PHYSICAL REVIEW B VOLUME 14, NUMBER 7 1 OCTOBER 1976

Mössbauer study of the lattice properties of the system $V_3Ga_{1-x}Sn_x$ †

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(Received 21 October 1975)

The temperature dependence of the ^{119}Sn Mössbauer shift and the relative recoil-free fraction has been measured in the A-15 pseudobinary compounds $V_3Ga_{1-x}Sn_x$ (x = 0.9, 0.5, 0.1). A two-Debye model for the phonon spectra describes the Sn vibrational motion, $\langle v^2\rangle$ and $\langle x^2\rangle$. For $V_3Ga_{0.9}Sn_{0.1}$ a deviation of the thermal shift from Debye behavior is shown to be due to lattice softening; that is, phonon mode shifting is observed for the Ga-rich high-T_c compound. Comparison with heat-capacity results indicates that the vibrational motion of the vanadium atom also softens at low temperature. Moreover, a consideration of the concentration dependence of the Sn and Ga phonon contribution to the mass enhancement λ suggests that the vanadium site controls the dependence of λ, and hence T_c, on concentration.

I. INTRODUCTION

Binary or ternary compounds based on the A-15 (Cr_3O) crystal structure have high superconducting transition temperatures and large critical fields.[1] In the vanadium-based A-15 compounds in which one component is a nontransition element, the high values of the electron-phonon coupling parameter λ, and therefore, the high values of the superconducting transition temperature T_c are associated with large values of the electronic density of states at the Fermi level, $N(0)$, and with temperature-dependent phonon properties. The high-T_c compounds V_3Ga and V_3Si have been found to have a Fermi energy E_F that lies on a sharp edge in the electronic density of states leading to anomalous temperature dependences of the spin susceptibility, ^{51}V Knight shift and nuclear spin-lattice relaxation rate, and the electronic specific heat.[2] It has also been found that the softening of certain phonons with decreasing temperature in these compounds leads to unusual behavior of the elastic constants and the lattice heat capacity.[3,4]

A Mössbauer study has been undertaken to examine the lattice properties of high- and low-T_c superconducting compounds with the A-15 (Cr_3O) structure. The relative recoil-free fraction f, which is related to the mean-square displacement, and the thermal shift δ_{th}, which is related to the mean-square velocity of the absorbing atom, have been measured by means of the ^{119}Sn Mössbauer effect in the V_3Ga-V_3Sn system. The determination of the temperature dependence of the Sn vibrational motion in these compounds allows one to systematically study the variation of certain moments of the vibrational spectra and to contrast their behavior in high- and low-T_c compounds. A phenomenological model is used to address the question of the microscopic nature of the anharmonicity and the contribution to λ from the electron-ion interaction at the tin site.

Shier and Taylor[5] have studied the temperature dependence of the Mössbauer fraction and shift of ^{119}Sn in Nb_3Sn. From their value of the absolute recoil-free fraction they find that the Sn vibrational motion is highly anharmonic. Moreover, an anomalous temperature-dependent change in shift is observed near the temperature of the phase transition in Nb_3Sn, which they attribute to an isomer shift due to interband charge transfer. We note that the observed change in shift at low temperature in Nb_3Sn is in the direction expected on the basis of lattice softening.

Our approach will be to analyze the experimental data by means of the harmonic or quasiharmonic approximation; that is, we ignore the imaginary part of the phonon self-energy, and at any temperature, we treat the phonons as δ functions peaked at frequencies ω_q that have different values as a function of temperature. In Sec. II we briefly review the harmonic theory of the mean-square displacement and velocity. In Sec. III we describe the experimental technique and results, and make use of a two-Debye model to describe the vibrational spectra. In Sec. IV we discuss the results with respect to the macroscopic specific-heat data and the systematics of λ.

II. REVIEW OF HARMONIC THEORY

Here we follow the treatment of Housley and Hess.[6] The equations of motion can be written in the form $M\ddot{x}+Lx=0$, where M and L are the mass and atomic force-constant matrices, respectively. A unitary transformation B is made which transforms the particle coordinates x to a set of normal coordinates $y = BM^{1/2}x$. The mean-square displacement of the kth atom of mass M_k in direction j is $\langle x_{jk}^2\rangle$ and the corresponding mean-square velocity is $\langle v_{jk}^2\rangle$. It can be shown that

$$\langle v_{jk}^2\rangle = \frac{\hbar}{M_k}\sum_i \left[\tfrac{1}{2} + N(\omega_i)\right] b_{jki}^2\,\omega_i \tag{1}$$

and

$$\langle x_{jk}^2\rangle = \frac{\hbar}{M_k}\sum_i \left[\tfrac{1}{2} + N(\omega_i)\right]\frac{b_{jki}^2}{\omega_i}, \tag{2}$$

where b_{jki} is the appropriate element of B, ω_i is a normal mode (phonon) frequency, and $N(\omega_i) = (e^{\hbar\omega_i/k_BT} - 1)^{-1}$ is the Bose-Einstein distribution.

To simplify the terminology, weighted mean frequencies are defined by the relationship

$$\omega_{jk}(n) = \left(\sum_i b_{jki}^2\,\omega_i^n\right)^{1/n}. \tag{3}$$

Then, the high-temperature expansion of Eq. (1) and (2) leads to

$$\langle v_{jk}^2\rangle = \frac{k_BT}{M_k}\left[1 + \frac{1}{12}\left(\frac{\hbar}{kT}\right)^2 \omega_{jk}^2(2) - \cdots\right] \tag{4}$$

and

$$\langle x_{jk}^2\rangle = \frac{k_BT}{M_k}\left[\frac{1}{\omega_{jk}^2(-2)} + \frac{1}{12}\left(\frac{\hbar}{kT}\right)^2 - \cdots\right]. \tag{5}$$

The zero-temperature values of Eqs. (1) and (2) are

$$\langle v_{jk}^2\rangle = (\hbar/2M_k)\,\omega_{jk}(1) \tag{6}$$

and

$$\langle x_{jk}^2\rangle = (\hbar/2M_k)[1/\omega_{jk}(-1)]. \tag{7}$$

Making use of the mathematical properties of B, it can be shown that the microscopic properties can be related to the properties of the crystal as a whole,

$$\sum_{jk} M_k\langle v_{jk}^2\rangle = \sum_i \left[\tfrac{1}{2} + N(\omega_i)\right]\hbar\omega_i, \tag{8}$$

$$\sum_{jk} M_k\langle x_{jk}^2\rangle = \sum_i \left[\tfrac{1}{2} + N(\omega_i)\right](1/\hbar\omega_i), \tag{9}$$

and

$$\sum_{jk} \omega_{jk}^n(n) = \sum_i \omega_i^n = 3N\langle\omega^n\rangle, \tag{10}$$

where $3N$ is the number of degrees of freedom.

