

## Relationship between $T_c$ and $N(0)$ : An NMR study of $V_3Ga_{1-x}Si_x$ <sup>†</sup>

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From the measured normal-state values of the  $^{51}V$  spin-lattice relaxation rate and nuclear-electric-quadrupole interaction in  $V_3Ga_{1-x}Si_x$ , we have determined the bare electronic density of states at the Fermi level,  $N(0)$ , using a tight-binding formalism. In the high- $T_c$  compositions,  $N(0)$  is dominated by the  $\pi$ -symmetry  $d$  subband that can be thought of as a narrow virtually localized state on the vanadium atoms (half-width  $\approx 20$  mRy) which is broadened by compositional fluctuations. It is found that the superconducting transition temperature normalized by the Debye temperature ( $T_c/\Theta_D$ ) for the  $V_3Ga_{1-x}Si_x$  and  $V_3Ga_{1-x}Sn_x$  compounds is a universal function of  $N(0)$ . The relationship between the mass renormalization  $\lambda$  and  $N(0)$  is considered in terms of the renormalization of the phonon frequencies due to electronic screening.

### I. INTRODUCTION

In recent years the numerical relationship of the superconducting transition temperature  $T_c$  to the Debye temperature  $\Theta_D$ , the electron mass renormalization  $\lambda$ , and the Coulomb pseudopotential  $\mu^*$  has been developed for many transition-metal systems.<sup>1,2</sup> Because  $\mu^*$  is a slow function of the bare density of states at the Fermi level,  $N(0)$ , with values between 0.1 and 0.2 for most transition metals,<sup>2</sup> attention has been brought to bear on the systematics of  $\lambda$ . McMillan<sup>1</sup> formulated an approximate expression for  $\lambda$  in terms of both the electron and phonon properties,

$$\lambda \approx \frac{N(0)\langle I^2 \rangle}{M\langle \omega \rangle / \langle \omega^{-1} \rangle},$$

where  $\langle I^2 \rangle$  is the double average over the Fermi surface of the squared electron-ion scattering matrix,  $M$  is the ion mass, and  $\langle \omega^m \rangle$  is the  $m$ th moment of the phonon spectrum. Based on experimental results for transition metals and alloys, McMillan<sup>1</sup> argued that  $N(0)\langle I^2 \rangle$  is roughly constant, and thus the details of the phonon spectrum dominate the variation of  $\lambda$ .

In high- $T_c$  transition-metal compounds such as  $V_3Ga$  and  $V_3Si$  of the  $A15$  ( $Cr_3O$ -type) structure, soft phonon modes and anharmonic behavior of the lattice modes are thought to play an important role in superconductivity.<sup>3</sup> In the high- $T_c$   $A15$  compounds  $V_3X$  and  $Nb_3X$ , an extremely high narrow peak in the density of electronic states near the Fermi level has also been postulated.<sup>4</sup> Since strongly coupled ( $\lambda \approx 1$ ) systems that are anharmonic can be expected to have finite phonon lifetimes, electron dressing of the phonons is thought to be quite important.<sup>5</sup>

In the  $A15$  structure, the vanadium atoms are situated on orthogonal linear chains on the cube faces. The first band calculations were simple one-dimensional tight-binding calculations that ig-

nored overlap between chains. The dominant feature is very high narrow peaks in the density of states.<sup>4</sup> Later, Mattheiss<sup>6</sup> used the augmented-plane-wave (APW) method to calculate the band structure of a number of  $V_3X$  compounds. He showed that large differences from the linear-chain model exist. He also noted that for  $X$ , a nontransition element, a rigid-band picture was fairly good. More recently, Goldberg and Weger<sup>7</sup> have used a tight-binding calculation to extend the high-symmetry-point calculations of Mattheiss to many more points in the Brillouin zone. They have also calculated the four  $d$ -subband densities of states for  $V_3Ga$ .

In a previous nuclear-magnetic-resonance (NMR) study of the pseudobinary compounds  $V_3Ga-V_3Sn$ , Fradin and Zamir<sup>8</sup> (hereafter referred to as FZ) found a correlation between the superconducting transition temperature  $T_c$  and the unrenormalized density of states at the Fermi level in the  $\pi$  subband,  $N^*(0)$ . The bare  $d$ -subband densities of states, determined from the spin-lattice relaxation rate and the electric field gradient (efg) at the  $^{51}V$  nucleus in the normal state, were found to be in qualitative agreement with the tight-binding band-structure calculations of Goldberg and Weger.<sup>7</sup> A rigid-band picture was assumed in comparing the experimentally determined values with the theoretical calculation for  $V_3Ga$ ; i.e., it was assumed that a Sn atom contributed one more electron to the conduction band than did a Ga atom.

The  $T_c$  value drops monotonically with increasing Sn concentration in the  $V_3Ga_{1-x}Sn_x$  compounds from a high of about 15 °K to a low of about 4 °K at  $V_3Sn$ . Although Si and Sn are in the same column in the Periodic Table,  $V_3Si$  has a value of  $T_c$  near 17 °K. On the basis of the Mattheiss<sup>6</sup> APW calculation, some indication exists that the band structure of  $V_3Si$  is more similar to  $V_3Ga$  than to  $V_3Sn$ . Considerable controversy exists concerning the composition dependence of  $T_c$  in  $V_3Ga_{1-x}Si_x$ . Deaton

TABLE I. Irreducible representation of  $D_{2d}$  ( $l=2$ ).

Bases	Assignment	Atomic functions	Spherical <sup>a</sup> harmonics
$A_1$	$\sigma_x$	$(5/4\pi)^{1/2}(3z^2 - r^2)/2r^2$	$Y_2^0$
$E$	$\pi_{1x}$	$(15/4\pi)^{1/2}zx/r^2$	$Y_2^{1,c}$
$E$	$\pi_{2x}$	$(15/4\pi)^{1/2}zy/r^2$	$Y_2^{1,s}$
$B_1$	$\delta_{1x}$	$(15/16\pi)^{1/2}(x^2 - y^2)/r^2$	$Y_2^{2,c}$
$B_2$	$\delta_{2x}$	$(15/4\pi)^{1/2}xy/r^2$	$Y_2^{2,s}$

<sup>a</sup> $Y_1^{m,c} \equiv (Y_1^m + Y_1^{-m})/\sqrt{2}$ ;  $Y_1^{m,s} = -i(Y_1^m - Y_1^{-m})/\sqrt{2}$ ;  $Y_l^m(\theta, \phi)$  are normalized spherical harmonics. The polar angle  $\theta$  is measured with respect to a  $z$  axis parallel to the tetragonal or chain axis.

and Gordon<sup>9</sup> reported increases to 18.6 °K in  $T_c$  measured resistively at intermediate  $x$  in  $V_3Ga_{1-x}Si_x$ . However, Otto<sup>10</sup> and Matthias and co-workers<sup>11</sup> found  $T_c$  dropped to below 12 °K at intermediate values of  $x$ . Values of  $T_c$  measured both on our samples and a sample obtained from Deaton and Gordon are consistent with a drop in  $T_c$  at intermediate  $x$ .

