}$, and $n_s = [\exp(\beta \hbar \omega_s) - 1]^{-1}$. (The ω_s may now be considered quasi-normal-mode frequencies, borrowing terminology from the field of neutron inelastic scattering.) It has recently been demonstrated that Eq. (4) can also be obtained more generally by a variational approach, which is equivalent to summing perturbation theory to infinite order but omitting all diagrams that lead to a nonvanishing imaginary part of the self-energy.¹⁸

Thus, the constant-volume lattice heat capacity is given by

$$C_L = T \left(\frac{\partial S}{\partial T} \right)_v = k_B \sum_{s=1}^{3N} n_s (n_s + 1) (\beta \hbar \omega_s)^2 \left(1 - \frac{T \omega'_s}{\omega_s} \right),$$

where $\omega'_s \equiv [(\partial \omega_s)/(\partial T)]_v$. For small anharmonicity, $k_B T \sum \omega'_s / \omega_s \ll 1$, and, in the high-temperature limit,

$$C_L = 3R \left(1 - \frac{\hbar^2 \langle \omega_s^2 \rangle}{12 (k_B T)^2} \right) - k_B T \sum_{s=1}^{3N} \frac{\omega'_s}{\omega_s}, \quad (5)$$

where

$$\langle \omega_s^2 \rangle \equiv \frac{1}{3N} \sum_{s=1}^{3N} \omega_s^2.$$

Equation (5) indicates that the lattice heat capacity approaches the $3R$ classical limit with a T^{-2} temperature dependence, as in harmonic theory, and that, in addition, a linear term is associated with the anharmonicity. At the temperatures at which Eq. (5) is valid, the electronic heat capacity is approximately linear in temperature ($C_E \approx \gamma T$), and the electron-phonon renormalization effects are unimportant. (Grimvall¹⁹ and Fradin²⁰ have shown that this latter point is correct for a free-electron model and for a band shape more appropriate to V_3Ga , respectively.) Rearranging Eq. (5) and including the electronic heat capacity, we have

$$\frac{C_v - 3R}{T} = - \frac{R \hbar^2 \langle \omega_s^2 \rangle}{4 k_B^2 T^3} + (A + \gamma), \quad (6)$$

where

$$A \equiv - k_B \sum_{s=1}^{3N} \frac{\omega'_s}{\omega_s}. \quad (7)$$

In Fig. 2, $(C_v - 3R)/T$ versus T^{-3} is plotted above 0.7 of the Debye temperature for the vanadium-base compounds. The slope defines $\langle \omega_s^2 \rangle$, and the high-temperature characteristic phonon temperature is

$$\Theta_\infty = \left(\frac{5 \hbar^2 \langle \omega_s^2 \rangle}{3 k_B^2} \right)^{1/2}.$$

(Wallace²¹ has shown for many materials that values of $\langle \omega_s^2 \rangle$, determined essentially from such plots, are in agreement with the values of the second moment of the normal-mode frequencies determined

