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Superconducting transition temperature and pressure effect in bcc transition metals

A. Birnboim

The Racah Institute of Physics, The Hebrew University of Jerusalem, Jerusalem, Israel

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A previous calculation of the superconducting transition temperature T_c in a strong-coupling localized formulation that was performed on V, Nb, and Ta is extended to bcc transition-metal alloys in the $3d$, $4d$, $5d$ rows of the periodic table, giving a nice quantitative agreement with experiment. The pressure dependence of T_c for some elements and for Zr-Nb-Mo alloys is calculated and compared with experiment.

I. INTRODUCTION

In two previous papers[1,2] (hereafter referred to as I and II) we developed a model for the calculation of the superconducting transition temperature T_c for transition metals. The theory was based on a transformation of the electron-phonon interaction from the usual Bloch formulation to the Wannier representation[3] in order to take advantage of the localized nature of the d functions that are responsible for superconductivity in these elements. We refer the interested reader to these papers for a detailed description of the calculations and assumptions involved. The main result concerning the present paper is the solution of the Eliashberg[4] equations with a modified kernel appropriate to the localized description. It was shown that T_c for various electron-phonon coupling constants λ, Coulomb pseudopotentials μ^*, and three different phonon spectra is well described by the function

$$T_c = 1.78\omega_0 \exp\left(\frac{1.13[1+\lambda+\bar{\lambda}(T_c)]}{\lambda - 1.3\mu^*}\right), \tag{1}$$

$$\lambda = \frac{N(0)J^2}{M}\int \frac{d\nu F(\nu)}{\nu^2} \equiv \frac{N(0)J^2}{M}\langle \nu^{-2}\rangle, \tag{2}$$

$$\bar{\lambda}(T_c) = \frac{N(0)J^2}{M}\int \frac{d\nu F(\nu)}{\nu^2}\ln\frac{\nu+\omega_0}{\nu + T_c/1.134}, \tag{3}$$

where ω_0 is the maximum frequency of the phonon spectrum $F(\nu)$. $N(0)$ is the density of states per spin at the Fermi surface, M is the atomic mass, and J^2 is a given combination of the matrix elements of the ionic potential gradient between electronic wave functions centered on the neighboring ions. (There is no need for the usual averaging over the Fermi surface.)

Equations (1)–(3) are the localized analog to the form suggested by Leavens[5] to McMillan's[6] formula in order to account better for the details of the phonon spectrum and which is closely related[7] to the logarithmic phonon average proposed by Allen and Dynes. The accuracy of these equations is illustrated in Fig. 2 of II.

The proposed model for calculating λ using fundamental properties of a metal such as its phonon spectrum, band structure, and specific-heat constant gave without the use of any adjustable parameter values for λ of V, Nb, Ta that were 1.5 times bigger than those obtained from the inversion of Eq. (1) with the experimental T_c of these elements.

We note here that the importance of the localized atomic properties in determining λ in transition metals was first pointed out by Hopfield[8] and further developed in a series of papers by Evans *et al.*[9] Their formalism looks different because they expand the wave functions in spherical harmonics around the origin and express $N(0)J^2$ by the various phase shifts, densities of states, and the Fermi energy. The equivalence of resonance and tight-binding descriptions of the d bands in transition metals was recently discussed by Moriarty.[10] Such an equivalence also exists in the calculation of the electron-phonon coupling constant and we shall show in the near future[11] that for a suitable choice of the asymptotic form of the atomic wave function, one obtains in a tight-binding calculation the same functional form for $N(0)J^2$ as that given by Evans *et al.* from their phase-shift formalism. The modifications that would appear in this expression if one calculates λ in the rigid-ion approximation proposed by Frohlich and Mitra[12] and Barisic[13] and adopted in II will also be discussed there.