In the present NMR investigation of  $^{51}V$  in  $V_3Ga_{1-x}Si_x$ , we find that  $T_c$  again correlates with  $N^*(0)$ . In fact, the main variation with  $x$  is a broadening of the  $d$  subband at intermediate  $x$  with attendant drop in  $N^*(0)$ . The variation is discussed in terms of a Friedel-Anderson type of localized model. The resonance results for  $V_3Ga_{1-x}Sn_x$  and  $V_3Ga_{1-x}Si_x$  taken together show that  $(T_c/\Theta_D)$  is a universal functional of the bare density of states at the Fermi level.

In Sec. II, we review the theoretical background necessary for the interpretation of the  $^{51}V$  spin-lattice relaxation rate  $1/T_1$  and electric field gradient  $q$ . In Sec. III, the experimental procedure is described, and the results are presented and discussed in Sec. IV. Section V contains a discussion of a model detailing the role of the density of states at the Fermi level on the renormalization of the phonon frequencies and the resulting effect on the superconducting transition temperature.

## II. REVIEW OF THEORY

The  $A15$  ( $Cr_3O$ ) structure in which the  $V_3X$  compounds crystallize is a cubic lattice with the  $X$  atoms on a body-centered-cubic sublattice. We focus attention on the  $V$  sites that have tetragonal symmetry. The point group is  $D_{2d}(\bar{4}2m)$ , and the vanadium atoms lie on chains arranged in three orthogonal families. In Table I we list the irreducible representation of the  $d$  wave functions ( $l=2$ ) for a vanadium atom on a chain with axis parallel to the  $\bar{z}$  direction.

The important contributions to the observed re-

laxation rates in transition metals arise from core-polarization<sup>12</sup> and orbital<sup>13</sup> hyperfine interactions with the  $d$  component of the conduction-electron wave function at the Fermi level, as well as from the contact<sup>14</sup> hyperfine interaction with the  $s$  component. Conduction-electron contributions associated with magnetic dipole and electric quadrupole<sup>15</sup> hyperfine interactions are usually quite small. FZ<sup>8</sup> discussed the strong dependence of the various contributions to the spin-lattice relaxation rate on the point-group symmetry properties of the  $d$  component of the conduction-electron wave function, i. e., the ratio of the  $A_1$ ,  $E$ ,  $B_1$ , and  $B_2$  orbital admixtures, in tetragonal symmetry.

In the absence of  $s$ - $d$  mixing, spin-orbit coupling, and Coulomb enhancement effects, the spin-lattice relaxation rate  $R = (T_1 T)^{-1}$  in tight binding can be expressed as<sup>8</sup>

$$R = \frac{4\pi}{\hbar} (\gamma_n \hbar)^2 k_B [N(0)^2] \sum_i P_i^2 (K_i^{(1)} + K_i^{(2)} \sin^2 \theta), \quad (1)$$

where  $\gamma_n$  is the nuclear gyromagnetic ratio,  $k_B$  is the Boltzmann constant, and  $N(0)$  is the bare density of states at the Fermi level for *one* direction of spin. The sum is over the three hyperfine interactions:  $s$ -contact  $P_s = \rho H_{\text{hf}s}^s$ ,  $d$ -spin core polarization  $P_d = (1 - \rho) H_{\text{hf}s}^d$ , and  $d$ -orbital  $P_{\text{orb}} = (1 - \rho) H_{\text{hf}s}^{\text{orb}}$ . Here  $\rho$  is the average fractional  $s$  character at the Fermi level:

$$\rho = N_s(0)/N(0);$$

$\theta$  is the angle between the tetragonal axis and the applied field, and

$$\begin{aligned} K_s^{(1)} &= 1, \quad K_s^{(2)} = 0, \\ K_d^{(1)} &= (F^{A_1})^2 + \frac{1}{2}(F^E)^2 + (F^{B_1})^2 + (F^{B_2})^2, \\ K_d^{(2)} &= 0, \quad K_{\text{orb}}^{(1)} = 2F^E(F^{B_2} + F^{B_1} + 6F^{A_1}), \\ K_{\text{orb}}^{(2)} &= -F^E(F^{B_2} + F^{B_1} + 6F^{A_1} - \frac{1}{4}F^E). \end{aligned} \quad (2)$$

Summing over the three orthogonal vanadium chains in the cubic  $A15$  structure, we find the  $\theta$ -independent orbital reduction factor

$$K_{\text{orb}} = \frac{4}{3}F^E(F^{B_2} + F^{B_1} + 6F^{A_1} + \frac{1}{3}F^E), \quad (3)$$

with

$$F^{A_1} + 2F^E + F^{B_1} + F^{B_2} = 1. \quad (4)$$

The  $F^{\Gamma(m)}$  terms are the average values of the fractional admixture coefficients at the Fermi level that have the same value for all  $m$ , which form a basis for a given irreducible representation  $\Gamma(m)$ ,

$$F^{\Gamma(m)} = \sum_{\mu} \sum_k |C_{\mu m k}|^2 [\delta(E_{\mu k} - E_F)] [N(0)N]^{-1}, \quad (5)$$

where the  $C_{\mu m k}$  terms are the fractional admixture coefficients,  $E_{\mu k}$  is the energy of the electron with band index  $\mu$  and wave vector  $k$ ,  $E_F$  is the Fermi energy, and  $N(0)N$  is the total number of states per

unit energy interval at the Fermi level for *one* direction of spin.

If the  $A_1$  functions are expressed as linear combinations of the form  $\xi_{\mu\mathbf{k}} Y_0^0 + (1 - \xi_{\mu\mathbf{k}}^2)^{1/2} Y_2^0$ , the  $s$ - $d$  interference term is given by<sup>8</sup>

$$R_{s-d} = (8\pi/\hbar)(\gamma_n \hbar)^2 [N(0)]^2 H_{\text{hfs}}^{(s)} H_{\text{hfs}}^{(d)} \times \langle \langle (F_{\mu\mathbf{k}}^{A_1})^2 \xi_{\mu\mathbf{k}}^2 (1 - \xi_{\mu\mathbf{k}}^2) \rangle \rangle, \quad (6)$$

where the angular brackets denote an average over the Fermi surface. Since  $H_{\text{hfs}}^{(s)}$  and  $H_{\text{hfs}}^{(d)}$  are of opposite sign, this term interferes destructively with Eq. (1).

