

## Superconducting properties of $A$ -15 $V_{75-x}M_xGa_{25}$ compounds: $M = \text{Ti, Cr, Mn, Fe, Co, and Ni}$

D. U. Gubser

Naval Research Laboratory, Washington, D. C. 20375

H. R. Ott and K. Girgis

Eidgenössische Technische Hochschule, Zürich, Switzerland

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Superconducting transition temperatures  $T_c$  and their pressure derivatives  $dT_c/dp$  have been determined for  $V_3Ga$  based ternary compounds containing 3d-element substitutions for V. The superconducting transition temperatures decrease while the normalized pressure derivatives,  $(1/T_c)(dT_c/dp)$  increase systematically for all 3rd element additions. These results suggest that the form of the  $T_c$  equation is not affected by rapid variations in the electronic density of states  $N(E)$ , as suggested by some models for superconductors of the  $A$ -15-structure type. Analysis of the data in terms of the McMillan  $T_c$  equation and the more recent  $T_c$  equation of Birnboim show that the electron-phonon coupling parameter  $\lambda$  scales uniquely with the electron-per-atom ratio  $\mathfrak{z}$  and is approximately proportional to the electronic density of states at the Fermi level,  $N(E_F)$ . The volume derivative of  $\lambda$ , as determined from  $dT_c/dp$  data, remains approximately constant as the electron-per-atom ratio varies near that of  $V_3Ga$  ( $\mathfrak{z} = 4.5$ ). The only significant difference in the two model  $T_c$  equations, i.e., McMillan or Birnboim, is in the absolute values of the parameters  $\lambda$  and  $d \ln \lambda / d \ln V$ , not in systematic variations.

### I. INTRODUCTION

The highest reported superconducting transition temperatures are found among stoichiometric  $A_3B$  compounds possessing the  $A$ -15 crystal structure, where  $A$  is a transition-metal atom and  $B$  is a non-transition-metal atom. High transition temperatures in these compounds are generally ascribed either to large electronic density of states at the Fermi level,  $N(E_F)$ , or to anomalies in the phonon spectrum.<sup>1-3</sup> Density-of-states models for describing superconductivity in  $A$ -15 compounds apply particularly well to V-based compounds where the largest  $N(E_F)$  values are found.<sup>4</sup>

The functional form of  $T_c$  on  $N(E_F)$  is not, however, well established in high- $T_c$ ,  $A$ -15 compounds since  $N(E)$  varies rapidly over typical phonon energies in the region near  $E_F$ . These rapid variations influence normal-state properties, such as Knight shifts,<sup>1,3</sup> but their importance in determining the form of the  $T_c$  equation has not been demonstrated.

$V_3Ga$  has the highest known  $N(E_F)$  value of any  $A$ -15 compound and its measured Knight shift indicates considerable variation in  $N(E)$  near  $E_F$ .<sup>1,2</sup> Furthermore, studies of the  $V_{75}Ga_{25-x}Sn_x$  and  $V_{75}Ga_{25-x}Si_x$  systems<sup>4,5</sup> have previously shown that  $T_c$  correlates well with  $N(E_F)$ . Thus,  $V_3Ga$ -based ternary systems are ideal for experimentally testing the influence of rapid  $N(E)$  variations on the functional form of the  $T_c$  equation.

In the work reported here, V atoms in  $V_3Ga$  have

been systematically replaced with other 3d-transition-metal atoms denoted by  $M$ , where  $M = \text{Ti, Cr, Mn, Fe, Co, and Ni}$  to form  $V_{75-x}M_xGa_{25}$  compounds, where  $x$  is the atomic concentration of  $M$  atoms. Superconducting transition temperatures in  $V_{75-x}M_xGa_{25}$  compounds were first reported by Savitskii *et al.*<sup>6</sup>; however, only a relatively few compounds were measured, which vitiated an accurate determination of  $T_c$  as a function of  $M$  concentration. Subsequently, Girgis, Odoni, and Ott<sup>7</sup> reported a more complete study of the Cr, Mn, and Fe ternary systems which clearly showed systematic behavior in the  $T_c$  data. This article extends investigations of the  $T_c$  dependence in  $V_{75-x}M_xGa_{25}$  compounds to the Ti, Co, and Ni systems and also reports on the effects of hydrostatic pressure on  $T_c$ . Systematic variations of  $T_c$  and  $dT_c/dp$  are observed for all the  $M$  alloy series. The results are analyzed and compared with several theoretical forms of the  $T_c$  equation.