III. EXPERIMENTAL

The samples of $V_3Ga_{1-x}Sn_x$ used in this investigation were identical to those used in a nuclear-magnetic-resonance investigation.[2] They were prepared by either arc melting or levitation melting, followed by appropriate anneals. X-ray and metallographic examination indicated that the samples were at least 90% in the A-15 phase. The reported superconducting transition temperatures are for measurements on powders[2] that were also used as absorbers; T_c was measured with a calibrated Ge resistor and an induction bridge operated near 1 kHz.

The Mössbauer study requires accurate determination of the changes in absorber shift at low temperature, where changes in thermal energy are small with changing temperature. It is necessary to precisely fix the absorber temperature and to eliminate thermal drift in the source. The Mössbauer drive system, which included calibration source and absorber, and probe source, was thermally clamped to 273.56 ± 0.03 K.[7] The sample temperature was controlled to ± 0.05 K. To obtain the zero of velocity and velocity calibration, the spectrum of ^{57}Co in Fe vs Fe was measured simultaneously with the measurement of the Mössbauer parameters of the ^{119}Sn in the superconducting compounds. The probe source was $Ba^{119}SnO_3$ (15 mCi). A palladium foil of 25.4 μm thickness was used as a critical absorber. The precision of the measurements (repeatability) was ~ ± 0.002 mm/sec (three measurements over eight months). The accuracy of the measurements is lower, perhaps as large as 0.010 mm/sec because of systematic errors, e.g., histogram (finite velocity width/channel) and geometry effects. The linewidth (full width at half maximum) of a 12.7-μm natural iron absorber (99.999% pure, annealed) held in the cryostat in the same manner as the $V_3Ga_{1-x}Sn_x$ compounds was 0.201 ± 0.004 mm/sec. Typical absorption spectra are shown in Fig. 1. Mössbauer measurements were made as a function of temperature from 5 to 300 K for $V_3Ga_{0.9}Sn_{0.1}$ ($T_c \sim 11$ K), $V_3Ga_{0.5}Sn_{0.5}$ ($T_c \sim 6$ K), and $V_3Ga_{0.1}Sn_{0.9}$ ($T_c \sim 4$ K).

The A-15 structure is body-centered cubic; the V atoms (A atoms) occupy the cube faces in pairs and extend throughout the crystal in linear chains along the ⟨100⟩ directions with the chains in adjacent cube faces perpendicular to one another. The Sn and/or Ga atoms (B atoms) occupy the cube corners and cube center. Thus, the nearest neighbors of the Sn atoms are V atoms and the point symmetry at the Sn site is cubic. We note that the absorber line is somewhat broadened, however, probably due to isomer shift and nuclear-electric-quadrupole interactions that result from composition fluctuations on B sites and from defects. Nuclear magnetic resonance on the Ga nuclei indicate that the electric field gradients at the B sites are small.

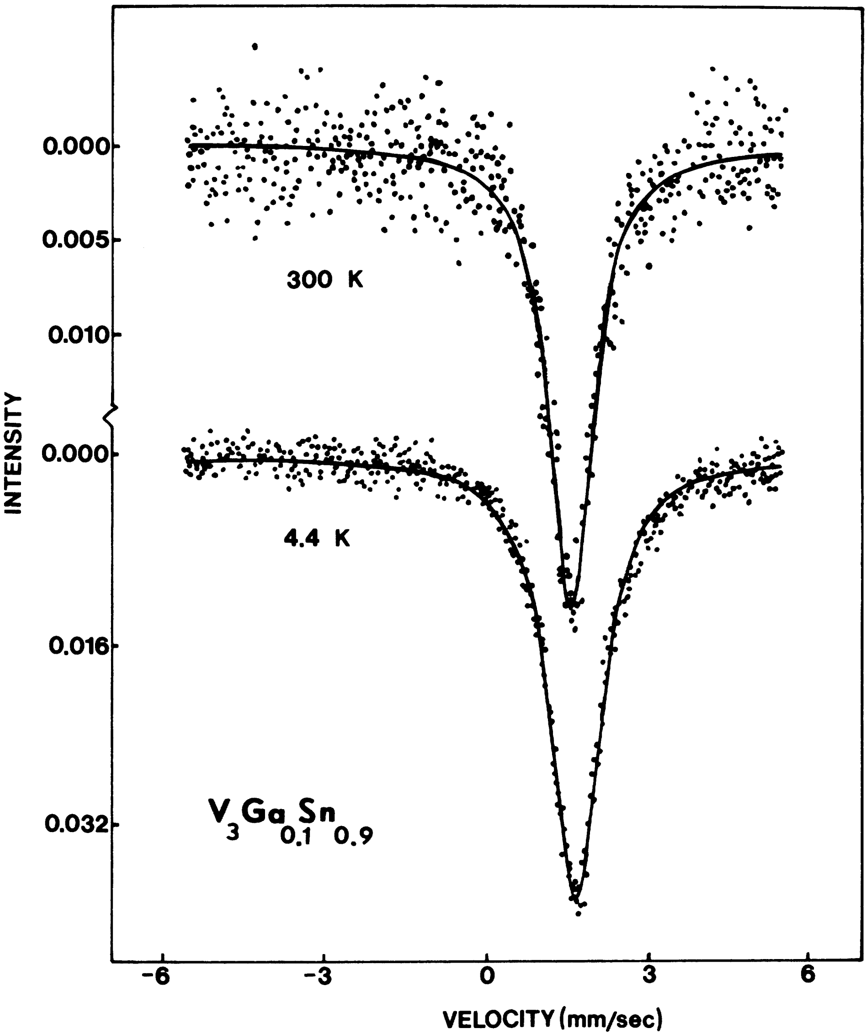

FIG. 1. Mossbauer spectra for $V_3Ga_{0.1}Sn_{0.9}$ at 4.4 and 300 K.