Although the relaxation rate for cubic-point symmetry is specified by a single  $d$ -electron orbital admixture parameter, and for hexagonal symmetry by two independent admixture parameters, the tetragonal-point symmetry requires three independent admixture parameters because of the lower symmetry.

The foregoing analysis contains two tacit assumptions. First, it was assumed that the expansion of the conduction-electron wave functions at the Fermi level could be limited to  $l=0$  and  $l=2$  atomic functions, i. e.,  $N(0) = N_s(0) + N_d(0)$ . It is likely, however, that the  $l=1$  admixture is often comparable to the  $l=0$  admixture. Nevertheless, the  $l=1$  hyperfine interaction may be safely neglected, since  $p$  hyperfine fields are generally quite small compared with  $s$  and  $d$  hyperfine fields. The major effect of an appreciable  $p$  admixture at the Fermi level is the reduction of  $N(0)$  relative to the total bare-electron density of states by an amount proportional to the fractional  $p$  character. This reduction is probably small since the density of states in transition metals is dominated by the  $d$ -band contributions. Second, a potentially more serious defect in the analysis is the assumption that the four  $d$  orbitals have identical radial dependences. In other words, the  $d$ -spin and  $d$ -orbital hyperfine fields are assumed to be constants. This assumption is reasonable only if the potential within the atomic volume is nearly spherically symmetric.

We have consciously ignored the effects of electron-electron exchange enhancement on  $T_1$ , because the relaxation rate is dominated by the orbital hyperfine interaction (see Sec. IV). The enhancement effect is spin coupled and would enter the orbital relaxation rate only by means of spin-orbit coupling, which is probably small in vanadium. In the absence of spin-orbit coupling, electron-electron enhancement would enter the relaxation rate through  $R_s$ ,  $R_d$ , and  $R_{s-d}$ . As is well known, phonon renormalization effects do not enter the relaxation rate.<sup>16</sup>

To extract the electric field gradient  $q$  from the measured nuclear-electric-quadrupole interaction, a value of the nuclear quadrupole moment  $Q$  must

be known. In our discussion we will use the value  $Q(^{51}\text{V}) = 0.052$  b determined by Childs and Goodman.<sup>17</sup> Following the treatment of Watson, Gosard, and Yafet<sup>18</sup> (WGY), we write the measured efg as

$$q = (1 - \gamma_\infty) q_{\text{latt}} + (1 - R_Q) q', \quad (7)$$

where  $(1 - \gamma_\infty)$  and  $(1 - R_Q)$  are the Sternheimer deshielding and shielding factors, respectively;  $q'$  is a local field gradient caused by the redistribution of occupied conduction-electron states near the Fermi surface, and  $q_{\text{latt}}$  is the point-charge contribution given by<sup>18</sup>

$$q_{\text{latt}} = (1/a_0)^3 (15.6 Z_V - 5.9 Z_X), \quad (8)$$

where  $a_0$  is the lattice parameter,  $Z_V$  and  $Z_X$  are the point charges of the vanadium and  $X$  sites, respectively. We neglect  $q_0$  and  $q''$  of WGY that arise from nonspherical potential and orbital distortion, respectively. The reader is referred to the paper by WGY<sup>18</sup> for the detailed discussion of  $q'$ . Briefly,  $q'$  is the shielding response of the conduction electrons within the spherical potential of the APW sphere to the external potential imposed by the field gradient of point charges. It is therefore linear in  $-q_{\text{latt}}$  and related to the densities of states at the Fermi level for the various bands. WGY show that, to order the phonon energy divided by the Fermi energy, the electron-phonon interaction can be neglected in the calculation of  $q'$ ; i. e.,  $q'$  is related to the bare density of states at the Fermi level  $N(0)$ .

### III. EXPERIMENTAL PROCEDURE

A series of pseudobinary compounds,  $\text{V}_3\text{Ga}_{1-x}\text{Si}_x$ , were prepared by arc melting. The ingots were annealed at 1000 °C for one week followed by a one-week anneal at 700 °C. Metallographic examination was made to determine the existence of second phases. In all cases, second phases accounted for less than 10–15% of the sample. Lattice parameters were determined from x-ray powder patterns. The  $T_c$  was measured on a Faraday balance.

The NMR measurements were made on powders crushed from the ingots. Two phase-coherent pulsed spectrometers with phase-sensitive detectors were used. Measurements at 4 and 12 MHz were made on a fixed-frequency spectrometer with radio-frequency magnetic field amplitude  $H_1$  between 100 and 150 Oe. The magnetic field was supplied by a Varian electromagnet with fieldial control. Measurements between 48 and 51 MHz were made on a variable-frequency spectrometer with  $H_1$  between 25 and 60 Oe. The magnetic field was supplied by a Westinghouse superconducting solenoid. Signal averaging was accomplished with either an analog or a digital dual-channel boxcar integrator.

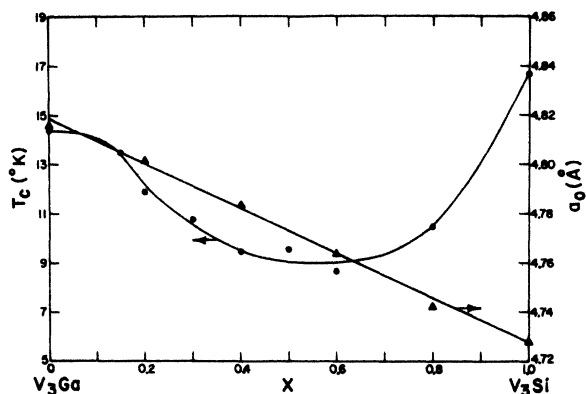


FIG. 1. Composition dependence of the superconducting transition temperature  $T_c$  and the lattice parameter  $a_0$  for the  $V_3Ga_{1-x}Si_x$  compounds.