### SAMPLE PREPARATION

Samples were prepared by melting the constituent elements in an atmosphere of high-purity argon. They were homogenized, subsequently wrapped in tantalum foil, and annealed under vacuum at 800°C for approximately four weeks. Solubility limits of the  $M$  atoms in  $A$ -15  $V_3Ga$  varied from complete solubility for Cr to only a very few atomic percent for Ni. Final compositions were determined from a microprobe analysis

( $\pm 0.5\%$ ) and lattice parameters  $a_0$  were measured by x-ray methods. Lattice parameters decreased linearly with Cr, Mn, Fe, Co, and Ni content and increased with Ti content. The magnitude of change in lattice parameters varied with  $M$  type in proportion to Pauling's atomic radii, except for Ni. Neutron diffraction studies were made to determine the distribution of  $M$  atoms and the degree of crystallographic long-range order.<sup>8</sup> It was observed that the  $M$  additions replaced mainly the V atoms, i.e., they occupied the 6c lattice sites. Complete details of the sample preparation and crystallographic and metallographic studies are reported elsewhere.<sup>7</sup>

#### TRANSITION TEMPERATURES $T_c$

Superconducting transition temperatures were measured inductively with a standard ac mutual-inductance bridge. The transition widths were typically 0.5 K wide.  $T_c$  was always defined as the midpoint of the transition.

All samples reported here had a final 800-°C thermal ordering anneal; however, the effects of a lower-temperature ordering anneal were examined in some of the samples. The largest effect was noted in binary  $V_3Ga$  where the 800-°C annealed sample had a  $T_c$  of 14.1 K while the 600-°C sample had a  $T_c$  of 14.7 K. Such ordering effects are well documented in the literature<sup>9</sup> and are due to an increase in the degree of crystallographic long-range order, i.e. V atoms on the 6c lattice sites and Ga atoms on the 2a sites. As  $M$  atoms are added, systematic differences in  $T_c$  between the two anneals rapidly disappear and were unobservable at concentrations of 5% or greater. This result is consistent with the fact that at higher  $M$  concentrations, a small percentage of the  $M$  atoms occupy the Ga 2a lattice sites. For instance, in  $V_{67.5}Fe_{7.5}Ga_{25}$ , approximately 95% of the Fe atoms were on the 6c sites while the remaining 5% were on the 2a sites. This  $M$  disorder dominates over thermal disorder at large  $M$  concentrations; thus, longer-time lower-temperature thermal anneals have little systematic effect on  $T_c$  in the higher-concentration compounds.

The results of these investigations are shown in Fig. 1 where  $T_c$  is plotted against  $M$  concentration  $x$ . Definite families of curves, parametrized by the  $M$  type, appear when the data are plotted in this manner (similarly, plots of  $T_c$  versus the lattice parameter  $a_0$  gave families of curves depending on  $M$  type). The initial change of  $T_c$  with  $M$  concentration is shown in Table I. Since these numbers refer to initial slopes of  $T_c$  with respect to concentration, values will depend slightly on the ordering anneal; however, in the Co system,

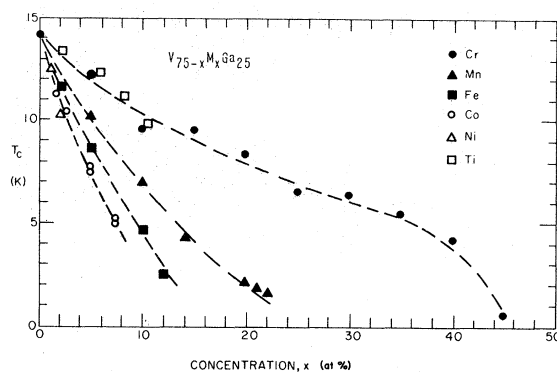


FIG. 1.  $T_c$  vs concentration for  $V_{75-x}M_xGa_{25}$  compounds. (Dashed lines are merely to guide the eye).

where such effects were most extensively studied, the difference in initial slope determinations for samples with an 800-°C versus a 600-°C anneal was small—approximately equal to the uncertainty in the quoted value itself.

If one converts these  $dT_c/dx$  values into  $dT_c/dz$  values, where  $z$  is the valence-electron-per-atom ratio, then, to within experimental error,

$$\left| \frac{dT_c}{dz} \right| \approx 40 \text{ K}/z,$$

a constant for all systems. Thus universal  $z$  dependence persists, in fact, over most of the alloy concentration ranges as shown in Fig. 2. Only the high-concentration Cr data deviate slightly from the universal behavior. (This effect in Cr, as will be discussed later, is most likely due to a concentration-induced change in the phonon frequencies.) It thus appears that the superconducting transition temperatures for these ternary A-15 systems are controlled predominantly by the number of valence electrons per atom. This result is consistent with expectations of density-of-states models describing superconductivity in A-15-structure-type compounds.