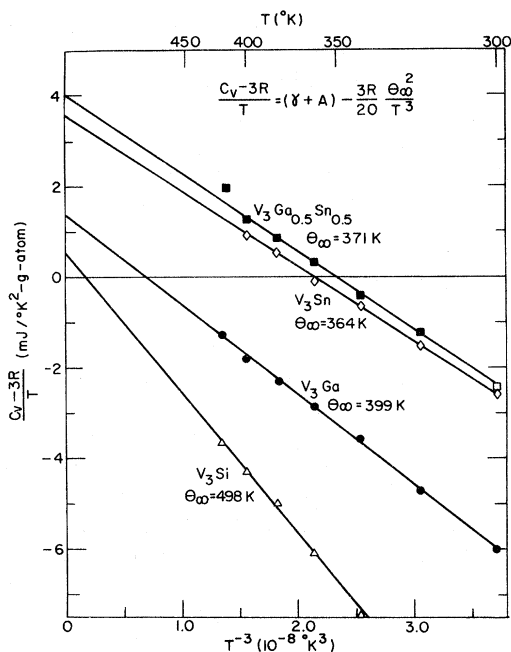


FIG. 2. Heat capacities of the indicated vanadium-base A-15 superconductors plotted as $(C_v - 3R)/T$ vs T^{-3} . The slopes provide the values of $\langle \omega_s^2 \rangle$, and hence Θ_∞ . The $T^{-3} = 0$ intercepts provide the combined electronic and anharmonic linear heat-capacity coefficients at high temperature.

by neutron inelastic-scattering measurements.) The curve labeled Debye in Fig. 1 is a harmonic-lattice heat capacity using the Debye model with Θ_∞ found graphically in Fig. 2. (The harmonic-lattice heat capacity above $\frac{1}{2}\Theta_\infty$ is not sensitive to the details of the phonon model used.) The high-temperature intercepts in Fig. 2 represent $A + \gamma$, the sum of the anharmonic and electronic contributions. Note that for V_3Ga and V_3Si these intercepts are close to zero (Fig. 2), whereas their electronic heat-capacity coefficients should be at least as large as those of V_3Sn (see, for example, Table II). In Fig. 3 C_v is plotted versus T/Θ_∞ . Note that V_3Ga and V_3Si have smaller high-temperature heat capacities than the low- T_c materials V_3Sn and $V_3Ga_{0.5}Sn_{0.5}$. This could only result from large negative anharmonic contributions to the heat capacities of the high- T_c materials.

A major problem in interpreting high-temperature heat-capacity data for metals is the decoupling of the electronic and anharmonic contributions. In the present analysis, the sum $A + \gamma$ was decoupled in two steps. (i) The low-temperature γ_b was obtained from the expression $\gamma_b = \gamma_0(1 + \lambda)^{-1}$, using λ obtained from McMillan's formula¹¹

$$T_c = \frac{\Theta}{1.45} \exp\left(-\frac{1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)}\right), \quad (8)$$

where $\Theta = \Theta_\infty$ and $\mu^* = 0.13$. (ii) The high-temperature γ was then obtained using γ_b , measured temperature dependencies of the magnetic susceptibility and T_1T (where T_1 is the ^{51}V nuclear spin-lattice relaxation time), and results of model density-of-states computations of the relative temperature dependence of the band-structure γ , Pauli susceptibility χ_p , and T_1T . At $T = 0$ K, χ_p and the band structure $\gamma = \gamma_b$ are proportional to $N(\epsilon_F)$, and $(T_1T)^{-1}$ is proportional to $N(\epsilon_F)^2$. At finite temperatures, the three quantities could be calculated if the density of states was known, since in the energy-space representation

$$\gamma = \frac{C_E}{T} - \gamma_1(T) \propto \frac{1}{T} \frac{\partial}{\partial T} \int_{-\infty}^{\infty} \epsilon N(\epsilon) f(\epsilon) d\epsilon, \quad (9)$$

$$\chi_p \propto \frac{1}{T} \int_{-\infty}^{\infty} N(\epsilon) f(\epsilon) [1 - f(\epsilon)] d\epsilon, \quad (10)$$

and

$$(T_1T)^{-1} \propto \frac{1}{T} \int_{-\infty}^{\infty} [N(\epsilon)]^2 f(\epsilon) [1 - f(\epsilon)] d\epsilon, \quad (11)$$

where $f(\epsilon)$ is the Fermi function and $\gamma_1(T)$ contains the electron-phonon many-body effects,^{19,20} which, for our purposes, can be ignored at high temperatures. The strong temperature dependence of the measured magnetic susceptibility χ for V_3Ga and

