Debye approximation is determined by

$$G(\vec{n}_* - \vec{n}'_*) = \frac{a^2}{2\pi}\int_0^{k_{\max}} \frac{J_0\{k_* |\vec{n}_* - \vec{n}'_*|\}}{\omega_k^2 - \omega^{2+}} k_*\, dk_* .$$

For $(\vec{n}_* - \vec{n}'_*) \to \infty$,

$$J_0\{k_* |\vec{n}_* - \vec{n}'_*|\} = \left(\frac{2}{\pi k_* |\vec{n}_* - \vec{n}'_*|}\right)^{1/2}$$

$$\times \cos\{k_* |\vec{n}_* - \vec{n}'_*| - \tfrac{1}{4}\pi\} .$$

Thus, after replacing the upper limit by ∞,

$$G^+(\vec{n}_* - \vec{n}'_*) = \frac{e^{i\pi/4} e^{ik_* n_*}}{2\eta(2\pi k_* n_*)^{1/2}}\, e^{i\vec{q}_*\cdot\vec{n}'_*} , \qquad \text{(A9)}$$

where $n_* \gg n'_*$, and $\vec{q}_* = (k_*/n_*)\vec{n}_*$ is a vector of magnitude $|k_*|$ in the direction of the radius vector $\vec{n}_*$.

---

[1] V. L. Bonch-Breuevich and V. B. Glasko, Fiz. Tverd. Tela 3, 36 (1960) [Soviet Phys. Solid State 3, 26 (1961)].

[2] I. Kobori, Progr. Theoret. Phys. (Kyoto) 33, 614 (1965).

[3] O. Litzman and K. Kunc, J. Phys. Chem. Solids 26, 1825 (1966).

[4] W. Ludwig, in *Theory of Crystal Defects* (Academica, Prague, 1966).

[5] R. A. Brown, Phys. Rev. 156, 692 (1967).

[6] R. A. Brown, Phys. Rev. 156, 889 (1967).

[7] O. Litzman and J. Cely, Czech. J. Phys. B18, 847 (1968).

[8] K. Ohashi, J. Phys. Soc. Japan 24, 437 (1968).

[9] R. L. Sproull, M. Moss, and H. Weinstock, J. Appl. Phys. 30, 334 (1959).

[10] M. Moss, J. Appl. Phys. 36, 3308 (1965).

[11] A. Taylor, H. R. Alberts, and R. O. Pohl, J. Appl. Phys. 36, 2270 (1965).

[12] P. G. Klemens, Proc. Phys. Soc. A68, 1113 (1955).

[13] P. Carruthers, Rev. Mod. Phys. 33, 92 (1961).

[14] P. Charsley and J. A. M. Salter, Phys. Status Solidi 9, K101 (1965).

[15] W. R. G. Kemp, P. G. Klemens, and R. J. Tonish, Phil. Mag. 4, 845 (1959).

[16] J. N. Lower and H. M. Rosenberg, Phil. Mag. 4, 467 (1969).

[17] Bal Krishna Agrawal, J. Phys. C 3, 1002 (1970).

[18] A. Granato, Phys. Rev. 111, 740 (1958).

[19] Bal Krishna Agrawal, J. Phys. C 2, 252 (1969).

[20] Bal Krishna Agrawal, Phys. Rev. 186, 712 (1969).

[21] R. H. Chambers, Appl. Phys. Letters 2, 165 (1963).

[22] C. L. Bauer and R. B. Gordon, J. Appl. Phys. 33, 672 (1962).

[23] M. Kusunoki and H. Suzuki, J. Phys. Soc. Japan 26, 932 (1969).

[24] B. R. Felix, L. Passell, and H. B. Silsbee, Phys. Rev. 100, A1808 (1955).

[25] G. M. Graham, Proc. Roy. Soc. (London) 248, 522 (1958).

[26] R. Zeyfang, Phys. Status Solidi 24, 221 (1967).

[27] P. Gruner and H. Bross, Phys. Rev. 172, 583 (1968).

[28] P. D. Mannheim, Phys. Rev. 165, 1011 (1968).