The shift in the centroid of the Mössbauer pattern is given by $\delta(T)=\delta_{is}(T)+\delta_{th}(T)$, where $\delta_{is}(T)$, the isomer shift, is related to the electrostatic energy between the electronic and nuclear charge and $\delta_{th}(T)$, the thermal shift, is related to the lattice energy. The electron density at the nucleus, and thus the isomer shift, changes with temperature due to thermal expansion and to changes with temperature of the character of the electrons occupying the valence states. Pressure experiments on Sn indicate that the isomer shift decreases with decreasing volume; that is, shielding effects overcome the increased electron density.[8] Below 40 K the coefficient of thermal expansion for the A-15 compounds is quite small, and at higher temperature it is positive.[9] Above 40 K, as T increases, the solid expands and the change in charge density causes an increase in isomer shift.[8] Bader and Knapp[9] have measured the coefficient of thermal expansion and the compressibility for $V_3Ga_{1-x}Sn_x$ between 80 and 300 K; using their values and the pressure dependence[8] of the ^{119}Sn shift for Sn in Pd (where the isomer shift is close to that for Sn in $V_3Ga_{1-x}Sn_x$), we estimated the changes in isomer shift to be $\Delta\delta$(0–80 K)~0.001 mm/sec, $\Delta\delta$(80–160 K)~0.001 mm/sec, and $\Delta\delta$(160–300 K)~0.002 mm/sec. These corrections are opposite in sign to the thermal shift and smaller than the statistical error in the experimental value of the shift.

We must now estimate changes in isomer shift due to changes in electron character resulting from temperature-dependent smearing at the Fermi level. An electronic density-of-states function $N(E)$, that reproduces the temperature and composition dependence of the susceptibility and spinlattice relaxation rate of ^{51}V in $V_3Ga_{1-x}Sn_x$, has been constructed (se Fig. 2).[4,10] From the

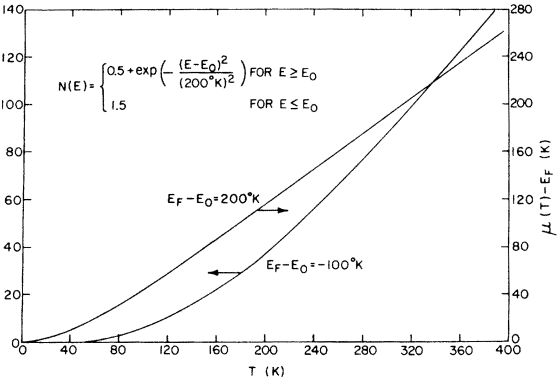

FIG. 2. Shift in the chemical potential with temperature for $V_3Ga_{0.9}Sn_{0.1}$ ($E_F-E_0=-100$ °K) and $V_3Ga_{0.5}Sn_{0.5}$ ($E_F-E_0=200$ °K). Calculations are based on model density of states $N(E)$ that yields the temperature dependence of the susceptibility and ^{51}V nuclear spin-lattice relaxation rate.

temperature-independent constraint

$$n=\int_0^\infty N(E)f(\mu,T)dE, \tag{11}$$

where n is the total number of conduction electrons in a given compound and $f(\mu,T)$ is the Fermi function, the chemical potential μ is found to increase with increasing temperature (see Fig. 2). Taking the shift at 300 K as the isomer shift and the rate of change of shift with s occupation near this value from Ruby,[11] the corrections for temperature-dependent changes in isomer shift due to changes in band occupation are obtained. At low temperature the corrections are small but increase with Sn concentration [$\Delta\delta$(10–100 K) ~ 0.0006 to 0.002 mm/sec]. At higher temperature the corrections are larger and again increase with increasing Sn concentration [$\Delta\delta$(100–300 K) ~ 0.004 to 0.008 mm/sec]. The changes of isomer shift from both thermal expansion and changing band occupation are therefore small, smoothly varying with temperature and of opposite sign to the changes due to the thermal shift.

The thermal shift is proportional to the mean-squared velocity of the Mössbauer atom

$$\delta_{th}(T)=\frac{\langle v_k^2\rangle}{2c}=\sum_j\frac{\langle v_{jk}^2\rangle}{2c}. \tag{12}$$

Using the harmonic approximation and a Debye formulation of the Sn vibrational motion,

$$\langle v_k^2\rangle=\langle v_k^2\rangle_0+\frac{9k_BT^4}{\Theta_\delta^3M_k}\int_0^{\Theta_\delta/T}\frac{x^3dx}{e^x-1}, \tag{13}$$

where

$$\langle v_k^2\rangle_0=9k_B\Theta_\delta/8M_k.$$

Note that $\delta_{th}(T)-\delta_{th}(0)$ is a measure of the change in thermal energy in the harmonic approximation and determines the Debye temperature Θ_δ. At high temperature ($T>\Theta_\delta$), $\langle v^2_k\rangle$ approaches $3k_BT/M_k$ and is independent not only of the Debye temperature but also of the thermal model of the solid. Thus, an extrapolation from high temperature ($T\sim\Theta_\delta$) to $T=0$ K allows an absolute measurement of the thermal shift.

The temperature dependence of the shift is shown for $V_3Ga_{0.1}Sn_{0.9}$ and $V_3Ga_{0.9}Sn_{0.1}$ in Figs. 3 and 4, respectively. Note, that the results reported are the averages of three independent temperature scans for each composition. For example, for $V_3Ga_{0.9}Sn_{0.1}$, the data at 78 K in the analysis are the average of three runs with values of $\delta=1.647\pm0.004$, 1.652 ± 0.003, and 1.651 ± 0.003. The solid lines are the Debye curves for a least-squares fit to Θ_δ and $\delta_{is}(0)$. The fit to the $V_3Ga_{0.9}Sn_{0.1}$ data, however, shows systematic deviation from Debye behavior.