An important advantage of the model described in II, is that it enables to obtain J^2 directly from the band structure (by algebraic operations) without explicitly calculating the transfer integrals. This procedure is particularly suitable for the discussion of the variation of T_c along the rows of the Periodic Table —the so-called Matthias[14] rule— which is the purpose of the present paper. As the calculations in I and II are based on bcc lattices, our discussion here will be restricted to such alloys only, which means that the number of electrons per atom, Z, varies in the interval $4.5 \lesssim Z$

TABLE I. Several phonon averages used in obtaining Eq. (4) as described in the text.

	a	b (°K^{-1})	ω_0/Θ_D	$\Theta_D/(1/\langle\nu^{-2}\rangle)^{1/2}$
V	1.27	0.0057	1.03	1.88
Nb	1.37	0.0095	1.11	1.77
Ta	1.18	0.0083	0.95	1.78
Average	1.27	···	1.03	1.81

$\lesssim 6.5$. In spite of this, much insight may be gained from this partial group, as the experimental T_c, in the $4d$ row, say, varies in this neighborhood from 10.8 °K ($Z \simeq 4.75$) to 0.016 °K ($Z = 5.7$) and back to 12.6 °K ($Z = 6.5$).

The ideal situation would be if we had band structures, phonon spectra and specific-heat measurements for different values of Z. However, as the experimental situation is far from that ideal, one has to deduce approximate information from more measurable properties such as the Debye temperature Θ_D, lattice spacing, etc. In Sec. II we construct a model for calculating the variation of T_c in a given row where the variation of J^2 is deduced from lattice spacing and the variation of $\langle\nu^{-2}\rangle$ from Θ_D. The basic approach is to use a minimal number of adjustable parameters. This line is followed also in Secs. III and IV where we present attempts to account for the interesting pressure dependence of T_c in transition-metal elements and alloys. As the influence of pressure on T_c is very complicated,[15] the *a priori* chance to get a reasonable fit to experiment in a simple model seems small. From this point of view the agreement with experiment obtained in these sections is encouraging. Section V is devoted to a discussion.

II. TRANSITION TEMPERATURE IN bcc ALLOYS

We want to bring Eqs. (1)–(3) to an approximate form which will enable us to calculate T_c for a continuum of alloys without needing all the details of the phonon spectrum and band structure of each alloy.

We expand $\bar{\lambda}(T_c)$ defined in Eq. (3) in T_c/ν (for not too soft phonons) and get

$$\bar{\lambda}(T_c) = \bar{\lambda}(T_c = 0) - \frac{N(0)J^2}{1.13M}\, T_c \int \frac{d\nu\, F(\nu)}{\nu^3}$$
$$\equiv \lambda(a - bT_c)\,.$$

The ratio $\bar{\lambda}(T_c)/\lambda$ may be computed directly for a given phonon spectrum and indeed we find it to decrease linearly with T_c, where the constants a, b for V, Nb, Ta are given in Table I. As b is small we have for $T_c \lesssim 10$ °K

$$1 + \lambda + \bar{\lambda}(T_c) = 1 + \lambda(1 + a - bT_c)$$
$$\lesssim 1 + \lambda(1 + a) \simeq 1 + 2.25\lambda\,.$$

The relations between Θ_D and ω_0 and $\langle\nu^{-2}\rangle$ are also given in Table I. The fact that $\Theta_D/(1/\langle\nu^{-2}\rangle)^{1/2}$ is nearly equal for the three elements suggests that we use the average value, which is close to $\sqrt{3}$, as predicted by the Debye model, to approximate

$$\lambda = \frac{N(0)J^2}{M} \int \frac{d\nu\, F(\nu)}{\nu^2} \simeq \left(\frac{1.81}{\Theta_D}\right)^2 \frac{N(0)J^2}{M}$$

(especially if we remember that V and Ta have significantly different phonon spectra and Debye temperatures).

By performing a similar scaling for ω_0 we obtain the approximate formula for T_c

$$T_c = 1.83\Theta_D \exp\left(\frac{-1.13(1 + 2.25\lambda)}{\lambda - 1.3\mu^*}\right)\,, \tag{4}$$

with λ defined above.