[29] G. Benedek and G. F. Nardelli, Phys. Rev. 155, 1004 (1967).

[30] A. K. Srivastava and Bal K. Agrawal, J. Phys. C 3, L20 (1970).

[31] M. D. Tiwari, Phys. Letters 32A, 213 (1970).

PHYSICAL REVIEW B VOLUME 3, NUMBER 6 15 MARCH 1971

Electronic Specific Heats and Superconductivity in the Group-V Transition Metals*

M. Ishikawa and Louis E. Toth
Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455

(Received 9 June 1970; revised manuscript received 14 September 1970)

Electronic specific heats of Nb-V alloys were measured from 1.5 to 14 °K and on the basis of these measurements superconductivity parameters were calculated. Both the McMillan and the Hopfield theories were used to try to understand the cause of the broad minimum in T_c with alloying composition. The McMillan theory indicates that the cause is due to a weakening of the electron-phonon interaction parameter. The Hopfield theory could not adequately predict the existence of the minimum in these alloys.

I. INTRODUCTION

The superconducting behavior of Nb-V solid-solution alloys is unusual. Whereas the superconducting transition temperatures of Nb and V are both relatively high, 9.2 and 5.5 °K, respectively, the variation of T_c in the alloys goes through a pronounced minimum at a composition of about $Nb_{0.50}V_{0.50}$. The effect cannot be correlated with Matthias's *e/a* factor, since both Nb and V belong to group 5. This minimum, furthermore, occurs in solid solutions of compounds in which Nb and V are the principal constituents. For example, in NbN-VN solid solutions with the NaCl crystal structure, the T_c of $(NbN)_{0.5}(VN)_{0.5}$ is only 2 °K compared to a T_c of 17.3 °K for NbN and 8.5 °K for VN.[1]

In order to understand the cause of this minimum, low-temperature specific heats were measured in order to determine γ and Θ_D values which were then used to calculate electron-photon interaction parameters V_{ph}. These parameters were also calculated for Nb-Ta alloys by using the low-temperature specific-heat data of Corsan and Cook.[2] Both the theories of McMillan[3] and Hopfield[4] were used to interpret the data. The McMillan theory explains the minimum in T_c in the alloys by a rapid decrease in V_{ph} as Nb is alloyed with V. The Hopfield theory could not be used to explain the broad minimum. In fact, this theory predicts a maximum in T_c in Nb-V alloys.

II. EXPERIMENTAL

All samples were prepared by arc melting under a pure argon atmosphere and by homogenizing for several hours at temperatures between 1330 and 1980 °C in a vacuum of about 2×10^{-5} mm Hg. The starting materials were niobium −325 mesh powder, obtained from the Wah Chang Corp., Albany Ore., and vanadium lumps, from the United Mineral & Chemical Corp., N. Y. Their chemical analyses are listed in Table I.

The lattice parameters were measured with a diffractometer using Fe radiation. The results were in fairly good agreement with the literature values.[5] The relatively sharp superconducting T_c's indicated that the homogeneity of the samples was good.

Low-temperature specific heats were measured from 1.5 to 15 °K with an adiabatic calorimeter. The operation and calibration of this instrument is described elsewhere.[6] Magnetic fields of 10- to 11.5-kG magnet were applied to quench the super conducting state in the high T_c alloys (Nb, $Nb_{0.90}V_{0.10}$, V).

TABLE I. Chemical analyses of starting materials.

Nb (in ppm)							
Al	<20	Cu	<40	Mo	<20	Ta	300
B	<1	Fe	<50	N	55	Ti	<40
C	<40	H	20	Ni	<20	V	<20
Cd	<5	Hf	<80	O	1320	W	210
Co	<10	Mg	<20	Pb	<20	Zr	100
Cr	<20	Mn	<20	Si	<50	Sn	<10
V (metallic impurities only) (in ppm)							
Al	92						
Fe	<50						
Mg	35						
Mo	<20						
Si	188						

III. RESULTS AND DISCUSSION

The experimental C_p data are shown in Fig. 1. Values of γ, T_c, and Θ_D, as determined from the graphs of C_p/T vs T^2 and the least-squares analysis of the data in the temperature range 2–7 °K, are given in Table II and also Fig. 2. Similar data for the Nb-Ta system, as reported by Corsan and Cook[2] are also shown in Fig. 2. The temperature dependence of Θ_D for V and Nb, as calculated from the ratio $(C_p-\gamma T)/T^3$, agrees very well with earlier literature reports.[7,8] Θ_D remains constant to 2.5 and 3.0 °K, respectively, and at slightly higher temperatures an abrupt decrease occurs.