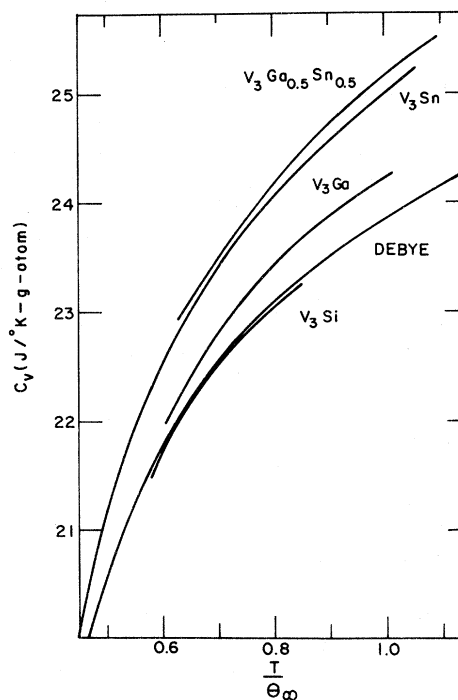


FIG. 3. Heat capacity of the indicated vanadium-base A-15 superconductors plotted as C_v vs reduced temperature T/Θ_∞ . The curve labeled Debye is a Debye lattice heat capacity.

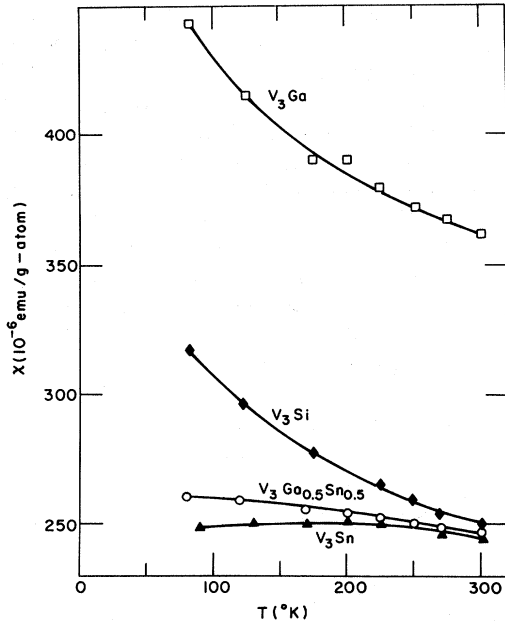


FIG. 4. Magnetic susceptibility vs temperature for the indicated vanadium-base A-15 compounds.

V_3Si (Fig. 4) indicates that γ also will be strongly temperature dependent. Of course, the measured χ cannot easily be related to χ_b , and hence γ , because of Van Vleck-type orbital paramagnetism and exchange-enhancement effects. T_1T measurements,^{9,10} however, are quite valuable for our purposes since they are independent of these effects. T_1T in these compounds is dominated by the contribution of the orbital hyperfine field due to the vanadium-derived d wave function. Because spin-orbit effects are expected to be weak, spin-coupled exchange-enhancement effects on T_1T should be negligible. Also, Kadanoff²² has shown that the electron-phonon interaction does not affect T_1T .

An example of a model calculation of $(T_1T)^{-1/2}$, γ , and χ_b that is consistent with the temperature dependence of the spin-lattice relaxation time and susceptibility of V_3Ga is shown in Fig. 5. The model of $N(\epsilon)$ in the vicinity (± 0.5 eV) of ϵ_F is given by $N(\epsilon) = N_0 \left[\frac{1}{3} + \frac{2}{3} \exp\left[-\frac{(\epsilon - \epsilon_0)^2}{(200 \text{ }^\circ\text{K})^2}\right] \right]$ for $\epsilon \geq \epsilon_0$ and $N(\epsilon) = N_0$ for $\epsilon < \epsilon_0$, where the chemical potential for $T=0$ °K, $\mu(0) = \epsilon_F = \epsilon_0$. The strong temperature dependencies, which are certainly beyond the lowest-order T^2 corrections, result both from the smearing effects of the Fermi function as temperature increases and the shift of the chemical potential with temperature, e.g., $\mu(300 \text{ }^\circ\text{K}) - \mu(0 \text{ }^\circ\text{K}) = 124 \text{ }^\circ\text{K}$. It should be noted that the model $N(\epsilon)$ is not unique, although the scale of structure in $N(\epsilon)$ near ϵ_F can be determined by this method. Other physical properties, such as the phonon-assisted interband-scattering contribution to the electrical