$N(0)$ is determined self-consistently with the final value of λ from the specific-heat coefficient Γ as described in II, i.e.,

$$\lambda = \tfrac{1}{2}\left[-1 + (1 + c\Gamma J^2/M\Theta_D^2)^{1/2}\right]\,, \tag{5}$$

where c is a constant.

A model for extracting J^2 from the band structure was presented in II. Gathering the formulas given there we obtain from nearest neighbors in a bcc lattice

$$\begin{aligned} J^2 &= \tfrac{16}{3}(5C_1^2 + 2C_2^2 + 2C_3^2)\,, \\ C_1 &= A(14 + 8x + 2x^2 + \tfrac{1}{3}x^3)\,, \\ C_2 &= A(2 + \tfrac{1}{3}x^3)\,, \\ C_3 &= A(-10 - 2x + x^2 + \tfrac{1}{3}x^3)\,, \\ A &= -\tfrac{1}{9}\sqrt{3}\,(B/\rho^4)\,e^{-x}\,; \quad x = Q\rho \end{aligned} \tag{6}$$

where ρ is the distance to the nearest neighbor, B is a certain atomic integral, and Q describes the exponential decay of the atomic wave function at large distance. In II B and Q were chosen to fit augmented-plane-wave band-structure calculations at high-symmetry points. As B and Q are atomic properties we assume that they do not change too much in this part of the periodic table where the crystal structure is bcc and use for the $3d, 4d, 5d$ rows the values we had in II for V, Nb, Ta, respectively. With this assumption we obtain J^2 for each alloy in the row from its lattice constant.

Thus we have a method to calculate λ and T_c for each alloy in a certain region of the Periodic Table using its lattice constant, specific-heat coefficient, atomic weight, and Debye temperature. We assume it to be a reasonable model for describing superconductivity in transition-metal alloys. As we had not used any adjust-

TABLE II. Quantities used in calculating λ and T_c in the $4d$ row of the Periodic Table.

Alloy	Lattice const (Å)	Θ_D(°K)	Γ (mJ/mole °K^2)	$10^{-2}\,J^2$ (a.u.)	λ	T_c (°K)	T_c^{exp} (°K)
$Zr_{0.5}Nb_{0.5}$	3.447	238	8.3	0.635	1.186	6.036	9.3
$Zr_{0.25}Nb_{0.75}$	3.375	246	8.9	0.826	1.403	8.727	10.8
Nb	3.306	277	7.8	1.067	1.302	(9.22)	9.22
$Nb_{0.85}Mo_{0.15}$	3.279	312	6.3	1.181	1.031	7.043	5.85
$Nb_{0.60}Mo_{0.40}$	3.232	371	2.87	1.409	0.522	1.797	0.60
$Nb_{0.40}Mo_{0.60}$	3.203	429	1.62	1.573	0.288	0.140	0.05
$Nb_{0.30}Mo_{0.70}$	3.190	442	1.46	1.653	0.261	0.080	0.016
$Nb_{0.20}Mo_{0.80}$	3.173	461	1.49	1.763	0.260	0.076	0.095
$Nb_{0.10}Mo_{0.90}$	3.160	487	1.67	1.853	0.270	0.081	0.30
Mo	3.146	460	1.83	1.955	0.332	0.352	0.92
$Mo_{0.5}Tc_{0.5}$	3.109	300	4.6	2.255	1.308	13.146	12.6

able parameter we got in II values of λ which were somewhat too big, and we correct this systematic deviation by multiplying J^2 by a constant factor such that we get the experimental T_c for the $Z=5$ element. Now, there exists a variety of empirical data for Θ_D and Γ and it is possible to improve the agreement with experiment by using data from different sources. In order to be consistent we always used the data used by McMillan.[6] (We changed only the $\Theta_D = 265$ °K of $Nb_{0.85}Mo_{0.15}$ which looks like a local minimum in McMillan's table. As it is clear[16] that Θ_D is monotonic in this region we choose $\Theta_D = 312$ °K following Hopfield.[8]) The lattice constants were taken from Ref. 17, the atomic mass and the number of electrons per atom were taken as the weighted averages of the elements constituting the alloy. The different quantities used in our calculation for the $4d$ row are given in Table II together with the calculated values of λ.