The observed T_c behavior in these alloy systems is unusual. Although we did not study dilute solutions of V or Ta in Nb, the present data indicate a sharp peak in T_c at the pure Nb composition. There is a much smaller but similar effect in the variation of γ values. The variation of γ and Θ_D in the Nb-V alloy system, in general, runs opposite the T_c behavior. Furthermore, on the basis of γ and Θ_D values alone, one would expect a higher T_c for V than for Nb, which, in fact, does not occur.

The variation of T_c with composition was analyzed with both the McMillan and Hopfield theories. The McMillan theory[3] enables one to calculate the electron-phonon interaction parameter from knowledge of γ, Θ_D, and T_c. According to McMillan, T_c is given by

$$T_c = (\Theta_D/1.45)e^{-1/g},$$

with

$$g = \frac{N(0)\{V_{ph} - V_C^*[1+0.62N(0)V_{ph}]\}}{1.04[1+N(0)V_{ph}]}.$$

Here $N(0)$ is the "bare" density of states or the band-structure density of states. $N(0)$ is related to the measured value of γ by the expression[9]

$$\gamma = \gamma_0[1+N(0)V_{ph}] = \tfrac{2}{3}\pi^2 k_B^2 N(0)[1+N(0)V_{ph}].$$

The product $N(0)V_C^*$ is the Coulomb pseudopotential of Morel and Anderson.[10]

In order to evaluate $N(0)$ and V_{ph} from the measured values of γ, Θ_D, and T_c, it is customary to assume that $N(0)V_C^*$ equals 0.13.[3] We show below that other experimental data support this assumption. Furthermore, the calculated values of $N(0)$ and V_{ph} do not depend critically upon the choice of $N(0)V_C^*$. Assuming then the 0.13 value, we show in Fig. 3 the variation of V_{ph} and $N(0)$ with composition in the V-Nb and Nb-Ta alloys. In calculating the parameters for Nb-Ta alloys we used the data of Corsan and Cook.[2] We decided, however, to modify their Θ_D values to those along the dotted line