NMR measurements were made at 77°K with the sample immersed in liquid nitrogen. The  $^{51}V$  nuclear-resonance profiles were obtained by integrating either the free-induction decay or the echo following a two-pulse sequence. A boxcar gate much greater than the free-induction-decay time was used while the magnetic field was swept. The  $T_1$  values were obtained by saturating the nuclear-spin system with a comb of rf pulses and measuring the recovery of the longitudinal magnetization  $M(\tau)$  at a time  $\tau$  later. Single exponential recovery was found in all cases, and nearly complete saturation was obtained.

Spectrum parameters were determined by comparing the experimental spectra with computer-(IBM 360/195) generated synthetic powder-pattern spectra involving distributions of electric field gradients and axial Knight shifts.<sup>10</sup>

#### IV. RESULTS AND DISCUSSION

In Fig. 1, the composition dependences of the superconducting transition temperature and the lattice parameter are shown for the samples used in the present investigation. A sample of  $V_3Ga_{0.25}Si_{0.75}$  supplied by Deaton and Gordon with a reported<sup>9</sup>  $T_c$  near 18.6°K was found to have a broad bulk transition between 7.1 and 11.5°K with a trace near 15.5°K. The 15.5°K transition temperature could be due to a trace of  $V_3Si$  second phase in their sample.

Figure 2(a) is a field sweep at 4 MHz through the  $\frac{1}{2} \rightarrow -\frac{1}{2}$  transition of  $^{51}V$  in  $V_3Ga_{0.8}Si_{0.2}$ . Figure 2(b) is the computer-generated<sup>8</sup> synthetic resonance profile for the central transition with the parameters given in Table II. Figure 3(a) is the field sweep at 51 MHz through the  $\frac{1}{2} \rightarrow -\frac{1}{2}$  transition of  $^{51}V$  in  $V_3Ga_{0.8}Si_{0.2}$ . Figure 3(b) is the corresponding synthetic resonance profile with the same parameters as in Fig. 2(b).

The composition dependence of the spin-lattice relaxation-rate-reciprocal-temperature product  $R \equiv (T_1 T)^{-1}$  at 77°K is shown in Fig. 4. Note the similarity of the composition dependence of  $T_c$  and  $R \equiv (T_1 T)^{-1}$ . This relationship was also observed in the  $V_3Ga_{1-x}Sn_x$  compounds.<sup>8</sup>

In Table II, we list the axial Knight shift  $K_{ax}$ , the nuclear-electric-quadrupole interaction  $e^2q_0Q/h$ , and the width  $\Delta q/q_0 = \Delta K_{ax}/K_{ax}$  of the distribution (assumed Gaussian) of these parameters. These parameters were determined by fitting the experimental spectra obtained at 4 and near 51 MHz with the computer-generated synthetic resonance absorption spectra,<sup>8</sup> e.g., see Figs. 2 and 3. The mean electric field gradient  $q_0$  has a weak composition dependence. Figure 5 illustrates the com-

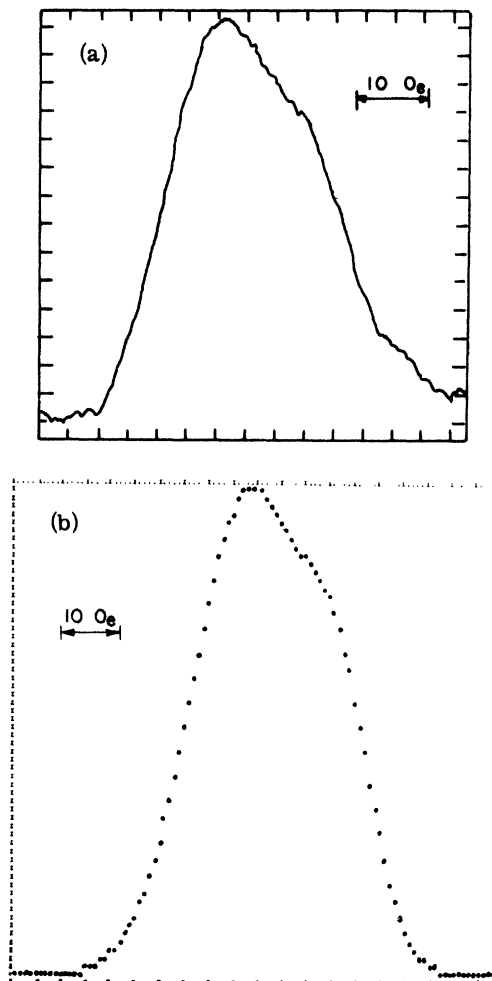


FIG. 2. (a) Field sweep through the  $^{51}V$  central ( $\frac{1}{2} \rightarrow -\frac{1}{2}$ ) transition in  $V_3Ga_{0.8}Si_{0.2}$  at 4 MHz and 77°K. Magnetic field increases to the left. (b) Synthetic resonance profile for the  $^{51}V$  central transition obtained with  $e^2q_0Q/h = 2.9$  MHz,  $K_{ax} = -0.015\%$ , and  $\Delta q/q_0 = \Delta K_{ax}/K_{ax} = 0.4$ . Magnetic field increases to the left.

TABLE II. Spectrum-fitting parameters and electric-field-gradient calculation.

	$V_3Ga$	$V_3Ga_{0.8}Si_{0.2}$	$V_3Ga_{0.6}Si_{0.4}$	$V_3Ga_{0.4}Si_{0.6}$	$V_3Ga_{0.2}Si_{0.8}$	$V_3Si$
$K_{ax}$ (%)	-0.06	-0.015	-0.01	+0.01	+0.03	+0.025
$e^2q_0Q/h$ (MHz)	3.11	2.9	2.5	2.9	3.3	2.95
$\Delta q/q_0 = \Delta K_{ax}/K_{ax}$	0.1	0.4	0.6	0.4	0.3	0.05
$q_0(10^{24} \text{ cm}^{-3})$	1.72	1.6	1.5	1.6	1.8	1.63
$q_0 a_0^3$	192	177	164	173	192	172
$-q'/q_{latt}$	8.5	9.9	11.2	10.3	8.5	10.4
$4F^6 {}_2F^*N(0)$ (states/Ry V-spin)	7	8	9	8	7	8

position dependence of  $K_{ax}$ , which changes sign near  $x=0.5$ , and the fractional width of the Gaussian distribution of  $q$  and  $K_{ax}$ , which peaks near  $x=0.4$ . The isotropic Knight shifts  $K_{iso}$  are determined after the shape of the spectra are fit with the computer-generated synthetic powder patterns and reported relative to  $\nu/H=(11.193 \text{ MHz})/(10 \text{ kOe})$ . The absolute magnetic fields are measured with respect to pure aluminum. Figure 6 illustrates the composition dependence of  $K_{iso}$ .