High-T_c compounds with the A-15 structure tend to undergo lattice softening with decreasing temperature and often undergo phase transitions.[1,3] Specific-heat and susceptibility measurements for the samples used in the Mössbauer investigation do not indicate a phase transition in this system. We attribute the systematic deviation of the shift from Debye behavior at low temperature to

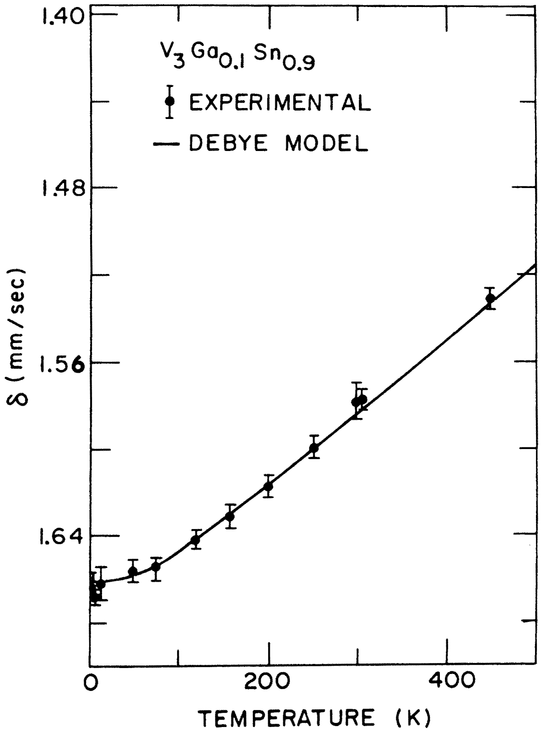

FIG. 3. Shift $\delta(T)$ vs temperature for $V_3Ga_{0.1}Sn_{0.9}$. The solid line is a Debye curve for $\langle v_k^2\rangle$ with $\Theta_\delta=174$ °K.

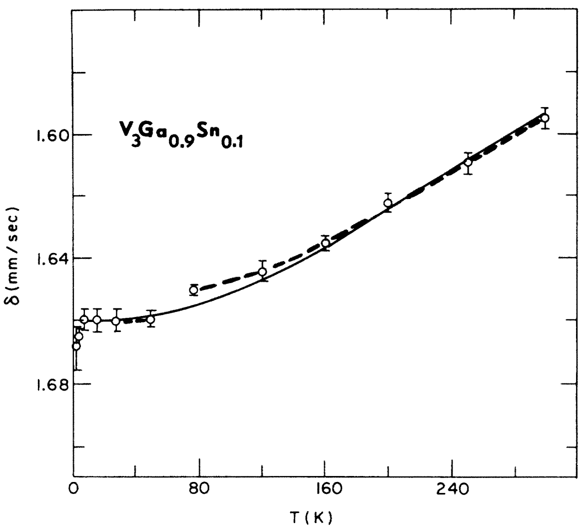

FIG. 4. Shift $\delta(T)$ vs temperature for $V_3Ga_{0.9}Sn_{0.1}$. The solid line is a Debye curve for $\langle v_k^2\rangle$ with $\Theta_\delta = 350\,°K$. The dashed line is a fit to the model shown in Figs. 8(a) and 8(b).

phonon shifting in the Ga-rich compounds. Testardi[3] has reported phonon softening in polycrystalline V_3Ga. We therefore treat the Debye temperature as temperature dependent; i.e., we treat the shift for $V_3Ga_{0.9}Sn_{0.1}$ in a quasiharmonic approximation. A family of Debye curves for Θ_δ spanning all possible values of thermal shift (normalized to 300 K) are generated. The experimental shifts are placed on this plot. The resulting temperature dependence of Θ_δ is shown in Fig. 5.

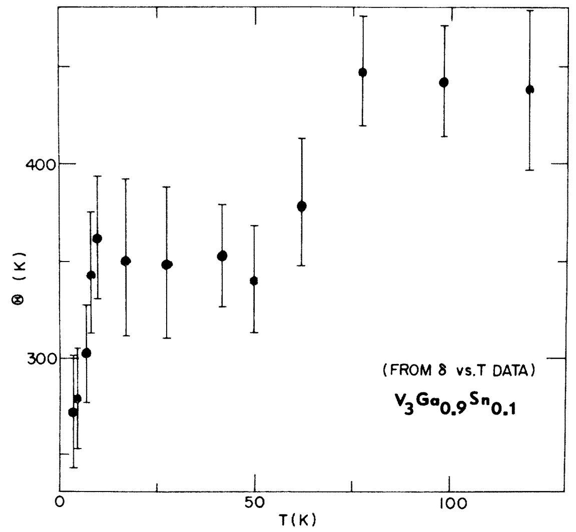

FIG. 5. Debye temperature vs temperature in quasiharmonic model from thermal shift for $V_3Ga_{0.9}Sn_{0.1}$. (This plot includes data at several temperatures for which only one run was made.)

Based on this analysis, phonon softening occurs between 50 and 80 K in the $V_3Ga_{0.9}Sn_{0.1}$ compound. We note that previous Mössbauer studies of the anharmonic nature of vibrational spectra have treated f, not $\delta_{th}(T)$, that is, $\langle x^2\rangle$, not $\langle v^2\rangle$.[12,13] Hui and Allen[14] have recently shown in a variational approach that the thermodynamic properties of strongly anharmonic systems can be calculated from a quasiharmonic model.

The area of Mössbauer absorption is related to the Debye-Waller factor in a harmonic solid,

$$-\ln A \sim -\ln f = K^2 \langle x_{jk}^2\rangle$$

where f is the Mössbauer fraction and K is 2π divided by the wavelength of the γ ray. For a Debye formulation of the Sn vibrational motion

$$\langle x_{jk}^2\rangle = \frac{\hbar^2}{M_k k_B \Theta_f}\left[\frac{1}{4} + \left(\frac{T}{\Theta_f}\right)^2 \int_0^{\Theta_f/T} \frac{x\,dx}{e^x - 1}\right] \tag{14}$$

and for $T > \Theta_f$,

$$\langle x_{jk}^2\rangle = \frac{\hbar^2}{M_k k_B}\,\frac{T}{\Theta_f^2} + \langle x_{jk}^2\rangle_0 , \tag{15}$$

where $\langle x_{jk}^2\rangle_0$ is the zero-point motion. The mean-square displacement is linear in temperature at high temperature with a slope proportional to Θ_f^{-2}. Thus, at high temperature the slope of $-\ln A$ vs T is very sensitive to the value of Θ_f. In the experiments reported here no correction has been made for background radiation. The samples are thin powders, i.e., particles of 5 μm or less laid in a monoparticular layer. Consequently, only a relative value of the Debye-Waller factor is obtained. The intensity ratio of Mössbauer spectra for 5 and 300 K is in approximately the same ratio as the harmonic recoil-free fraction, as calculated from the measured Debye temperature Θ_f.