#### PRESSURE EFFECTS $(1/T_c)(dT_c/dp)$

The apparatus for measuring the effects of pressure on  $T_c$ , shown schematically in Fig. 3, was a standard piston-cylinder clamp apparatus where-

TABLE I. Initial changes of  $T_c$  with  $M$  additions.

	$dT_c/dx$ (K/at.%)	$dT_c/dz$ (K/ $z$ )
Ti	$-0.40 \pm 0.05$	$40 \pm 5$
Cr	$-0.40 \pm 0.03$	$-40 \pm 3$
Mn	$-0.85 \pm 0.04$	$-42 \pm 2$
Fe	$-1.05 \pm 0.1$	$-35 \pm 4$
Co	$-1.6 \pm 0.1$	$-40 \pm 4$
Ni	$-1.7 \pm 0.2$	$-34 \pm 5$

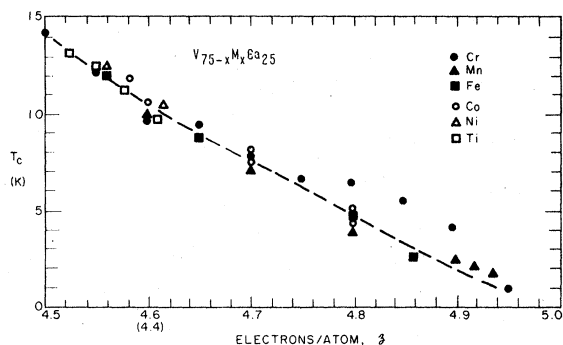


FIG. 2.  $T_c$  vs  $z$  ratio for  $V_{75-x}M_xGa_{25}$  compounds.  $z$  values for Ti alloys are indicated by a decreasing scale shown in parentheses below the abscissa. (Dashed line is merely to guide the eye.)

by hydrostatic pressures to approximately 20 kbar could be applied to the sample. The pressure cylinder was hardened BeCu having a 5-mm bore while the piston material was tungsten carbide. The sample, along with a pressure calibrant and the pressure transmitting fluid (glycerine), were all contained inside a nylon cell. Pressure was applied at room temperature in order to ensure a hydrostatic environment, whose importance in pressure studies of  $A-15$  compounds has been emphasized by Smith,<sup>10</sup> and retained by a lock-nut mechanism. Pressures were determined at low temperatures by simultaneously measuring  $T_c$  of the In calibrant whose  $T_c(p)$  curve is well documented.<sup>11</sup>  $T_c$  was measured inductively while slowly sweeping the temperature which was determined with a germanium resistance thermometer.

The effect of pressure on  $A-15$  compounds is not large, in fact, the total shift for the compounds reported here is less than the width of the transition temperature itself. Nevertheless, the shapes of the transitions proved invariant under pressure, indicative of a hydrostatic environment, and the

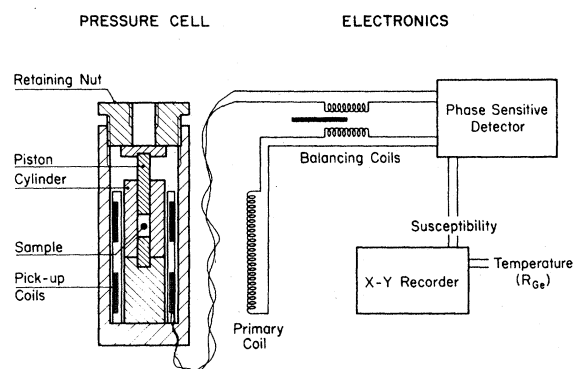


FIG. 3. Schematic of pressure cell and magnetic-susceptibility detection bridge.

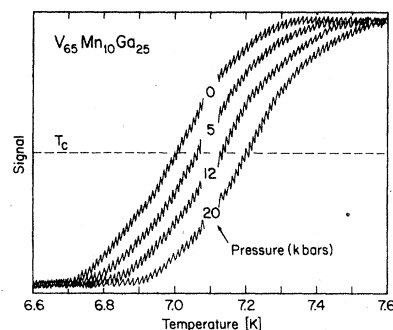


FIG. 4. Magnetic susceptibility vs temperature showing the superconducting- to normal-state transition as a function of pressure.

midpoint was reproducibly defined to about 20 to 30 mK. Since the total shifts were from 0.05 K to approximately 0.25 K at 20 kbar, such an accuracy is necessary to obtain reliable  $dT_c/dp$  values. Fig. 4 shows actual data for the  $V_{65}Mn_{10}Ga_{25}$  sample as a function of pressure. From data such as these, values for  $T_c$  and  $dT_c/dp$  were obtained.