Following FZ,<sup>8</sup> we set  $(1-R_Q)$  equal to 1 and  $(1-\gamma_\infty)$  equal to 27 in Eq. (7) and use point-charge assignments  $Z_V=+1.8$  and  $Z_{Ga}=+3$  in Eq. (8). If by analogy to Sn, we set  $Z_{Si}=+4$  we obtain an unphysical result for  $q'$ ; i. e., we find a negative density of states at the Fermi level  $N(0)$ . A physical result obtains if we decrease the valence by 1 so that  $Z_{Si}=+3$ . This value has the virtue of being consistent with the band calculations of Mattheiss<sup>6</sup> in that the  $V_3Si$  bands are more similar to those of  $V_3Ga$  than to  $V_3Sn$ . The value of the total density of states at the Fermi level is only weakly dependent on the assumptions made in the calculation of  $q$ , and is determined principally by the value of  $R=(T_1T)^{-1}$ . The calculated values of  $4F^6 {}_2F^*N(0)$  determined from case (a) of Fig. 4 of WGY<sup>18</sup> for the calculated values of  $q'/q_{latt}$  are shown in Table II.

Following the tight-binding calculations of Goldberg and Weger,<sup>7</sup> we will assume, as in the earlier work of FZ, that  $N^{d1}(0)=0$  and that  $N^o(0)$  is essentially constant at 5 states/(Ry V-spin). We also assume for the  $V_3Ga_{1-x}Si_x$  alloys that the  $s$ -band density of states at the Fermi level  $N_s(0)$  does not vary with composition. In the work of FZ,  $N_s(0)$  was set equal to zero. However, the use of a value of  $N_s(0)$  of between about 1 and 2 states/(Ry V-spin) does not qualitatively affect the composition dependences of the  $d$ -subband densities of states at  $E_F$ , but has the virtue of bringing the total density of states into better quantitative agreement with the values of  $\lambda$  determined from  $T_c$  and the low-temperature electronic specific-heat coefficient.

The calculation of  $R$  is illustrated in Table III,

where we have used the values of  $4F^6 {}_2F^*N(0)$  of Table I and Eqs. (1) and (6). Note the slight minimum in the total density of states  $N(0)$  that reflects

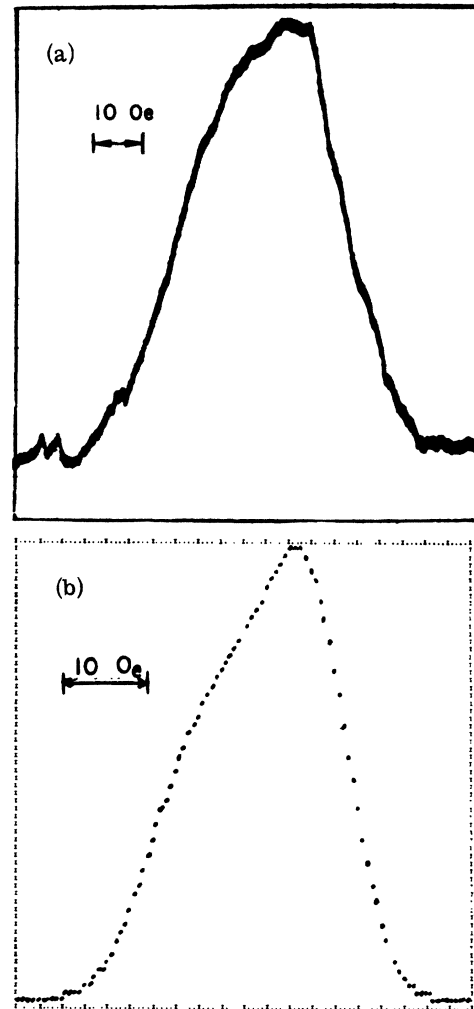


FIG. 3. (a) Field sweep through the  $^{51}V$  central transition in  $V_3Ga_{0.8}Si_{0.2}$  at 51 MHz and 77 K. Magnetic field increases to the left. (b) Synthetic resonance profile obtained with the same parameters as in Fig. 2(b). Magnetic field increases to the left.

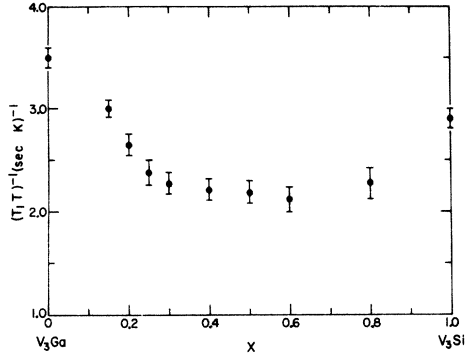


FIG. 4. Composition dependence of the spin-lattice relaxation-rate-reciprocal-temperature product at 77 °K for  $^{51}\text{V}$  in the  $\text{V}_3\text{Ga}_{1-x}\text{Si}_x$  compounds.

the minimum in  $N^*(0)$ ; the composition dependence of  $N(0)$  and  $N^*(0)$  correlates with the composition dependence of  $T_c$ . As in the  $\text{V}_3\text{Ga}_{1-x}\text{Sn}_x$  alloys,<sup>8</sup> the relaxation rate is dominated by the orbital term.

We assume the width of the distribution in the efg is due to local variations in the magnitude of the  $\pi$ -subband density of states, which dominates  $N(0)$ . Here we treat the  $\pi$  subband as a virtually localized state on the vanadium atoms. The sharpness of the peak in the  $\pi$  subband<sup>8</sup> suggests that the  $d$ - $d$  overlap is relatively modest.<sup>7</sup> We therefore suggest that in both  $\text{V}_3\text{Ga}$  and  $\text{V}_3\text{Si}$  the  $\pi$  subband can be treated as a nearly resonant virtually localized state associated with the vanadium atoms. The position of the peak  $E_i$  relative to the Fermi energy, as well as the width of peak  $W$ , can be affected by the local atomic environment of the vanadium atoms in the alloy. The statistical variation in local environment in the  $\text{V}_3\text{Ga}_{1-x}\text{Si}_x$  alloys,

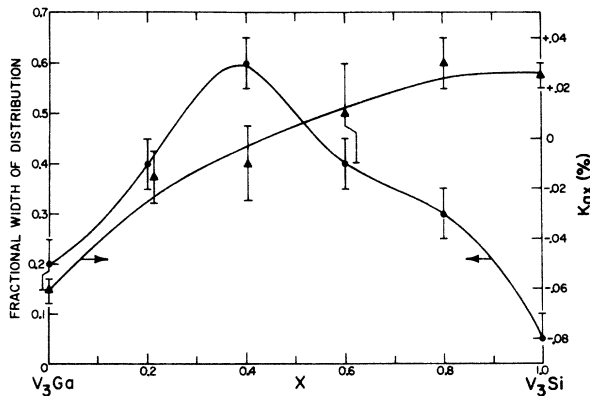


FIG. 5. Composition dependence of the mean axial Knight shift  $K_{ax}$  and the fractional width of the Gaussian distribution of the electric field gradient and  $K_{ax}$  in the  $\text{V}_3\text{Ga}_{1-x}\text{Si}_x$  compounds.