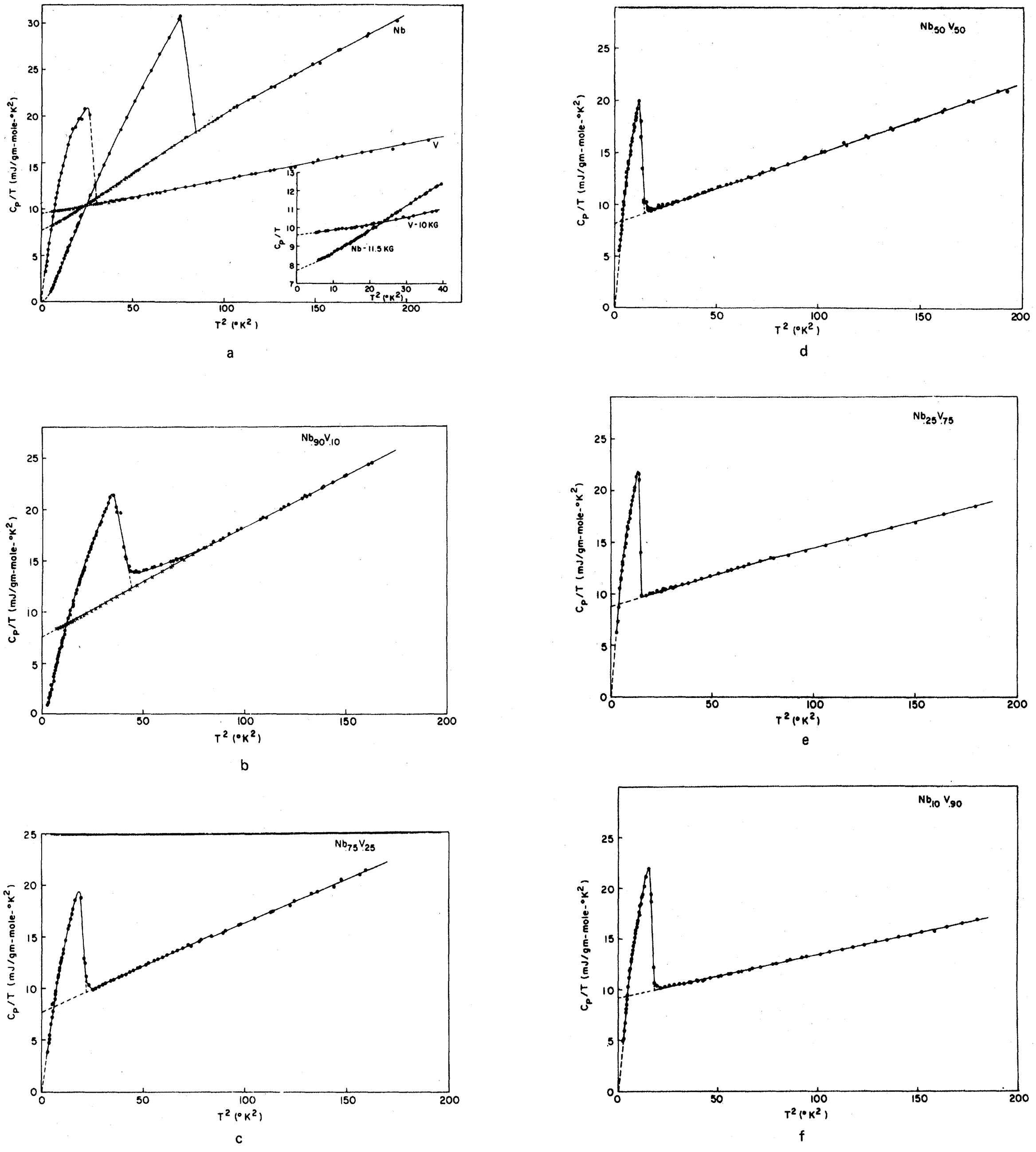

FIG. 1. Low-temperature specific heats of Nb-V alloys.

in Fig. 2. Their value of Θ_D for Nb is considerably smaller than the present value and other literature values. We therefore took Θ_D values corresponding to the dotted line in Fig. 2.

There are two interesting features of the above analysis as shown in Fig. 3. First, the variation of $N(0)$ or γ_0 with composition is nearly linear, decreasing almost monotonically from V to Nb to Ta. The observed values for $N(0)$ for V, Nb, and Ta were 1.28, 0.90, and 0.75 (eV atom)$^{-1}$, respectively. These values are in fairly good agreement with Mattheiss's augmented-plane-wave (APW) calculations.[11] The observed compositional variation for $N(0)$ is in agreement with susceptibility measurements,[12,13] which also vary in a nearly linear manner. This linear variation indicates that no drastic changes in the band structure occur with alloying. It is also clear that the observed variation for T_c cannot be correlated with the variation for $N(0)$.

The second interesting feature of Fig. 3 is the rapid decrease in V_{ph} when Nb is alloyed with V. The variation of V_{ph} is similar to that of T_c in the

TABLE II. Values of γ, Θ_D, and T_c for Nb-V alloys.

at.% Nb	γ (mJ mole^{-1}K^{-2})	Θ_D(°K)	T_c (°K)
0	9.63	423.0	5.52
10	9.23	361.4	4.25
25	8.80	319.5	3.87
50	8.16	305.3	3.85
75	7.65	278.1	4.70
90	7.42	263.0	6.69
100	7.72	277.0	9.18