resistivity ρ_{s-d} , can serve as a check on the model density of states. Thus, some uncertainty exists in the temperature dependence of γ relative to that of T_1T , although, for our purposes, the bounds on γ are fairly small.

Since T_1T has been measured^{9,10} at 77 and 300 °K for all samples of interest, we chose a functional form for

$$\gamma = \frac{\gamma_b}{1 + (T/\phi)}$$

that gives the proper ratio of T_1T at these two temperatures and is, in general, consistent with the temperature dependence of χ_b based on the calculations of Eqs. (9)–(11). Numerical calculations using various model band shapes that reproduce the temperature dependencies of χ and T_1T for a given V_3X compound show that the ratio of γ at 77 and 300 °K is between 1.2 and 2.0 times the corresponding ratio of $(T_1T)^{1/2}$. Hence a range of possible ϕ values, and therefore of high-temperature γ values and anharmonic A values, exists. The values of the relevant parameters and the error limits associated with the uncertainty in ϕ can be found in Table III. Note that the γ values at high temperatures are approximately the same for the four materials, whereas the low-temperature γ_0 and γ_b values are much larger for the high- T_c compounds V_3Ga and V_3Si (see Table II).

IV. DISCUSSION

The λ values can be calculated from the McMillan expression for T_c [Eq. (8)], as mentioned previously. The accuracy of these λ values may be lim-

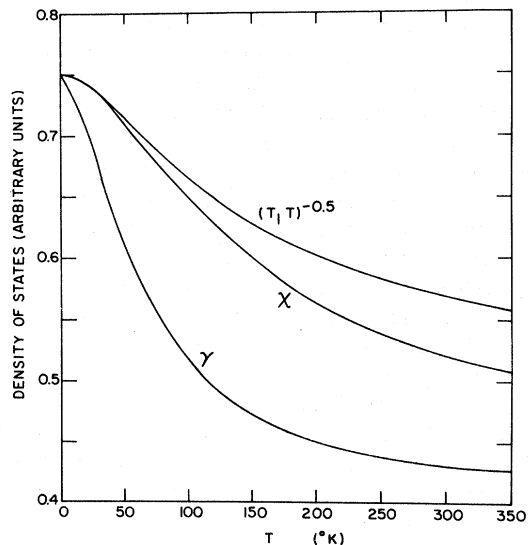


FIG. 5. Calculated temperature dependencies of the electronic heat-capacity coefficient γ , the spin susceptibility χ , and the spin-lattice relaxation time T_1 for V_3Ga .

TABLE III. Various parameters found in the high-temperature analysis of the heat-capacity data. See text for the definitions of the parameters. The γ values were evaluated at $\sim 360^\circ\text{K}$. The units of γ and A are $\text{mJ}/^\circ\text{K}^2$ g atom.

Compounds	Θ_∞ ($^\circ\text{K}$)	Φ ($^\circ\text{K}$)	γ	A
V_3Si	498	540 ± 150	5.4 ± 0.6	-4.9 ± 0.6
V_3Ga	399	390 ± 120	5.6 ± 0.6	-4.2 ± 0.9
$\text{V}_3\text{Ga}_{0.5}\text{Sn}_{0.5}$	371	4061 ± 320	5.8 ± 0.8	-1.8 ± 0.5
V_3Sn	364	5500 ± 1500	4.3 ± 0.2	-0.7 ± 0.5