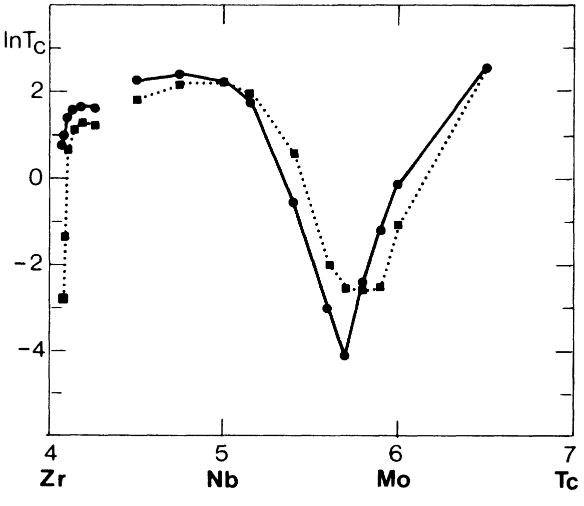

FIG. 1. Experimental (dots) and calculated (squares) values of $\ln T_c$ vs the number of electrons per atom, Z, in the $4d$ row of the Periodic Table. The points with $4.07 \leq Z \leq 4.26$ represent data of Zr-Mo alloys (Ref. 35).

For elements with small values of λ the calculated T_c is governed by the model used to describe the Coulomb pseudopotential μ^*. If, following McMillan,[6] we assume a constant μ^* we get for $Z \approx 5.7$, T_c of about 10^{-4} °K. Following Jensen,[18] we write $\mu^* = N(0)U_c$, where U_c is approximately constant along the row, and is chosen so that we get $\mu^* = 0.149$ for Nb as in Ref. 6, i.e., for a $4d$ alloy with certain λ and Γ,

$$\mu^* = 0.149\,(\Gamma/\Gamma_{\text{Nb}})(1+\lambda_{\text{Nb}})/(1+\lambda).$$

The results thus obtained for T_c are given in Table II and plotted in Fig. 1 versus Z on a semilogarithmic scale which emphasizes the agreement with experiment also for low values of T_c.

The agreement between the calculated and experimental values is astonishing if we remember that we used a very simple model and a single parameter that adjusted the T_c value of Nb. Similar quantitative agreement is obtained for the $3d$ and $5d$ rows as may be seen from Figs. 2 and 3, though the curves are less representative there,

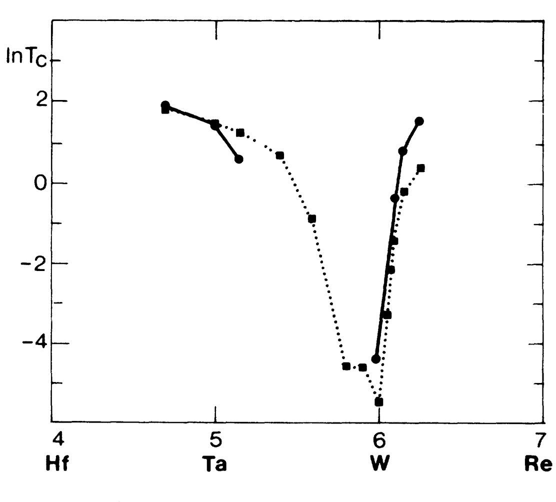

FIG. 2. Same as Fig. 1, for $5d$ alloys.