Nb-V system. The pronounced minimum in T_c results from the rapid and nonlinear decrease in V_{ph} as V is added to Nb. In the Nb-Ta alloys, V_{ph} is nearly constant and T_c decreases with increasing Ta content because of decreasing $N(0)$ values. One possible explanation for the lower V_{ph} value in V is that the d band in V is narrower than it is in Nb or Ta.[11,14]

It is possible to show that the value of $N(0)\,V_C^*$ used above is consistent with other experimental data.[15] We may express V_C^* as[16]

$$V_C^* = \frac{V_C}{1 + N(0)\,V_C \ln(\epsilon_F / k_B \Theta_D)} ,$$

where V_C is the matrix element of the screened Coulomb interaction averaged over the Fermi surface, and ϵ_F is the Fermi energy. V_C is related to the spin paramagnetic susceptibility χ_s by[17]

$$\chi_s = 2\mu_B^2 N(0)/[1 - N(0)\,V_C] .$$

For this calculation, the spin paramagnetic susceptibility χ_s must be separated from the total measured susceptibility because the orbital contribution is known to be fairly large for transition metals.[18-20] Although this separation has not been performed for Nb-V alloys, Butterworth,[19] using nuclear-magnetic-resonance data for V, has shown that the spin contribution (4s-3d) is approximately 50% of the total magnetic susceptibility. Therefore, the value of χ_s for V was taken as[12] 143×10^{-6} emu/mole and all other values of χ_s were obtained by assuming the same ratio of χ_s to χ_{total} as that for V. Values of the Fermi energy ϵ_F were approximated by linearly interpolating between 6.8 eV for V[21] and 9.47 eV for Nb.[11] Following this procedure we found that $N(0)V_C^*$ was very nearly equal 0.13 for all Nb-V alloys as we had originally assumed.

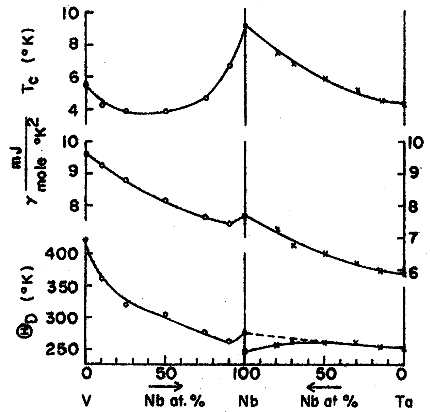

FIG. 2. Variations of γ, T_c, and Θ_D of V-Nb and Nb-Ta alloys.

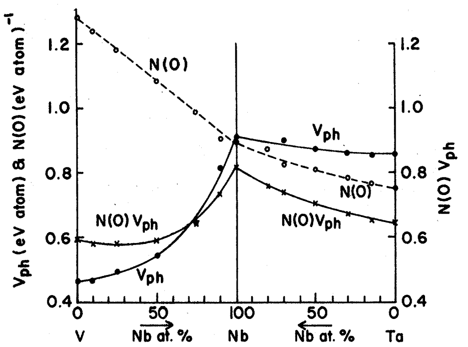

FIG. 3. Variations of V_{ph}, $N(O)\,V_{ph}$, and $N(O)$ calculated with McMillan's formula [with $N(O)\,V_C^* = 0.13$].

An attempt was made to analyze the data in terms of Hopfield's recent theory[4] for predicting T_c's on the basis of a short-range or strictly chemical property. In this theory $N(0)\,V_{ph}$ is given by the expression

$$N(0)V_{ph} = \eta / A \langle \Theta^2 \rangle ,$$

where A is the atomic number and $\langle \Theta^2 \rangle$ is an averaged squared phonon frequency expressed in units of temperature. Θ is correlated to the Debye temperature in these calculations. The parameter η is given by

$$\eta = \frac{1}{M_{\text{proton}}} \left(\frac{\hbar}{k_B} \right)^2 \left(\frac{d\mu}{dz} \right)^2 N_p(0) .$$

Here $d\mu/dz$ is a matrix element of the gradient of the atomic potential and it is assumed to be primarily a property of the atomic species involved; $N_p(0)$ is the density of p states at the Fermi level.