Table II lists the results of pressure measurements where  $T_c$ , the pressure derivative  $dT_c/dp$ , and the relative pressure derivative  $(1/T_c)(dT_c/dp)$  are shown as functions of the parameters  $x$  and  $z$ . The relative pressure derivatives are related to volume derivatives of  $T_c$  through the relation

$$\frac{d \ln T_c}{d \ln V} = -\frac{1}{\kappa} \frac{T_c}{T_c} \frac{dT_c}{dp}, \quad (1)$$

where  $\kappa$  is the isothermal compressibility of the sample. For purposes of comparing data from a variety of samples, this volume derivative is more

TABLE II. Values of  $T_c$ ,  $dT_c/dp$ ,  $(1/T_c)(dT_c/dp)$ , and  $z$  for  $V_{75-x}M_xGa_{25}$  compounds.

Sample	$T_c$ (K)	$\frac{dT_c}{dp}$ ( $10^{-6} \text{ bar}^{-1}$ )	$\left(\frac{1}{T_c}\right)\left(\frac{dT_c}{dp}\right)$ ( $10^{-5} \text{ K/bar}$ )	$z$
$(V_3Ga)$	14.1	1.2	0.80	4.50
$Fe_2$	11.8	1.0	0.85	4.56
$Co_2$	11.4	0.9	0.80	4.58
$Ti_{2.5}$	12.4	1.2	0.95	4.47
$Fe_5$	8.5	1.0	1.2	4.65
$Mn_5$	10.1	1.2	1.2	4.60
$Cr_5$	12.1	1.3	1.1	4.55
$Co_5$	7.2	0.8	1.1	4.70
$Ti_{7.5}$	11.3	1.2	1.1	4.42
$Mn_{10}$	7.0	1.0	1.4	4.70
$Mn_{15}$	4.2	0.6	1.4	4.80
$Cr_{15}$	9.9	1.4	1.4	4.65
$Co_{7.5}$	4.2	0.5	1.2	4.80
$Cr_{30}$	6.4	0.65	1.0	4.80

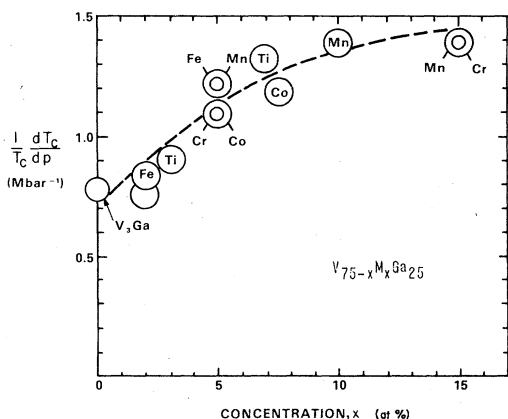


FIG. 5. Relative pressure derivations of  $V_{75-x}M_xGa_{25}$  compounds vs  $M$  concentration,  $x$ .

meaningful than the pressure derivative alone. The value of  $(1/T_c)(dT_c/dp)$  for binary  $V_3Ga$  determined in this study  $[(0.8 \pm 0.1) \times 10^{-6} \text{ bar}^{-1}]$  agrees quite well with the value determined previously by Smith<sup>10</sup>  $[(0.75 \pm 0.03) \times 10^{-6} \text{ bar}^{-1}]$ .

Figure 5 shows the relative derivatives plotted against  $x$ . In spite of the experimental scatter, it is immediately apparent that the relative pressure derivatives increase as one adds  $M$  atoms, rising to a value that is almost double that of binary  $V_3Ga$ .

#### DISCUSSION AND ANALYSIS

Since  $T_c$  correlates best with the  $\bar{z}$  ratio, rather than  $M$  type or concentration  $x$ , it suggests that  $T_c$  is dominated by electronic properties such as the electronic density of states  $N(E)$ . The electronic density of states affects  $T_c$  through the electron-phonon coupling parameter  $\lambda$  according to the formula<sup>12</sup>

$$\lambda = N(E_F) \langle I^2 \rangle / M \langle \omega^2 \rangle, \quad (2)$$

where  $N(E_F)$  is the electronic density of states at the Fermi level,  $\langle I^2 \rangle$  is an electron-phonon matrix element,  $M$  is the atomic mass, and  $\langle \omega^2 \rangle$  is an average phonon frequency.  $E_F$  itself is a function of the  $\bar{z}$  ratio.