The temperature dependence of $-\ln A$ for $V_3Ga_{0.9}Sn_{0.1}$ and $Va_3Ga_{0.1}Sn_{0.9}$ is shown in Figs. 6(a) and 6(b), respectively. The solid line is the least-squares fit to a Debye model. As is usual, Θ_f from $\langle x^2\rangle$ is different from Θ_δ for $\langle v^2\rangle$ due to the fact that these parameters are related to different moments of the tin vibrational spectral density. Therefore, to fit δ and $-\ln f$ simultaneously, a more complex spectral density than a single-Debye model is needed.

We now simulate the tin vibrational spectral density with a model which will reproduce the observed temperature dependence of $\langle v^2\rangle$ and $\langle x^2\rangle$. The model allows a simple and familiar analytical formulation of the temperature dependence of the vibrational spectra. We chose a model comprised of two Debye spectra; i.e.,

$$F(\omega) = a g_1(\omega) + (1 - a) g_2(\omega), \tag{16}$$

where, for $\omega > \omega_i$ $g_i(\omega) = 0$, and, for $\omega < \omega_i$ $g_1(\omega)$

$=9N\omega^2/\omega_1^3$, $g_2(\omega)=9N\omega^2/\omega_2^3(\omega_2>\omega_1)$, and $\int_0^{\omega_2}F(\omega)d\omega=3N$. The fraction of $3N$ modes in $g_1(\omega)$ is a; the remaining $(1-a)\,3N$ modes are in $g_2(\omega)$. The shift $\delta_{\text{th}}(T)$ and $-\ln A(T)$ are now simultaneously fitted for $\Theta_1(=\hbar\omega_1/k_B)$, $\Theta_2(=\hbar\omega_2/k_B)$, a, and the zero-temperature parameters. Figures 7(a) and 7(b) show the results for $V_3Ga_{0.1}Sn_{0.9}$ and $V_3Sn_{0.5}Ga_{0.5}$, respectively. The spectral density shown for these compounds fit the experimental data over the entire temperature range studied. Hence, any frequency shifts are small. Note, however, for $V_3Ga_{0.1}Sn_{0.9}$ that $a<0$, indicating that there is little spectral density for $\omega<2\times10^{13}$/sec.

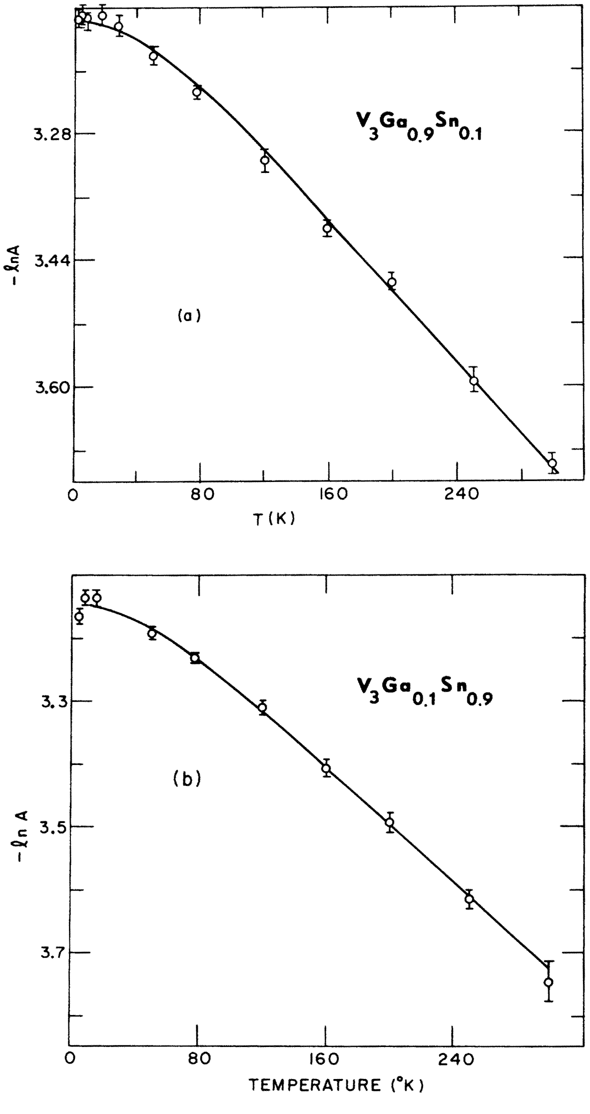

FIG. 6. (a) Temperature dependence of $-\ln A$ for $V_3Ga_{0.9}Sn_{0.1}$. The solid line is a Debye curve for $\langle x_{jk}^2\rangle$ with $\Theta_f=269$ °K. (b) Temperature dependence of $-\ln A$ for $V_3Ga_{0.1}Sn_{0.9}$. The solid line is a Debye curve for $\langle x_{jk}^2\rangle$ with $\Theta_f=264$ °K.

However, for $V_3Ga_{0.9}Sn_{0.1}$ the data for $T<50$ and $T>80$ K must be fitted separately as shown in Figs. 8(a) and 8(b), respectively; shifts in the spectral density which were indicated by the temperature dependence of Θ_6 are clearly seen for the very anharmonic high-T_c compound. Although the quantitative results in Fig. 8 are dependent on the use of the two-Debye model, the qualitative conclusion regarding the importance of anharmonicity is consistent with heat-capacity results as discussed in Sec. IV. It is interesting to note that although the average trend is toward softening as the temperature is reduced, the low-frequency Debye cutoff hardens. The Debye temperature associated with the low-frequency peak is $\Theta_1\sim6T_c$. This latter value is in the region of the maximum in the calculation of Bergmann and Rainer[15] for