ited by the simplicity of the $\mu^* = 0.13$ approximation, but it should be emphasized that they do illustrate the observed trend with T_c . The following discussion will show that this variation in λ can be calculated utilizing the phonon properties obtained from the heat-capacity measurements. McMillan has demonstrated empirically that for transition-metal alloys¹¹

$$\lambda \approx \frac{c}{M\langle\omega^2\rangle}, \quad (12)$$

where c is a constant, M is the gram atomic weight, and $\langle\omega^2\rangle$ is an average of the phonon frequencies squared at $T=0^\circ\text{K}$. [Formally, the $\langle\omega^2\rangle$ of Eq. (12) is a different average of the phonon frequencies than the $\langle\omega^2\rangle$ of Eq. (6). For the accuracy we need, we will ignore the difference.] The λ values for V_3Ga , V_3Si , and $\text{V}_3\text{Sn}_{0.5}\text{Ga}_{0.5}$ are listed in Table IV. The values in column (i) were calculated by means of Eq. (8) and in column (ii) $\lambda = c/M\langle\omega^2\rangle$, where c was fixed by the λ value for V_3Sn obtained from Eq. (8). [Using Bennemann and Garland's²³ estimates of μ^* would tend to increase the λ values in column (i) of Table IV by ~ 0.1 , but would not significantly affect the trends in λ with T_c .] Note that the values of λ found with the high-temperature $\langle\omega^2\rangle$ values are almost the same for the four materials. The $\langle\omega_s^2\rangle$ values that should have been used in Eq. (12) are those obtained from the phonon spectrum at $T=T_c$. For anharmonic materials, it is not surprising that the high-temperature second moments of the phonon frequencies do not predict the correct trend for the low-temperature λ values. The magnitudes of the high-temperature anharmonic heat-capacity coefficients for V_3Si and V_3Ga indicate substantial shifts of the phonon modes with temperature. We will now attempt to determine the effects of these shifts on the λ values in column (ii) of Table IV.

Allen and Cohen have shown¹² that λ varies with shifting phonon-mode frequencies caused by alloying, pressure, etc.,

$$\lambda_2 = \lambda_1 + [(6N)N(\epsilon_2)\Delta\epsilon]^{-1} \sum_{s=1}^{3N} \left[\left(\frac{\omega_{1s}}{\omega_{2s}} \right)^2 - 1 \right], \quad (13)$$

where λ_1 and λ_2 are the low-temperature electron-

phonon mass enhancements of materials 1 and 2 with phonon modes ω_{1s} and ω_{2s} , respectively, $N(\epsilon_2)$ is the electronic density of states at the Fermi level of material 2, and $\Delta\epsilon$ is the difference in electronic cutoff energies of materials 1 and 2. Analogously, temperature can cause phonon-mode frequencies to shift in much the same way as alloying or pressure. Therefore, if we use the high-temperature $\langle\omega_s^2\rangle$ to define $\lambda_2 = c/M\langle\omega_s^2\rangle$, we can then identify λ_1 with the $T=0$ electron-phonon mass enhancement λ . Equation (13) can now be rewritten

$$\lambda = \frac{c}{M\langle\omega_s^2\rangle} - [18Nk_B T N(\epsilon_F)]^{-1} \sum_{s=1}^{3N} \left[\left(\frac{\omega_s(0)}{\omega_s(T)} \right)^2 - 1 \right], \quad (14)$$

where $N(\epsilon_F)$ is the electronic density of states at the Fermi level and $\Delta\epsilon$ is taken to be the energy width of thermal smearing of ϵ_F which we set equal to $3kT$. To obtain λ we now need to determine the sum

$$\sum_{s=1}^{3N} \left[\left(\frac{\omega_s(0)}{\omega_s(T)} \right)^2 - 1 \right].$$