To obtain  $\lambda$  from  $T_c$  data, one must have an equation relating  $\lambda$  to  $T_c$ . Standard forms of the  $T_c$  equation assume a phonon-limited range for the attractive electron-electron interaction; however, for materials possessing the  $A-15$  crystal structure, many alternative equations have been proposed<sup>13-18</sup> based on an electronically limited interaction. These equations assume (i) that  $N(E_F)$  is large and sharply peaked near  $E_F$  falling essentially to zero within an energy range of less than 1 mRy (<150 K), and (ii) that such a functional

dependence of  $N(E)$  will alter the basic form of the interaction.

The effects of hydrostatic pressure can be used to test the validity of these electronically limited  $T_c$  equations. Such models predict positive pressure derivatives of  $T_c$ .<sup>19</sup>  $V$ -based  $A-15$  compounds (but not  $Nb$ -based compounds) have positive pressure derivatives<sup>10</sup> and are thus in qualitative agreement with these models assuming large and sharply peaked  $N(E)$  at  $E_F$ . As one adds extra electrons to the  $d$  band, in  $V_{75-x}M_xGa_{25}$  compounds, the Fermi energy moves away from the region of sharply varying  $N(E)$  and the relative pressure derivative  $(1/T_c)(dT_c/dp)$  should decrease. The increase in  $(1/T_c)(dT_c/dp)$ , with  $\bar{z}$  ratio as shown in Fig. 5 clearly violates the predictions of these models. Thus, even though positive pressure shifts in  $V_3Ga$  compounds are in accord with those models requiring sharp structure in  $N(E)$ , systematics of the pressure derivatives are not compatible with them. Hence, sharp structure in  $N(E)$  near  $E_F$  does not appear to alter the basic form of the phonon-limited  $T_c$  equation.

The equation for  $T_c$  assuming a phonon-limited energy range for the attractive electron-phonon interaction, has the general form

$$T_c \sim \Theta \exp -1/g(\lambda\mu^*), \quad (3)$$

where  $\Theta$  is an average phonon frequency and  $g$  is the net electron-electron interaction which depends on the repulsive Coulomb parameter  $\mu^*$  and the attractive electron-phonon parameter  $\lambda$ . Nettleton<sup>20</sup> has suggested that  $\lambda$  is not strongly effected by sharp electronic structure since it involves an average over the phonon energy range, i.e.,  $\lambda - \bar{\lambda}$ , where  $\bar{\lambda}$  is given by Eq. 8 in Ref. 20.

The most common specific form for  $\Theta$  and  $g$  was given by McMillan<sup>12</sup> in 1967 based upon a solution of the Eliashberg equations for the  $Nb$  phonon spectrum:

$$\begin{aligned} \Theta &= \Theta_D / 1.45, \\ g^{-1} &= 1.04(1 + \lambda) / [\lambda - \mu^*(1 + 0.62\lambda)], \end{aligned} \quad (4)$$

where  $\Theta_D$  is the Debye temperature. Further computer modeling by Allen and Dynes<sup>21</sup> based on the same approach as used by McMillan, but generalizing to different phonon spectra and to larger  $\lambda$ , has led to a different  $\Theta$  in Eq. (4), but for  $\lambda < 1.5$  the difference is only in the type of phonon average used to obtain  $\Theta$ . More recently, Birnboim and Gutfreund<sup>22-24</sup> formulated another  $T_c$  equation based on the ideas of Appel and Kohn<sup>25</sup> who suggested that the natural way to describe the electron-phonon interaction in materials with transition metals is by employing the Wannier or atomic-site representation rather than the Bloch representation.

Using this localized description of electronic states in narrow- $d$ -band compounds, Birnboim and Gutfreund again solved the Eliashberg equations under the same assumptions as used by McMillan to obtain

$$\Theta = 1.83\Theta_D$$

and

$$g^{-1} = 1.13(1 + 2.25\lambda)/(\lambda - 1.3\mu^*). \quad (5)$$

This relation should be valid over the same  $\lambda$  range as is McMillan's since similar assumptions about the phonon spectrum were made.