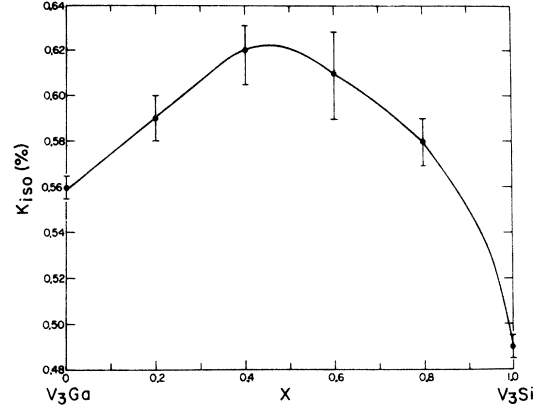


FIG. 6. Composition dependence of the isotropic Knight shift in the  $\text{V}_3\text{Ga}_{1-x}\text{Si}_x$  compounds.

due to the disorder on the nontransition-metal sublattice, can have a strong effect on the localized state through a variation in hybridization of the  $d$  state with the  $s$  and  $p$  derived states in the conduction band. With this model, we calculate the logarithmic variation of the efg in terms of the variation in the  $\pi$ -subband density at  $E_F$ ,  $\delta N^*(0)$ ,

$$\frac{\Delta q}{q_0} = \frac{4KF^{62}\delta N^*(0)}{(1-\gamma_\infty) - 4KF^{62}F^*N(0)}, \quad (9)$$

where we have made use of Eq. (7) and case (a) of WGY. Here  $K$  is a constant equal to 1.25 for the range of  $N(0)$  of interest.<sup>18</sup> The values of  $\delta N^*(0)$  that correspond to the experimental values of  $\Delta q/q_0$  are given in Table IV. For numerical purposes, we assume the localized peak has a Gaussian shape

$$N_0^*(E - E_i) = \left(\frac{2}{\pi}\right)^{1/2} \frac{n}{W} e^{-2(E-E_i)^2/W^2}, \quad (10)$$

with width  $W$  and area  $n$  states/V-spin. We also assume that statistically the position of the peak centroid  $E_i$  is distributed according to a Gaussian distribution of second moment  $\Delta^2$ ,

$$G(E_i) = \left(\frac{2}{\pi}\right)^{1/2} \frac{1}{\Delta} e^{-2E_i^2/\Delta^2}. \quad (11)$$

Folding  $N_0^*(E - E_i)$  with  $G(E_i)$ , we find the shape of  $N^*(E)$  for each alloy,

$$N^*(E) = \left(\frac{2}{\pi}\right)^{1/2} \frac{n}{(\Delta^2 + W^2)^{1/2}} e^{-2E^2/(\Delta^2 + W^2)}, \quad (12)$$

where  $n$  is taken as one electron per spin direction per vanadium atom in the  $\pi$  subband.<sup>8</sup> With this model, the composition dependences of  $W$ ,  $\Delta$ , and  $N_0^*(0)$  are obtained (Table IV and Fig. 7). It can be seen from the variation in  $W$ , and therefore  $N_0^*(0)$ , that the local peak in the  $\pi$  subband varies by about a factor of 2 in amplitude. This probably indicates the importance of  $d$ - $d$  overlap, which has been ignored in this localized model of  $N_0^*(E)$ . The

TABLE III. Calculated spin-lattice relaxation rates and derived densities of states.

(Ry V-spin) <sup>-1</sup>	V <sub>3</sub> Ga	V <sub>3</sub> Ga <sub>0.8</sub> Si <sub>0.2</sub>	V <sub>3</sub> Ga <sub>0.6</sub> Si <sub>0.4</sub>	V <sub>3</sub> Ga <sub>0.4</sub> Si <sub>0.6</sub>	V <sub>3</sub> Ga <sub>0.2</sub> Si <sub>0.8</sub>	V <sub>3</sub> Si
$N_s(0)$	2.0	2.0	2.0	2.0	2.0	2.0
$N^d(0)$	5.0	5.0	5.0	5.0	5.0	5.0
$N^f(0)$	27.0	19.0	14.0	15.0	18.0	22.0
$N^{d^2}(0)$	4.8	6.4	9.0	7.3	5.6	6.0
$N(0)$	38.8	32.4	30.0	29.3	30.6	35.0
(sec °K) <sup>-1</sup>						
$R_{orb}^a$	2.56	1.86	1.45	1.49	1.72	2.14
$R_d^b$	0.36	0.29	0.34	0.28	0.25	0.32
$R_s^c$	0.95	0.95	0.95	0.95	0.95	0.95
$R_{s-d}$	-0.50	-0.50	-0.50	-0.50	-0.50	-0.50
$R_{tot}$	3.37	2.60	2.24	2.22	2.42	2.91
$R_{expt}$	3.43	2.62	2.22	2.17	2.36	2.91

$$^a H_{hfs}^{(orb)} = 0.14 \times 10^6 \text{ Oe.}$$

$$^b H_{hfs}^{(d)} = -0.117 \times 10^6 \text{ Oe.}$$

$$^c H_{hfs}^{(s)} = 1.12 \times 10^6 \text{ Oe.}$$

width of the distribution  $\Delta$  varies by about a factor of 5, indicating the importance of compositional fluctuations on broadening  $N^f(E)$ . Note that  $\Delta$  is considerably larger for V<sub>3</sub>Ga than for V<sub>3</sub>Si, which is in accord with the fact that V<sub>3</sub>Ga forms with a much broader range of stoichiometry. The value of  $\Delta$  is always small compared with the intrinsic width  $W$ , indicating the nearly resonant character of the localized state.