To predict T_c's in alloys, Hopfield first determines the parameters η and $\langle \Theta^2 \rangle$ for the component elements. $\langle \Theta^2 \rangle$ is determined from the phonon density of states given by McMillan[3] and then η is calculated from the experimental T_c with the McMillan formula for T_c and his assumed value of $N(0)V_C^*$. In alloys, η is assumed to vary linearly between component end points and $\langle \Theta^2 \rangle$ is related to the experimentally determined Θ_D values. Hopfield has successfully used his theory to show that maxima in T_c

TABLE III. Comparison of observed transition temperatures of Nb-V and Nb-Ta alloys with those calculated by the Hopfield theory. (Throughout these calculations, the present experimental values were used for T_c and Θ_D. For the parameter A, atomic weights were used instead of atomic numbers as in the Hopfield's calculations.)

Alloy	$\eta(10^6\,°K^2)$	T_c (calculated) (°K)	T_c (observed) (°K)
V	2.560	(5.52)	5.52
$V_{0.90}Nb_{0.10}$	2.677	10.14	4.25
$V_{0.75}Nb_{0.25}$	2.853	12.76	3.87
$V_{0.50}Nb_{0.50}$	3.146	11.08	3.85
$V_{0.25}Nb_{0.75}$	3.439	11.72	4.70
$V_{0.10}Nb_{0.90}$	3.614	12.23	6.69
Nb	3.731	(9.18)	9.18
$Nb_{0.80}Ta_{0.20}$	3.665	7.38	7.42
$Nb_{0.70}Ta_{0.30}$	3.631	7.00	6.80
$Nb_{0.50}Ta_{0.50}$	3.565	5.71	5.93
$Nb_{0.30}Ta_{0.70}$	3.498	4.57	5.15
$Nb_{0.15}Ta_{0.85}$	3.448	4.44	4.58
Ta	3.398	(4.33)	4.33

should occur in the Ti-Zr and Nb-Zr alloy systems, and to show that the proper T_c variations can be calculated in the Nb-Mo, Ta-W, and other systems.

Using Hopfield's suggested procedure, we calculated the T_c's for the Nb-V alloys. The results, given in Table III, show that the theory predicts a maximum in T_c in the alloys as opposed to the observed minimum.

It is rather difficult to find alloy systems in which a critical test can be made to distinguish between alternate theories for predicting T_c and to verify the Hopfield model. Hopfield argues that $N(0)$ is *not* the major parameter of interest in determining T_c but rather that $\langle\Theta^2\rangle$ is. Since $\langle\Theta^2\rangle$ has not been determined experimentally in most alloys, the variation of Θ_D in alloys becomes the means for predicting T_c. Qualitatively, a negative deviation of Θ_D from a linear behavior in binary alloys leads to a positive deviation in T_c as can be seen in Fig. 4. Unfortunately, it is difficult to separate the effects of Θ_D on T_c from those of γ on T_c in most alloy systems. The correlation between the variation of γ and T_c in the transition series has been noted by many investigators. A positive deviation of γ from a linear behavior in a binary solid solution is frequently accompanied by a positive deviation in T_c as can be seen from Figs. 4 and 5.[22]

When many binary alloy systems are studied, one finds that γ and Θ_D values for any one system generally vary with composition in an opposite manner[22]: A positive deviation of γ is usually accompanied by a negative deviation in Θ_D. Thus, for most binary solid solutions, the variation of Θ_D and γ would both predict the same type of behavior for T_c. Opposite variations of γ and Θ_D are found