Debye temperatures for  $V_3Ga$  and  $Cr_3Ga$  have been reported<sup>2</sup> as 310 K and 584 K respectively; hence, a change in  $\Theta_D$  is expected in ternary compounds. Debye temperatures for the ternary systems reported here, however, were not experimentally measured. It was therefore necessary to estimate their values from results of previous measurements on an analogous A-15 system. For the  $V_{75-x}Cr_xSi_{25}$  alloy system,  $T_c$  and  $\Theta_D$  have been determined as a function of  $x$ .<sup>26</sup> The data show that  $\Theta_D$  increases approximately linearly with  $x$  for  $x < 30$  and then remains constant at the value of  $\Theta_D(Cr_3Si)$  over the remainder of the composition range. For the  $V_{75-x}M_xGa_{25}$  alloy systems it was assumed that  $\Theta_D$  varied in a similar manner between the end points of 310 and 584 K, i.e.,

$$\Theta_D \approx 310 + 9x, \quad x < 30$$

$$\Theta_D \approx 584, \quad x > 30.$$

The electron-phonon parameter  $\lambda(\mathfrak{z})$  was determined for the alloys reported here by inverting the  $T_c$  equations of McMillan and of Birnboim. In order to reduce the effects of uncertainties in the absolute values of  $\Theta_D$  and/or  $\mu^*$ , systematic vari-

ations in  $\lambda$  were obtained by normalizing to the value of binary  $V_3Ga$ , i.e.  $\lambda(4.5)[T_c(4.5) = 14.1 \text{ K}]$ . Figure 6 shows the  $\mathfrak{z}$  systematics of  $\lambda(\mathfrak{z})$  as analyzed by both the McMillan and the Birnboim formulations. All data fall on a universal  $\mathfrak{z}$  curve. The Cr data points which did not follow the same  $T_c(\mathfrak{z})$  curve as that of the other  $M$  alloys are no longer distinguishable when  $\lambda(\mathfrak{z})$  are compared. This result is due to the fact that  $\Theta_D$  is a function of  $x$ . Although  $T_c$  depends slightly on  $x$  (from  $\Theta_D$ ),  $\lambda$  appears uniquely determined by the  $\mathfrak{z}$  value. Differences in  $\lambda(\mathfrak{z})/\lambda(4.5)$  for the two models are small and can be reduced by slight changes in the prefactors of the  $T_c$  equation; hence, one cannot differentiate between the models on the basis of these  $\mathfrak{z}$  systematics.

Also shown in Fig. 6 is the ratio  $N(\mathfrak{z})/N(4.5)$  as determined from recent band-structure calculations of Klein *et al.*<sup>27</sup> The curve represents a hand-drawn smoothed curve approximating the calculated density of states. According to Eq. (2),  $N(\mathfrak{z})/N(4.5)$  should be directly comparable to  $\lambda(\mathfrak{z})/\lambda(4.5)$  provided that the rigid-band-model approximation is valid and that the quantity  $\langle I^2 \rangle / M \langle \omega^2 \rangle$  is constant. For V-based compounds where other 3d-transition-metal atoms are substituted for V, the product  $\langle I^2 \rangle / M \langle \omega^2 \rangle$  may be expected to remain approximately constant due to the similarity in the 3d-electron-shell configuration.<sup>5</sup> The data analyzed by either method do indeed follow the general trends of the theoretical  $N(E)$  calculation although numerical agreement is not exact. Agreement could perhaps be improved by plotting the ratios of  $\bar{N}(\mathfrak{z})$  as suggested by Nettles,<sup>20</sup> where  $\bar{N}(\mathfrak{z})$  is the density of states averaged over the phonon spectrum. These data, however, are not available. The qualitative agreement of Fig. 6 suggests that to a first approximation, the rigid-band assumptions and the assumed constancy of  $\langle I^2 \rangle / M \langle \omega^2 \rangle$  are valid in these V-based ternary systems.

Pressure derivative measurements give information about the volume dependence of  $\lambda$ . Differentiating Eq. (2), one obtains

$$\frac{d \ln \lambda}{d \ln V} = \frac{d \ln N(E_F)}{d \ln V} + \frac{d \ln \langle I^2 \rangle}{d \ln V} + 2\gamma, \quad (6)$$

where  $\gamma = -d \ln \Theta / d \ln V$ . Differentiating Eq. (3) (assuming  $d\mu^*/dV = 0$ ), one obtains  $d \ln \lambda / d \ln V$  in terms of experimentally measured parameters:

$$\frac{d \ln \lambda}{d \ln V} = \left[ \gamma - \left( \frac{1}{\kappa T_c} \right) \left( \frac{dT_c}{dP} \right) \right] / \left[ \left( \ln \frac{\Theta}{T_c} \right) f(\lambda \mu^*) \right], \quad (7)$$

where  $f(\lambda \mu^*) = (1/g)(dg/d\lambda)$ .