#### V. RELATIONSHIP BETWEEN $T_c$ AND $N(0)$

In Fig. 8 we illustrate the main result of the present work. We have plotted the values of  $T_c$  normalized by  $\Theta_D$  as a function of the total density of states at the Fermi level. These data represent values of  $N(0)$  taken from the V<sub>3</sub>Ga<sub>1-x</sub>Sn<sub>x</sub> system,<sup>8</sup> which have been recalculated to allow a value of  $N_s(0)$  of 2 states/(Ry V-spin), as well as from the V<sub>3</sub>Ga<sub>1-x</sub>Si<sub>x</sub> system presented in Sec. IV. As we have argued in Sec. II, these values of  $N(0)$  represent bare or unrenormalized values of the density of states. The values of  $\Theta_D$  are taken from a fit to the peak in the  $C_p/T$ -versus- $T$  data of Knapp and

Culbert.<sup>20</sup> The quite surprising result is that  $T_c/\Theta_D$  appears to be a universal function of  $N(0)$  for two A15 alloy systems that exhibit marked differences in their composition dependences of  $T_c$  and  $\Theta_D$ .

The electron-phonon mass enhancement is defined by<sup>1</sup>

$$\lambda \equiv 2 \int_0^\infty \alpha^2(\omega) \frac{F(\omega)}{\omega} d\omega. \quad (13)$$

Here  $\alpha^2(\omega)$  is an average of the electron-phonon interaction, and  $F(\omega)$  is the phonon density of states.

Gomersall and Gyorffy<sup>21</sup> have shown that the generalization of McMillan's approximation to  $\lambda$  for systems with more than one atom per unit cell is given in the rigid-atom approximation by

$$\lambda \simeq \frac{N(0)}{\langle \omega^2 \rangle} \sum_i \frac{\langle I_i^2 \rangle}{M_i}. \quad (14)$$

The density of states in the V<sub>3</sub>X compounds is dominated by the states derived from the vanadium atomic  $d$  levels. If we assume the dominant electron-ion scattering is from the nearly resonant

TABLE IV. Parameters of the localized peak in the  $d$  band.

	V <sub>3</sub> Ga	V <sub>3</sub> Ga <sub>0.8</sub> Si <sub>0.2</sub>	V <sub>3</sub> Ga <sub>0.6</sub> Si <sub>0.4</sub>	V <sub>3</sub> Ga <sub>0.4</sub> Si <sub>0.6</sub>	V <sub>3</sub> Ga <sub>0.2</sub> Si <sub>0.8</sub>	V <sub>3</sub> Si
$N^f(0)$ (Ry V-spin) <sup>-1</sup>	27.0	19.0	14.0	15.0	18.0	22.0
$\delta N^f(0)$ (Ry V-spin) <sup>-1</sup>	1.4	2.7	1.7	2.1	2.9	0.4
$W$ (mRy)	29	40	55	51	42	36
$\Delta$ (mRy)	5	12	14	15	13	3
$N_s^f(0)$ (Ry V-spin) <sup>-1</sup>	27.5	19.9	14.5	15.6	19.0	22.2

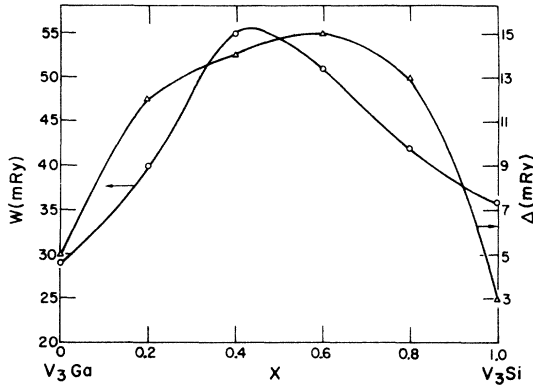


FIG. 7. Composition dependence of the localized vanadium  $d$ -state peak width  $W$  and root second moment  $\Delta$  of the Gaussian distribution of peak centroids in the  $V_3Ga_{1-x}Si_x$  compounds.

vanadium  $d$  state in the  $V_3X$  compounds, the electron-phonon interaction is given by

$$\lambda \approx \frac{N(0) \langle I_V^2 \rangle}{\langle \omega^2 \rangle M_V}, \quad (15)$$

and the variation in  $\lambda$  is due to the variation in  $N(0) \langle I_V^2 \rangle / \langle \omega^2 \rangle$ . If we follow McMillan and assume  $N(0) \langle I_V^2 \rangle$  is nearly constant, then the dependence of  $T_c / \Theta_D$  and therefore  $\lambda$  on  $N(0)$  (Fig. 8) must be through the phonon renormalization. The phonon spectra are temperature dependent,<sup>3</sup> in part, because of temperature dependence of the electronic screening in the high- $T_c$  A15 compounds. Therefore, we have no reliable means of estimating the zero-point moments of the phonon spectra entering Eq. (15).

Allen and Silbergliitt<sup>22</sup> have recently discussed the effect of the full dynamic nature of the phonon spectral function  $B(q, \omega)$  that is of importance when the phonons have finite lifetimes and temperature-dependent frequency shifts due to the self-energy corrections. They find that

$$\lambda = [N(0)/M] \langle \langle |I(\vec{k}, \vec{k}')|^2 / \omega_{\vec{k}-\vec{k}'}^2(0) \rangle \rangle, \quad (16)$$

where

$$I(\vec{k}, \vec{k}') = \vec{\epsilon} \cdot \langle \vec{k} | \nabla \vec{V} | \vec{k}' \rangle \quad (17)$$

is the electron scattering matrix element and the angular brackets indicate averaging  $\vec{k}$  and  $\vec{k}'$  over the Fermi surface. They emphasize that  $\omega_{\vec{q}}(0)$  is the frequency the phonon would have if the real part of the phonon self-energy were frequency independent (i.e., if the restoring force at the phonon frequency were the same as the restoring force to static deformations). The frequency  $\omega_{\vec{q}}(0)$  differs from the experimental frequency  $\omega_{\vec{q}}$ , which is defined as the frequency at which the phonon spectral function peaks. If the phonon self-energy results

from electron-phonon interactions only, the equality of  $\omega_{\vec{q}}^2$  and  $\omega_{\vec{q}}^2(0)$  is a statement of the adiabatic approximation. Recent experiments<sup>23</sup> on the high- $T_c$  compound  $Nb_3Sn$  have shown  $\omega_{\vec{q}}^2$  differs markedly from  $\omega_{\vec{q}}^2(0)$  for certain phonons. For the  $\langle 110 \rangle$  transverse-acoustic branch,  $\omega_{\vec{q}}^2(0)$  is found to be much smaller than  $\omega_{\vec{q}}^2$ .