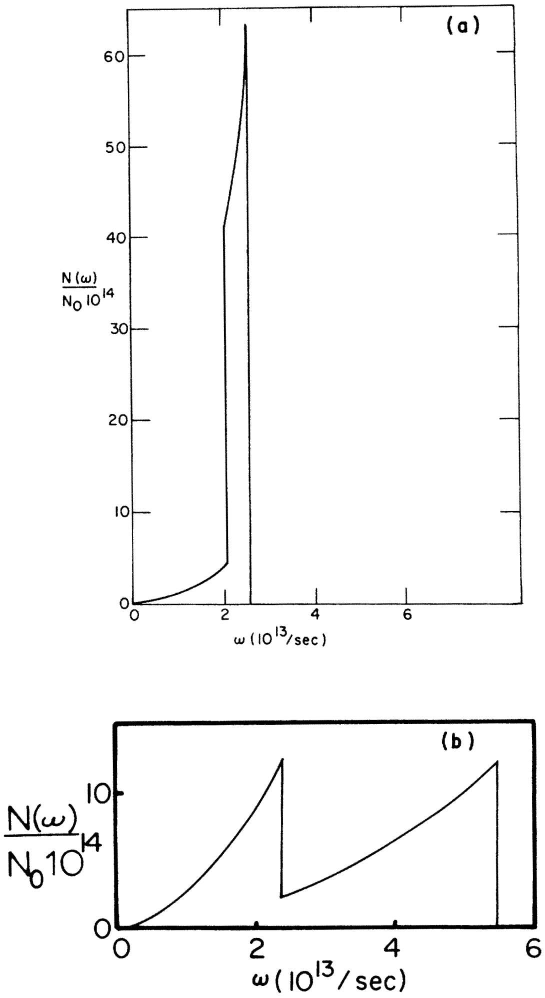

FIG. 7. Phonon spectral density from simultaneous fit to $\delta(T)$ and $-\ln A$ on basis of two-Debye model (a) $V_3Ga_{0.1}Sn_{0.9}$ with $a=-0.825$, $\Theta_1=157$ K, and $\Theta_2=197$ K; (b) $V_3Ga_{0.5}Sn_{0.5}$ with $a=0.265$, $\Theta_1=181$ K, and $\Theta_2=417$ K.

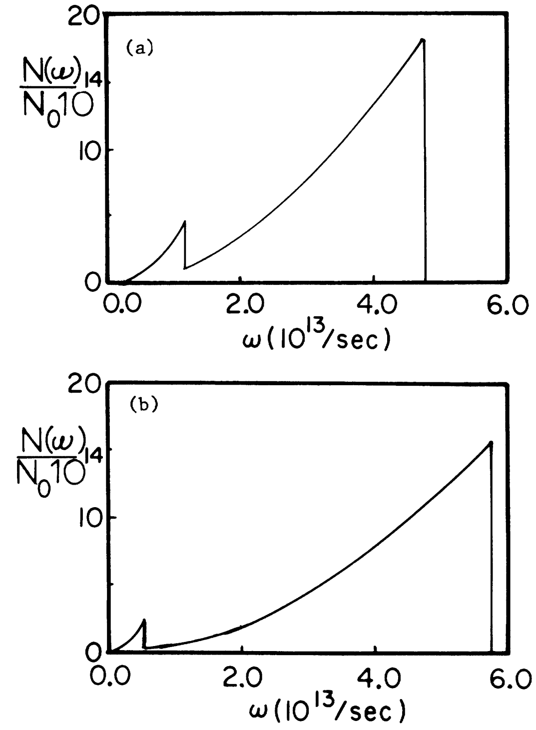

FIG. 8. Phonon spectral density from simultaneous fit to $\delta(T)$ and $-\ln A$ on the basis of two-Debye model for $V_3Ga_{0.9}Sn_{0.1}$ for (a) $T < 50$ K, $a = 0.045$, $\Theta_1 = 90$ K, and $\Theta_2 = 364$ K; (b) $T > 50$ K with $a = 0.014$, $\Theta_1 = 43$ K, and $\Theta_2 = 437$ K.

$\delta T_c / \delta[\alpha^2(\omega)F(\omega)]$ vs ω/T_c, where $\alpha^2(\omega)$ is the electron-ion coupling strength. That is, the low-frequency tin vibrations have moved into a region where their impact on T_c is optimized.

IV. DISCUSSION

The relationship of the atomic motion of the tin atoms to that of the crystal as a whole must be addressed: further, the questions of the microscopic source of the phonon frequency shifts and the contributions to the variation in λ with composition discussed. First, we calculate the second moment for the Sn atom and compare it to the macroscopic second moment derived from the approach of the lattice heat capacity to the classical $3R$ high-temperature limit. Housley and Hess[6] show that $\omega_{jk}(2)$ is proportional to $M_k^{-1/2}$, independent of the other masses, and proportional to the force constant $\phi_{jkjk}^{1/2}$, independent of the other force constants. Here ϕ_{jkjk} is the force constant obtained if only the kth atom is displaced in the jth direction, all other atoms being held fixed. Since in the vanadium-gallium-tin ternary $V_3Ga_{1-x}Sn_x$, the microscopic results $\omega_{jk}(2)$ are obtained only for tin, we will assume $\omega_{jk}(2)$ for the Ga scales as

$$\omega_{j\mathrm{Ga}}(2) = \omega_{j\mathrm{Sn}}(2)(M_{\mathrm{Sn}}/M_{\mathrm{Ga}})^{1/2}, \qquad (17)$$

i.e., the same average value of ϕ_{jkjk} is assumed for the Ga and Sn randomly placed on the bcc sublattice. Then in temperature units we calculate from Eq. (10),

$$3\Theta_V(2)^2 + [(1-x)M_{\mathrm{Sn}}/M_{\mathrm{Ga}} + x]\Theta_{\mathrm{Sn}}(2)^2 = 4\Theta_\infty(2)^2, \qquad (18)$$

where x is the atomic fraction of Sn on the bcc sub-sublattice and $\Theta_\infty(2)$ is the second moment from high-temperature heat capacity.[4] Note, for a Debye model $\omega_{jk}(n) = [3/(n+3)]^{1/n} k_B \Theta_{jk}(n)/\hbar$. The results of this calculation are listed in Table I. Note that the Ga-rich, high-T_c compound has the largest value of $\Theta_{\mathrm{Sn}}(2)$ and the smallest value calculated for $\Theta_V(2)$.