The volume dependence of the appropriate av-

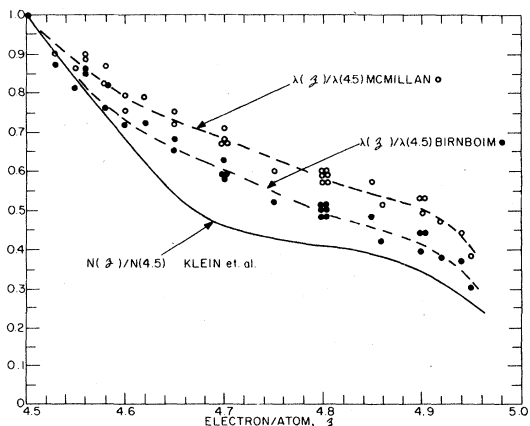


FIG. 6. Ratios of  $\lambda(\mathfrak{z})/\lambda(4.5)$  as determined by both the McMillan and Birnboim models (data plus dashed lines) and  $N(\mathfrak{z})/N(4.5)$  from calculations of Klein *et al.* (solid line) vs  $\mathfrak{z}$  value.

erage phonon frequency  $\gamma$  is an additional unknown parameter which complicates interpretation of pressure data. In the alloy systems studied here, the quantity  $\langle I^2 \rangle / M \langle \omega^2 \rangle$  appears to be approximately constant, independent of  $\beta$ ,  $x$ , and  $a_0$ ; hence, the volume change of  $\langle I^2 \rangle / M \langle \omega^2 \rangle$  is expected to be small, i.e.,

$$\frac{d \ln \langle I^2 \rangle}{d \ln V} \approx - \frac{d \ln (1 / \langle \omega^2 \rangle)}{d \ln V} \approx -2\gamma \quad (8)$$

For A-15 materials,

$$- \frac{d \ln \langle I^2 \rangle}{d \ln V} \approx \frac{2}{3} a_0 q < 2$$

(Refs. 10 and 19;  $q$  is a constant describing the exponential decay of the localized  $d$  wave function). Hence, the value of  $\gamma$  is expected to be less than 1, which is approximately one order of magnitude smaller than the term  $(1/\kappa T_c)(dT_c/dp)$  in Eq. (7) [ $\kappa \approx 0.14 \times 10^{-6} \text{ bar}^{-1}$  (Ref. 28)]. Using Eq. (8) and the fact that  $\gamma$  is small compared with  $(1/\kappa T_c)(dT_c/dp)$ , Eqs. (6) and (7) reduce to

$$\begin{aligned} \frac{d \ln \lambda}{d \ln V} &\approx \frac{d \ln N(E_F)}{d \ln V} \\ &\approx \left[ - \left( \frac{1}{\kappa T_c} \right) \left( \frac{dT_c}{dp} \right) \right] / \left[ \left( \ln \frac{\Theta}{T_c} \right) f(\lambda \mu^*) \right]. \end{aligned} \quad (9)$$

Smith<sup>29</sup> has recently shown that no correlation exists between Grüneisen parameters  $\gamma_c$  and the pressure derivatives of  $T_c$  in various samples of  $V_3\text{Si}$ . This lack of correlation gives additional support to the approximation of neglecting  $\gamma$  in Eq. (7).

As with extracting  $\lambda$  from  $T_c$  data, it is imperative to have specific forms for  $\Theta$  and  $g$  before  $d \ln \lambda / d \ln V$  can be obtained from the data using Eq. (9). With the McMillan formula, one has

$$\Theta = \Theta_D / 1.45$$

and

$$f(\lambda \mu^*) = \frac{(1 + 0.38 \mu^*)}{(1 + \lambda)(\lambda - \mu^* - 0.62 \lambda \mu^*)}, \quad (10)$$

while with the Birnboim formula

$$\Theta = 1.83 \Theta_D$$

and

$$f(\lambda \mu^*) = \frac{1 + 2.93 \mu^*}{(\lambda - 1.3 \mu^*)(1 + 2.25 \lambda)}. \quad (11)$$

Figure 7 shows the experimentally determined values of  $d \ln \lambda / d \ln V$  normalized to the value for