Chan and Heine<sup>24</sup> have shown that the renormalized frequency  $\omega_{\vec{q}}$  is related to the bare frequency  $\Omega_{\vec{q}}$  by the generalized linear response function of the conduction electrons given by

$$\chi_{\vec{q}} = \sum_{\vec{k}} \frac{f_{\vec{k}} - f_{\vec{k}+\vec{q}}}{E_{\vec{k}+\vec{q}} - E_{\vec{k}}}. \quad (18)$$

We take an approximate form for  $\omega_{\vec{k}-\vec{k}'}^2(0)$  suggested by the work of Chan and Heine,

$$\omega_{\vec{k}-\vec{k}'}^2(0) = \Omega_{\vec{k}-\vec{k}'}^2 (1 - B\chi_{\vec{k}-\vec{k}'}), \quad (19)$$

where  $\Omega$  is the bare-phonon frequency, and  $B$  is a constant. In the limit of  $T \rightarrow 0$ , Eqs. (16) and (19) yield, after factorization and appropriate averaging,

$$\lambda = \frac{N(0) \langle \langle I_V^2 / \Omega^2 \rangle \rangle}{M_V (1 - BN(0))}. \quad (20)$$

Although some phonon modes may stiffen while others soften, Eq. (20) indicates the manner in which we expect  $\lambda$  to vary.

We have used Eq. (20) and the two-square-well form for  $T_c$ ,

$$T_c / \Theta_D = \frac{1}{1.45} e^{-(1+\lambda) / (\lambda - \mu^*)}, \quad (21)$$

to fit the data in Fig. 8. Here we have used Benne-

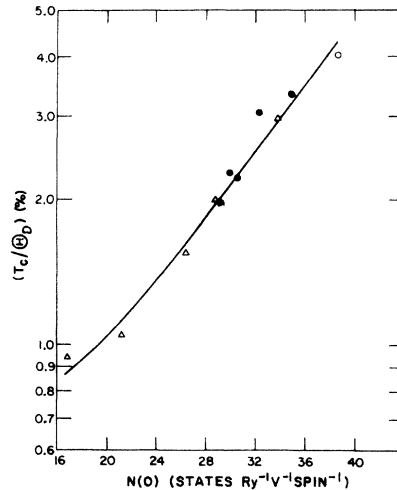


FIG. 8. Superconducting transition temperature normalized by the Debye temperature as a function of the bare density of states at the Fermi level. Open circle,  $V_3Ga$ ; closed circles,  $V_3Ga-V_3Si$  compounds; triangles,  $V_3Ga-V_3Sn$  compounds. Solid curve is a fit to the data obtained with a two-square-well model and  $\lambda = \lambda_0 / [1 - BN(0)]$  with  $\lambda_0 = 0.36$  and  $B = 0.015$  Ry V-spin.



TABLE V. Superconducting and normal-state parameters for  $V_3X$  compounds.

Compound	$N(0)$ (Ry V-spin) <sup>-1</sup>	$T_c$ (°K)	$\Theta_D$ (°K)	$\mu^*$	$\lambda$
$V_3Ga$	38.8	14.5	360	0.193	0.86
$V_3Si$	35.0	16.7	498	0.187	0.76
$V_3Ga_{0.9}Sn_{0.1}$	33.9	10.7	360	0.186	0.73
$V_3Ga_{0.9}Si_{0.2}$	32.4	11.9	388	0.183	0.70
$V_3Ga_{0.2}Si_{0.8}$	30.6	10.5	472	0.180	0.67
$V_3Ga_{0.6}Si_{0.4}$	30.0	9.5	416	0.179	0.65
$V_3Ga_{0.1}Si_{0.6}$	29.3	8.7	444	0.178	0.64
$V_3Ga_{0.7}Sn_{0.3}$	28.8	7.2	360	0.177	0.63
$V_3Ga_{0.5}Sn_{0.5}$	26.4	5.6	360	0.172	0.60
$V_3Ga_{0.1}Sn_{0.9}$	21.3	3.8	360	0.159	0.53
$V_3Sn$	16.8	3.4	360	0.144	0.48

mann and Garland's<sup>2</sup> numerical approximation for  $\mu^*$ . The use of McMillan's equation<sup>1</sup> for  $T_c/\Theta_D$  results in only small numerical differences. We assume, for the  $V_3X$  compounds of interest, that  $\Omega$  and  $B$  are essentially independent of composition. Although a poor fit to the data in Fig. 8 is obtained if we use the full explicit dependence of  $\lambda$  on  $N(0)$ , i. e.,  $\lambda \sim N(0)/[1 - BN(0)]$ , a quite good fit is obtained if we treat

$$\lambda_0 \equiv [N(0)/M_V] \langle\langle I_V^2/\Omega^2 \rangle\rangle$$

as a constant. The parameters in the fitted curve in Fig. 8 are  $\lambda_0 = 0.36$  and  $B = 0.015$  Ry V-spin. The values of  $\mu^*$  and  $\lambda$  are given in Table V.

The constancy of  $\lambda_0$  can be understood if we fol-

low Hopfield<sup>25</sup> and assume  $\nabla V$  to be local interaction. Since overlap contributions are considered to be small for the  $d$  bands in the  $V_3X$  compounds, only  $p$ - $d$  matrix elements appear in Eq. (17). Thus  $\langle\langle I_V^2 \rangle\rangle$  has the form

$$\langle\langle I_V^2 \rangle\rangle \approx \frac{N_p(0)N_d(0)}{[N(0)]^2} (\nabla V)^2. \quad (22)$$

The dominant contribution to the density of states at the Fermi level arises from  $N_d(0)$ , whereas the  $p$  and  $s$  fractions  $N_p(0)$  and  $N_s(0)$  are small quantities that vary slowly. Thus

$$N(0) \langle\langle I_V^2 \rangle\rangle \approx N_p(0)(\nabla V)^2 \approx \text{const.}$$

In summary, we find that  $T_c/\Theta_D$  is a universal function of the bare density of states at the Fermi level for the  $V_3Ga$ - $V_3Sn$  and  $V_3Ga$ - $V_3Si$  pseudobinary compounds. A reasonably good account of the composition dependence of  $\lambda$  in the  $V_3X$  compounds is given by  $\lambda = \lambda_0/[1 - BN(0)]$ , where the bare density of states at the Fermi level is dominated by the vanadium  $d$  states of  $\pi$  symmetry. The functional form of  $\lambda$  is suggestive of the controlling nature of electron screening via the electron-phonon interaction in the phonon self-energy.

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