Following McMillan,[16] the electron mass renormalization is given by

$$\lambda = 2\int d\omega\, \omega^{-1}\alpha^2(\omega)F(\omega) = \frac{N(0)<I^2>}{M<\omega^2>}, \qquad (19)$$

where $\langle I^2 \rangle$ is a double average over the Fermi surface of the electron-ion matrix element, $N(0)$ is the electronic density of states at the Fermi level, M is the ion mass, and $\langle \omega^2 \rangle$ is given by

$$\begin{aligned}\langle \omega^2 \rangle &= \int d\omega\, \omega\alpha^2(\omega)F(\omega) \Big/ \int d\omega\, \omega^{-1}\alpha^2(\omega)F(\omega) \\ &\cong \int d\omega\, \omega F(\omega) \Big/ \int d\omega\, \omega^{-1}F(\omega) \\ &\simeq \omega(1)\omega(-1). \qquad (20)\end{aligned}$$

McMillan showed that the numerator in Eq. (19) is roughly constant for transition metals and alloys, and the controlling factor is the denominator which depends on the variation in phonon properties

The moments obtained from the Mössbauer measurements are averages over $F(\omega)$ and not over $\alpha^2(\omega)F(\omega)$. However, we will follow McMillan's[16] assumption that $\alpha^2(\omega)$ is almost frequency

TABLE I. High-temperature second moments and low-temperature phonon contributions to λ.

Composition	$\Theta_\infty(2)$ (K)	$\Theta_{\mathrm{Sn}}(2)$ (K)	$\Theta_V(2)$ (K)	$[\Theta_{\mathrm{Sn}}(1)\Theta_{\mathrm{Sn}}(-1)\overline{M}]^{-1}$ (10^{-7} g^{-1} K^{-2})
$V_3Ga_{0.1}Sn_{0.9}$	364[a]	225	398	2.39
$V_3Ga_{0.5}Sn_{0.5}$	371[b]	369	349	1.87
$V_3Ga_{0.9}Sn_{0.1}$	399[c]	433[d]	332	0.81[e]

[a] Value for V_3Ga from Ref. 4.
[b] Reference 4.
[c] Value for V_3Sn from Ref. 4.
[d] High-temperature value.
[e] Low-temperature value.

independent. There are plausible arguments on physical grounds for adopting this assumption for the A-15 compounds. Neutron inelastic scattering and tunneling measurements on Pb, a three-dimensional soft-phonon system, indicate that the frequency dependence of $\alpha^2(\omega)F(\omega)$ and $F(\omega)$ are similar.[17] In lower-dimensional solids larger differences between $\alpha^2F(\omega)$ and $F(\omega)$ are expected. However, on the basis of neutron-inelastic-scattering results in the high-T_c A-15 compound Nb_3Sn, the dispersion relations for the transverse acoustic branch shows phonon softening over a large range of q; this behavior is not typical of a Kohn anomaly, nor of the expectations for a low-dimensional solid.

For compounds in which the ionic mass ratios are substantial, the partition of λ suggested by Phillips,[18] Gomersal and Gyorffy,[19] and Klein and Papaconstantopoulos[20] is useful; that is, λ is written as the sum from the various atomic species

$$\lambda = \sum_k \frac{N(0)_k\langle I^2\rangle_k}{M_k\langle\omega^2\rangle_k}. \tag{21}$$

We will employ this approximation even though the mass ratios in the $V_3Ga_{1-x}Sn_x$ compounds are not large. We now evaluate $\langle\omega^2\rangle_k = \omega(1)_k\omega(-1)_k$. Housley and Hess demonstrate that $\omega_{jk}(1)$ and $\omega_{jk}(-1)$ scale approximately as $M_k^{-1/2}$, roughly independent of the other masses. Also they show that $\omega_{jk}(1)$ approximately depends only on ϕ_{jkjk}, independent of the other force constants. We assume for the Ga and Sn randomly placed on the bcc sublattice in the A-15 structure that $\omega_{jk}(1)$ and $\omega_{jk}(-1)$ scale simply as $M^{-1/2}$; i.e., the same average force constants apply. Thus, the contribution of the Ga and Sn to λ is simply proportional to

$$\frac{1}{[\Theta_{Sn}(1)\Theta_{Sn}(-1)]\overline{M}} = \frac{xM_{Sn} + (1-x)M_{Ga}}{[\Theta_{Sn}(1)\Theta_{Sn}(-1)]M_{Ga}M_{Sn}}, \tag{22}$$

where x is the atom fraction of Sn, $\omega_{Sn}(1)\omega_{Sn}(-1)$ is expressed in temperature units, and we have assumed the same numerators in Eq. (21). The values of $\{[\Theta_{Sn}(1)\Theta_{Sn}(-1)]\overline{M}\}^{-1}$ are listed in Table I. We note that although λ calculated from McMillan's equation for T_c increases monotonically with increasing Ga concentration, that $\{[\Theta_{Sn}(1)\Theta_{Sn}(-1)]\overline{M}\}^{-1}$, as well as $[\Theta_{Sn}(1)\Theta_{Sn}(-1)]^{-1}$, decreases with increasing Ga concentration. Assuming in Eq. (21) that the terms in the numerator involving the non-transition elements are roughly independent of Ga concentration, our results indicate that the variation of λ, and therefore of T_c, with composition is not controlled by the B-site vibrational contribution to λ. Thus, the systematics of λ must be controlled either by the electronic factors in λ or by the vibrational motion of the vanadium atoms or both.