First we will make the simple assumption concerning the shift in the phonon mode frequencies with temperature:

$$\omega_s(T) = \omega_s(0) + T\omega_s', \quad (15)$$

where $\omega_s' = \partial\omega_s/\partial T$ is assumed to be independent of temperature. Substituting Eq. (15) in Eq. (14) and dropping the second-order term,

$$\lambda = \frac{c}{M\langle\omega_s^2\rangle} + [9Nk_B T N(\epsilon_F)]^{-1} T \sum_s \omega_s'. \quad (16)$$

The sum in Eq. (16) is identical to the sum in the definition of the anharmonic term, Eq. (7), and hence

$$\lambda = \frac{c}{M\langle\omega_s^2\rangle} - A[9Nk_B^2 N(\epsilon_F)]^{-1}. \quad (17)$$

The λ values calculated using Eq. (17) appear in column (iii) of Table IV. Note that these λ values, which include corrections for anharmonicity, are in better agreement with the values from the McMillan equation for T_c , [column (i)] than are those

TABLE IV. Values of the electron-phonon mass enhancement obtained from different models for the indicated vanadium-base A-15 superconductors.

Compounds	(i) λ^a	(ii) λ^b	(iii) λ^c	(iv) λ^d
V_3Si	0.82	0.46	0.60	0.8
V_3Ga	0.85	0.57	0.68	0.9
$\text{V}_3\text{Ga}_{0.5}\text{Sn}_{0.5}$	0.62	0.59	0.62	0.6
V_3Sn	0.56	0.56	0.57	0.6

^a λ obtained from Eq. (8). ^c λ obtained from Eq. (17).

^b λ obtained from Eq. (12). ^d λ obtained from Eq. (22).

which do not include anharmonic corrections [column (ii)]. However, the λ values calculated for the high- T_c materials using Eq. (17) are still considerably smaller than are those calculated from the McMillan equation. This is due to the simplicity of the approximation of Eq. (15). To obtain better agreement between the trend in λ derived from McMillan's equation and the λ values obtained from the high-temperature phonon properties, we need a more realistic appraisal of the temperature dependence of the phonon frequencies than the constant ω'_s assumption of Eq. (15). For instance, Testardi's elastic-constant measurements for V_3Si reveal that, at least in the long-wavelength limit, ω'_s is not constant over the temperature range of interest.¹

Up until now, we have made no assumptions concerning the physical origin of the shifts in the phonon-mode frequencies. A variety of models have been proposed that address themselves to this concern, and they have been reviewed elsewhere.^{1,2} These models are microscopic in that they make assumptions concerning the electronic states and/or the phonon states, and the associated coupling. In the present study, we do not require a microscopic model of the electron or phonon states. However, to proceed with the analysis, we do require a model to describe the coupling that gives rise to the temperature dependence of ω'_s . The temperature dependence of ω'_s can be obtained by examining conduction-electronic screening of the bare-ion potentials, since such screening can be a prime cause of phonon-mode shifting in metals. An increase in the screening will result in softer phonons. Since within the Thomas-Fermi model screening becomes more effective as the electronic density of states increases, the general observation that, within a given class of superconductors, T_c increases as $N(\epsilon_F)$ increases can be qualitatively understood. Fradin and Williamson recently provided quantitative verification of this general observation for the vanadium-base superconductors of interest.¹⁰ Chan and Heine have indicated that in the adiabatic approximation the linear response function of the conduction electrons $\chi_s(T)$ is the appropriate function through which the electronic screening manifests itself.²⁴ To first order in $\chi_s(T)$,

$$[\omega_s(T)]^2 = \Omega_s^2 [1 - D_s \chi_s(T)], \quad (18)$$

where the bare frequencies Ω_s are taken to be independent of temperature and the D_s are constants. Assuming $\chi_s(T) \propto \chi_0(T) \propto \chi(T)$, Eq. (18) can be rewritten

$$[\omega_s(T)]^2 = [\omega_s(0)]^2 \{1 - B_s [\chi(T) - \chi(0)]\}, \quad (19)$$

where the frequencies $\omega_s(0)$ are now recognized as the screened phonon frequencies at $T=0$ °K and the