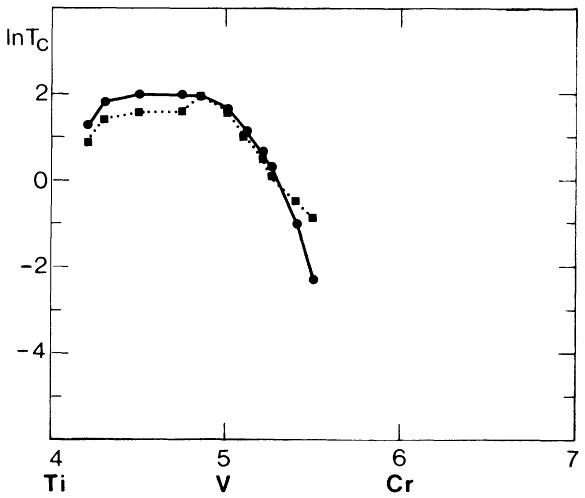

FIG. 3. Same as Fig. 1, for $3d$ alloys.

because of the small number of experimental points, especially for $3d$ alloys that become magnetic for $Z \geq 5.5$.

From Table II it becomes clear why T_c in the "central transition metals" follows qualitatively the specific-heat coefficient Γ. By passing from $Z=4.5$ to $Z=6$, J^2 increases by a factor of ~ 3, while Θ_D^2 increases by a factor of ~4, thus the ratio J^2/Θ_D^2 appearing in λ is essentially constant and λ is mainly determined by $N(0)$, i.e., Γ via Eq. (5). However, the other quantities are still important. For example, the last point, namely $Mo_{0.5}Tc_{0.5}$, has a higher value of T_c than Nb, say, which has higher Γ, and this is a consequence of its having a much larger value for J^2 than Nb. Compared to M_0, which has a similar value of J^2, this alloy has a much higher T_c, both because of its larger Γ and because of its relatively low Θ_D, which is connected with the instability associated with the change of lattice symmetry in this vicinity.

We note here that the last statement does not contradict the conclusion of Evans *et al.*[9] about the approximate constancy of $N(0)J^2$ because of the inverse correlation between $N(0)$ and Θ_D.[18] Thus we may equally well say that T_c in transition metals is determined by the phonon properties [a constant $N(0)J^2$], or by the electronic density of states (a constant J^2/Θ_D^2).

III. PRESSURE EFFECT OF ELEMENTS

As is well known the pressure effect of transition metals differs from that of nontransition metals in that it may be a small negative effect or even a positive one. The difficulty in understanding the influence of pressure lies in the fact that one has to account for its simultaneous effect on many quantities, none of which is fully understood in these materials. In the model we introduced in I, II, and the previous Sec. I and II, there is a decoupling between the phonon and electronic contributions to λ, and it enables us to distinguish between changes in T_c caused by electronic or phonon properties. In this section we illustrate this point by using the changes observed experimentally in T_c and lattice properties under pressure, to deduce the changes in the electronic behavior represented by $N(0)J^2 \equiv \eta$, and comparing to the predictions of our model.

We write Eq. (4) as

$$T_c = 1.83\Theta_D e^{-1/K}, \tag{7}$$

$$K = (\lambda - 1.3\mu^*)/1.13(1+2.25\lambda), \tag{8}$$

and differentiate (7) with respect to volume,

$$\frac{d\ln K}{d\ln V} = \left[\ln\left(\frac{1.83\Theta_D}{T_c}\right)\right]^{-1}\left(-\frac{1}{\chi T_c}\frac{dT_c}{dP} + \xi\right), \tag{9}$$

where χ is the isothermal compressibility and $\xi = -d\ln\Theta_D/d\ln V$ is the lattice Grüneisen parameter.[19] Differentiating (8), neglecting the dependence of μ^* on pressure, we have

$$\frac{d\ln K}{d\ln V} = f(\lambda,\mu^*)\frac{d\ln\lambda}{d\ln V},$$

$$f(\lambda,\mu^*) = \frac{\lambda(1+2.25\times 1.3\mu^*)}{(\lambda - 1.3\mu^*)(1+2.25\lambda)}, \tag{10}$$

where from (2)