A useful measure of the anharmonicity, or the change in phonon frequencies with temperature, is the logarithmic temperature derivative over the phonon spectrum

$$\mathcal{A} = -k_B\frac{d}{dT}\sum_i \ln\omega_i. \tag{23}$$

The high-temperature heat capacity of V_3Ga has been analyzed using the quasiharmonic formulation,[4]

$$C_v = 3R\left(1 - \frac{\hbar^2}{12k_B^2}\frac{\langle\omega_i^2\rangle}{T^2}\right) - \mathcal{A}T \tag{24}$$

to yield a value of $\mathcal{A} = -4.2(9)\,\mathrm{mJ/K^2}$ g-atom. To get an order of magnitude comparison, we define an average value of $\mathcal{A}_{Sn}$ for the $V_3Ga_{0.9}Sn_{0.1}$ sample over the 50–350 K temperature range:

$$\mathcal{A}_{Sn} \equiv -Nk_B\left(\Delta\sum_j \ln\omega_{j\,Sn}\Big/\Delta T\right). \tag{25}$$

We calculate from our two-Debye model phonon spectra

$$\Delta\sum_j \ln\omega_{j\,Sn} = \sum_j \ln\omega_{j\,Sn,\ \text{high temp}} - \sum_j \ln\omega_{j\,Sn,\ \text{low temp}} = 0.224$$

for the $V_3Ga_{0.9}Sn_{0.1}$ sample, and find a value $\mathcal{A}_{Sn} = -6.20\ \mathrm{mJ/K^2}$ g-atom. The sign of $\mathcal{A}_{Sn}$ indicates that the logarithmic average of the Sn vibrational motion softens as temperature is decreased. Since

$$\omega_{\ln} = \exp\left(\sum_i \ln\omega_i\right) = \lim_{n\to 0}\left(\sum_i \omega_i^n\right)^{1/n},$$

we can make use of Eq. (10) and write

$$\mathcal{A}(\omega_i) = \sum_k \mathcal{A}(\omega_{jk}). \tag{26}$$

Thus, if we assume the same logarithmic change of phonon frequencies for the Sn and Ga atoms on the bcc sites, we have for the average value of $\mathcal{A}$ between 50 and 350 K for the $V_3Ga_{0.9}Sn_{0.1}$

$$\mathcal{A}(\omega_i) = \tfrac{1}{4}\mathcal{A}_{Sn} + \tfrac{3}{4}\mathcal{A}_V, \tag{27}$$

which leads to

$$-4.2 \lesssim \tfrac{1}{4}(-6.2) + \tfrac{3}{4}\mathcal{A}_V,$$

where we have taken $\mathcal{A}(\omega_i)$ equal to the high-temperature heat-capacity value of $\mathcal{A}$ for V_3Ga. The inequality indicates our expectation that the anharmonicity is less in $V_3Ga_{0.9}Sn_{0.1}$ than in V_3Ga. We, therefore, find

$$\mathcal{A}_V \gtrsim -3.5\ \mathrm{mJ/K^2}\text{ g-atom}.$$

That is, we find the vanadium anharmonicity to be of the same sign and approximately the same magnitude as that of the tin. Thus, our picture of the high-T_c $V_3Ga_{1-x}Sn_x$ compounds, based on the phenomenological treatment, is one in which the vibrations of both the vanadium and the nontransition element atoms soften as temperature is lowered, but the dominant contribution to λ is due to the electron-ion interaction at the vanadium site.

V. CONCLUSIONS

The temperature dependence of the ^{119}Sn thermal shift and recoil-free fraction has been studied in the pseudobinary superconductors $V_3Ga_{1-x}Sn_x$. The Sn vibrational motion, $\langle v^2 \rangle$ and $\langle x^2 \rangle$, can be described by a simple two-Debye model for the phonon spectra. The Sn motion in the higher T_c, Ga-rich compound, softens at low temperature indicating phonon-mode shifting with temperature. A phenomenological comparison of the Mössbauer results with heat-capacity results on V_3Ga indithat the vibrational motion of the vanadium atom must soften at low temperature. Consideration of the Sn(Ga) vibrational contribution to the mass enhancement λ with varying concentration suggests that the vanadium site controls the dependence of λ, and hence T_c, on concentration.

ACKNOWLEDGMENTS

It is a pleasure to thank B. Dunlap and G. S. Knapp for many interesting and helpful discussions and G. Van Landuyt and S. P. Taneja for technical assistance.

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†Based on work performed under the auspices of the National Science Foundation and the Energy Research Development Administration (ERDA).

*Part of this work was submitted in partial fulfillment of the requirements for the Master of Science in Physics at Northern Illinois University.

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[1] M. Weger and I. B. Goldberg, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1973), Vol. 28, pp. 2–178.

[2] F. Y. Fradin and D. Zamir, Phys. Rev. B 7, 4861 (1973).

[3] L. R. Testardi, Rev. Mod. Phys. 47, 637 (1975).

[4] G. S. Knapp, S. D. Bader, H. V. Culbert, F. Y. Fradin, and T. E. Klippert, Phys. Rev. B 11, 4331 (1975).

[5] J. S. Shier and R. D. Taylor, Phys. Rev. 174, 346 (1968).

[6] R. M. Housley and F. Hess, Phys. Rev. 146, 417 (1966).

[7] C. W. Kimball, S. P. Taneja, L. Weber, and F. Y. Fradin, in *Mössbauer Effect Methodology*, edited by I. J. Gruverman, C. W. Seidel, and D. K. Dieterly (Plenum, New York, 1974), Vol. 9, pp. 93–112.

[8] H. S. Möller and R. L. Mössbauer, Phys. Lett. 24A, 416 (1967).

[9] S. D. Bader and G. S. Knapp (unpublished).

[10] F. Y. Fradin and J. D. Williamson, Phys. Rev. B 10, 2803 (1974).

[11] S. L. Ruby, in *Mössbauer Effect Methodology*, edited by I. Gruverman (Plenum, New York, 1967), Vol. 3, p. 203.

[12] R. H. Nussbaum, D. G. Howard, W. L. Nees, and C. F. Steen, Phys. Rev. 173, 653 (1968); J. G. Dash, D. P. Johnson, and V. M. Visscher, *ibid.* 168, 1087 (1968).

[13] A. A. Maradudin, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1966), Vol. 19, p. 2.

[14] J. C. Hui and P. B. Allen, J. Phys. C 8, 2923 (1975).

[15] G. Bergmann and D. Rainer, Z. Phys. 263, 59 (1973).

[16] W. L. McMillan, Phys. Rev. 167, 331 (1968).

[17] J. M. Rowell and R. C. Dynes, in *Phonons*, edited by M. A. Nusimovici (Flammarion, Paris, 1971), p. 150.

[18] J. C. Phillips, AIP Conf. Proc. 4, 339 (1972).

[19] I. R. Gomersall and B. L. Gyorffy, J. Phys. F 3, L-138 (1973).

[20] B. M. Klein and D. A. Papaconstantopoulos, Phys. Rev. Lett. 32, 1193 (1974).