B_s are constants. For the difference $\chi(T) - \chi(0)$, the experimental susceptibility is used. [The $\chi_s(T) \propto \chi_0(T)$ assumption requires that the Fermi surface not drastically change shape with temperature and that Kohn anomalies not be important in the appropriately averaged phonon quantity.] Using Eq. (19), Eq. (7) for the high-temperature anharmonic contribution to the heat capacity becomes

$$\frac{A}{k_B} = - \sum_s \frac{\omega'_s}{\omega_s} = \frac{1}{2} \frac{\partial \chi(T)}{\partial T} \sum_s B_s \left(\frac{\omega_s(0)}{\omega_s(T)} \right)^2, \quad (20)$$

and the second term in Eq. (14) for the change in λ with temperature becomes

$$[18Nk_B TN(\epsilon_F)]^{-1} \sum_s \left[\left(\frac{\omega_s(0)}{\omega_s(T)} \right)^2 - 1 \right] = [18Nk_B TN(\epsilon_F)]^{-1} \times [\chi(T) - \chi(0)] \sum_s B_s \left[\frac{\omega_s(0)}{\omega_s(T)} \right]^2. \quad (21)$$

Eliminating $\sum B_s [\omega_s(0)/\omega_s(T)]^2$ from Eqs. (20) and (21) and substituting into Eq. (14), we find

$$\lambda = \frac{c}{M\langle \omega_s^2 \rangle} - [9Nk_B TN(\epsilon_F)]^{-1} A \left(\frac{\chi(T) - \chi(0)}{\partial \chi / \partial T} \right). \quad (22)$$

(Note that the unknown B_s constants do not appear in Eq. (22). The only parameter is the constant c .) Using Eq. (22), λ values were calculated for the materials of interest, where the $\partial \chi / \partial T$ were evaluated at the same temperature at which the anharmonic heat-capacity coefficients were obtained (~ 300 °K). The results appear in column (iv) of Table IV. The agreement between these λ values and those derived from the McMillan equation [see column (i) of Table IV] is quite satisfactory. Given that a number of simplifying approximations were made in deriving Eq. (22), the precision with which the λ values of columns (i) and (iv) agree is perhaps fortuitous. However, we believe that the basic physics is correct; i.e., the anharmonicity A has a temperature dependence similar to $\partial \chi / \partial T$, and considerable phonon-mode softening occurs with decreasing temperature in V_3Ga and V_3Si . Although λ and A both depend on phonon modes throughout the Brillouin zone, it is interesting that the same average of the phonon shifts appears in Eqs. (20) and (21). Hence, it is unnecessary to know the details of a phonon spectrum to obtain a semiquantitative relationship between T_c and anharmonicity.

V. CONCLUSION

We have shown that the high- T_c materials V_3Ga and V_3Si have large negative anharmonic contributions to their heat capacities. The anharmonic contributions can be related to shifts in phonon-mode frequencies with temperature. By applying the theory of Allen and Cohen, a relationship between anharmonicity and T_c has been established. The unusually large change of phonon-mode frequencies

with temperature requires consideration of the influence of electronic screening on the temperature dependence of the phonon modes to establish the relationship between λ and anharmonicity, Eq. (22). For the high- T_c superconductors V_3Si and V_3Ga , the temperature dependence of the spin susceptibility γ and T_1T are caused by the thermal averaging about the Fermi energy of sharp structure in the d -band density of states. The same thermal effect on the electronic screening is a major cause of the temperature dependence of the phonon frequencies and the unusually large anharmonic heat-

capacity coefficient at high temperature. Indeed, the phonon-mode softening that occurs as temperature is lowered, which results from unusually large renormalization due to the electronic screening, is primarily responsible for the high superconducting transition temperatures of V_3Ga and V_3Si .

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