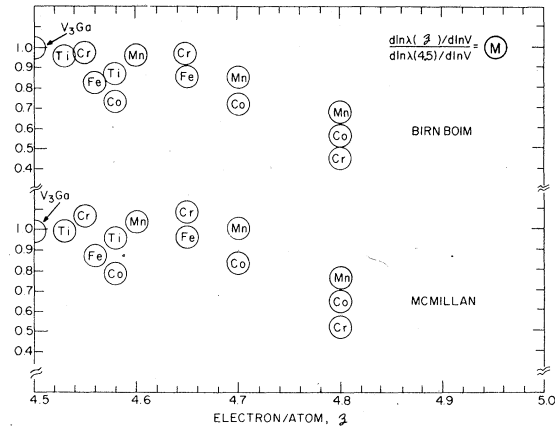


FIG. 7. Ratio of  $(d \ln \lambda / d \ln V) / [d \ln \lambda(4.5) / d \ln V]$  as determined by both the McMillan and Birnboim models.

$V_3\text{Ga}$ ,  $\beta = 4.5$ . Whereas the relative pressure derivatives increase with  $M$  additions, the strong  $\beta$  dependence of the normalizing function  $[\ln(\Theta/T_c)]f(\lambda \mu^*)$  causes the normalized relative derivatives, i.e.,  $d \ln \lambda / d \ln V$ , to remain approximately constant. The upper scale refers to the Birnboim analysis while the lower curve refers to the McMillan analysis. To within the scatter in the data there is no difference in the systematic variations of  $d \ln \lambda / d \ln V$  between the two approaches. The data show that  $d \ln \lambda / d \ln V$  is approximately constant until the  $\beta$  value becomes greater than 4.65 and then it begins to fall. As with  $T_c$ ,  $\beta$  appears the most appropriate parameter for describing the data since plots of  $d \ln \lambda / d \ln V$  against either  $x$  or  $a_0$  leads to families of curves whereas the  $\beta$  dependence is more universal to all  $M$  systems.

## CONCLUSIONS

The data on  $T_c$  and  $dT_c/dp$  presented here on the  $V_{75-x}M_x\text{Ga}_{25}$  alloy systems support the concept that the superconducting transition temperature is determined by a phonon-limited energy range for the attractive electron-phonon interaction and that sharp structure in the density-of-states curve has little effect on the functional form of the  $T_c$  equation. Our results show that, at least for the  $V_3\text{Ga}$ -based systems studied here,  $\lambda$  is directly related to  $N(E_F)$ , or perhaps more specifically for materials where  $N(E)$  varies rapidly with energy near  $E_F$ , to a density of states averaged over a typical phonon energy range in a manner as suggested by Nettle.<sup>20</sup> Likewise, it is suggested that for such a system, the volume derivative of  $\bar{\lambda}$  should be

TABLE III. Values of  $\lambda$  and  $d \ln \lambda / d \ln V$  for various  $\Theta_D$  and  $\mu^*$  according to the McMillan (*M*) and Birnboim (*B*) models.  $T_c(V_3Ga) = 14.1$  K.

$\mu^*$	$\Theta_D = 310$ K				$\Theta_D = 350$ K			
	$\lambda$	$\lambda$	$-d \ln \lambda / d \ln V$	$-d \ln \lambda / d \ln V$	$\lambda$	$\lambda$	$-d \ln \lambda / d \ln V$	$-d \ln \lambda / d \ln V$
	<i>M</i>	<i>B</i>	<i>M</i>	<i>B</i>	<i>M</i>	<i>B</i>	<i>M</i>	<i>B</i>
0.05	0.74	1.19	3.2	4.7	0.69	1.08	3.0	4.2
0.10	0.87	1.40	3.1	4.5	0.82	1.28	2.9	4.0
0.15	1.01	1.61	3.0	4.3	0.95	1.47	2.8	3.9

dominated by the volume derivative of  $\bar{N}(E_F)$ .

Determinations of  $\lambda$  from  $T_c$  as well as the determination of  $d \ln \lambda / d \ln V$  depend on the particular  $T_c$  equation employed. A comparison of McMillan's equation to that suggested recently by Birnboim show that the two equations behave in a similar systematic manner. Absolute values for  $\lambda$  and  $d \ln \lambda / d \ln V$  are, however, quite different for the two models. Table III lists values of  $\lambda$  and  $d \ln \lambda / d \ln V$  for  $V_3Ga$  determined by the two equations for several values of  $\Theta_D$  and  $\mu^*$ . Theoretical cal-

culations of  $\lambda$  and  $d \ln \lambda / d \ln V$  should be able to distinguish between the two models since the values differ significantly.

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