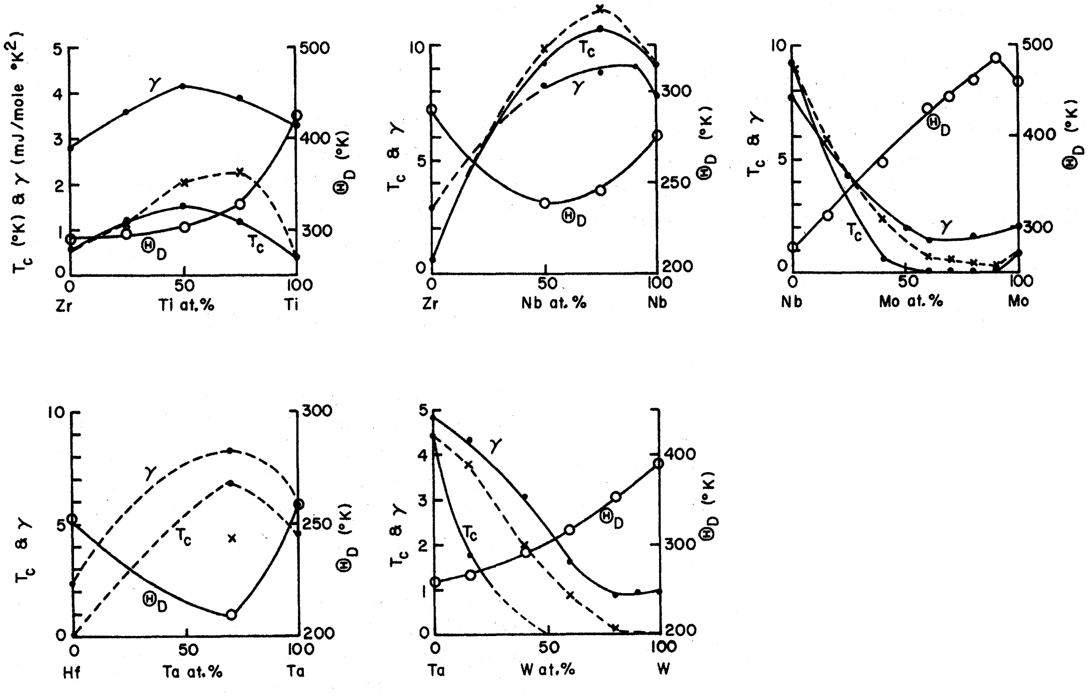

FIG. 4. Variation of T_c, γ, and Θ_D for several alloy systems. Both γ and T_c vary in the same general manner. In these systems positive deviations of γ from linear behavior are accompanied by negative deviations of Θ_D and vice versa. Hopfield's calculated values are denoted by X's and these values agree well with the experimental data.

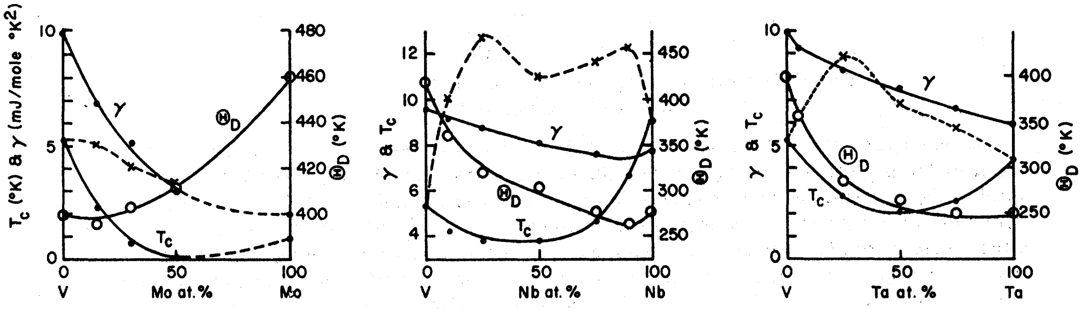

FIG. 5. In the V-Nb and V-Mo alloy systems, γ and Θ_D both show negative deviations from linear behavior. In these systems Hopfield's theory fails to predict adequately T_c. Hopfield's calculated values are denoted by X' s.

in the following alloy systems: Zr-Ti, Zr-Nb, Nb-Mo, Hf-Ta, and Ta-W (see Fig. 4). These systems were some of the ones used by Hopfield to substantiate his theory, but we maintain that such systems cannot adequately test the hypothesis, since they do not allow a separation of the effects on T_c of γ and Θ_D.

Several binary solid solutions can be found in which the variations Θ_D and γ with composition show the same type of deviation from linear behavior. These are Nb-V, Mo-V, and Ta-V . γ and Θ_D values and T_c's, both observed and calculated, are shown in Fig. 5. In the Mo-V and Ta-V alloys, the variation of calculated T_c's does not agree with the observed values. This discrepancy may again be due to the unusual nature of V or to the possibility that Θ_D is a poor indicator of $\langle\Theta^2\rangle$. In view of the objections raised by this experiment, however, it would be worthwile to investigate several other alloy systems to further test the theory.

While the Hopfield formula does not predict accurately the T_c's in the solid solutions of the Nb-V system, the theory does give a qualitative reason as to why $N(0)V_{\mathrm{ph}}$ is less for V than for Nb. The lower T_c in V may be due to the stiffer lattice for V as evidenced by the higher Θ_D value. Thus in the formula $N(0)V_{\mathrm{ph}}=\eta/A\langle\Theta^2\rangle$, the higher Θ_D or $\langle\Theta^2\rangle$ value reduces $N(0)V_{\mathrm{ph}}$ and thus T_c.

---

*Research sponsored by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, under AFOSR Grant No. 68-1369.

[1] L. E. Toth, *Transition Metal Carbides and Nitrides* (Academic, New York, to be published).

[2] J. M. Corsan and A. J. Cook, Phys. Letters 28A, 500 (1969).

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

[4] J. J. Hopfield, Phys. Rev. 186, 443 (1969).

[5] H. A. Wilhelm, O. N. Carlson, and J. M. Dickinson, J. Metals 6, 915 (1954).

[6] L. E. Toth, Technical Report No. AFOSR-68-0265, 1968 (unpublished); M. Ishikawa, M. S. thesis, University of Minnesota, 1968 (unpublished).

[7] E. Bucher, F. Heiniger, and J. Muller, in *Proceedings of the Ninth International Conference on Low Temperature Physics*, edited by J. G. Daunt *et al.* (Plenum, New York, 1965), p. 1059.

[8] B. J. C. van der Hoeven, Jr., and P. H. Keesom, Phys. Rev. 134, A1320 (1964).

[9] It was found that the enhancement due to spin fluctuations [N. F. Berk and J. R. Schrieffer, Phys. Rev. Letters 17, 433 (1966); in *Proceedings of the Tenth International Conference on Low Temperature Physics* (Vimiti, Moscow, USSR, 1967), Vol. II A] is not important for these alloys compared with the phonon enhancement, as expected for transition metals in the central portion in the Periodic Table.

[10] P. Morel and P. W. Anderson, Phys. Rev. 125, 1263 (1962).

[11] L. F. Mattheiss, Phys. Rev. B 1, 373 (1970).

[12] D. J. Lam, J. J. Spokas, and D. O. Van Ostenburg, Phys. Rev. 156, 735 (1967).

[13] S. Taniguchi, R. S. Tebble, and D. E. G. Williams, Proc. Roy. Soc. (London) A265, 502 (1962).

[14] T. K. Mitra, J. Phys. C 2, 52 (1969).

[15] K. Andres, E. Bucher, J. P. Maita, and R. C. Sherwood, Phys. Rev. 178, 702 (1969).

[16] J. R. Schrieffer, *Theory of Superconductivity* (Benjamin, New York, 1964).

[17] G. Gladstone, M. A. Jensen, and J. R. Schrieffer, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), Vol. 2.

[18] W. Hume-Rothery, in *Electronic Structure and Alloy Chemistry of the Transition Elements*, edited by P. A. Beck (AIME, New York, 1963).

[19] J. Butterworth, Proc. Phys. Soc. (London) 83, 71 (1964).

[20] A. M. Clogston, A. C. Gossard, V. Jaccarino, and Y. Yafet, Phys. Rev. Letters 9, 262 (1962).

[21] L. F. Mattheiss, Phys. Rev. 134, A970 (1964).

[22] F. Heiniger, E. Bucher, and J. Muller, Physik Kondensierten Materie 5, 243 (1966).