$$\frac{d\ln\lambda}{d\ln V} = \frac{d\ln J^2}{d\ln V} + \frac{d\ln N(0)}{d\ln V} + \frac{d\ln\langle\nu^{-2}\rangle}{d\ln V}$$

$$= \frac{d\ln\eta}{d\ln V} + 2\gamma(-2), \tag{11}$$

where[20]

$$\gamma(n) = -\frac{1}{n}\frac{d\ln\langle\nu^n\rangle}{d\ln V}.$$

From (9)–(11) we get

$$\frac{d\ln\eta}{d\ln V} = \left(\xi - \frac{dT_c}{dP}\Big/\chi T_c\right)\left[\ln\left(\frac{1.83\Theta_D}{T_c}\right)f(\lambda,\mu^*)\right]^{-1} - 2\gamma(-2). \tag{12}$$

One finds in the literature a variety of values for the Grüneisen constants. Many measurements were performed at temperatures that are not low enough, and the distinction between lattice and electronic contributions is impossible. In such measurements one gets a total Grüneisen constant from the ratio of the total thermal-expansion coefficient to the total heat capacity. In other mea-

TABLE III. Comparison between the empirical (emp), calculated by the model (calc), and the directly calculated (dir) $d\ln\eta/d\ln V$, for several transition-metal elements.

Element	λ	ξ (Ref. 19)	$\left(\frac{d\ln\eta}{d\ln V}\right)^{\text{emp}}$	γ_{el} (Ref. 19)	$\left(\frac{d\ln J^2}{d\ln V}\right)$	$\left(\frac{d\ln\eta}{d\ln V}\right)^{\text{calc}}$	$\left(\frac{d\ln N(0)}{d\ln V}\right)^{\text{dir}}$	$\left(\frac{d\ln J^2}{d\ln V}\right)^{\text{dir}}$	$\left(\frac{d\ln\eta}{d\ln V}\right)^{\text{dir}}$
V	0.860	1.2	−2.67	1.65	−3.60	−1.95	1.41 (Ret. 23)	−3.45	−2.04
Nb	1.302	1.6	−2.06	1.5	−4.14	−2.64	1.27 (Ref. 24)	−3.94	−2.66
Ta	0.953	1.7	−2.32	1.3	−4.29	−2.99	···	···	···
Mo	0.385	1.7	−2.29	1.5	−4.05	−2.55	···	···	···

surements[21] only the heat capacity was separated into its constituents. As we are explicitly interested in the distinction between $d\ln\langle\nu^{-2}\rangle/d\ln V$ and $d\ln N(0)/d\ln V$ we will use the data of Collins and White[19] that separated the phonon and electron contributions both in the thermal expansion and the specific heat.

The value of $\gamma(-2)$ is not found in the literature for transition metals, but it seems reasonable that

$$\gamma_\infty \equiv \gamma(0) \geqslant \gamma(-2) \geqslant \gamma(-3) \equiv \gamma_0\,,$$

where γ_0 and[19] γ_∞ are the lattice Grüneisen parameters at low and high temperatures, respectively. [From the work of Barron *et al.*[20] one finds that $\gamma(n)$ is monotonic in n, at least for ionic crystals, and that the difference $\gamma_\infty - \gamma_0$ is not large.] Since, however, we expressed in Secs. I and II $\langle\nu^{-2}\rangle$ by Θ_D we approximate $\gamma(-2) \simeq \gamma(0) \equiv \xi$.

The various quantities we used in the calculation of the empirical $d\ln\eta/d\ln V$ from (12) are given in Table III. T_c and dT_c/dP are taken from Ref. 22, Θ_D from Ref. 6 and χ from Ref. 21. The values of λ are given from the inversion of Eq. (4) with μ^* as described in Sec. II.

We turn now to a theoretic calculation of $d\ln\eta/d\ln V$. Neglecting the renormalization of Γ by the electron-phonon interaction (which is again a sort of coupling) we write

$$\frac{d\ln N(0)}{d\ln V} = \frac{d\ln\Gamma}{d\ln V} \equiv \gamma_{\text{el}}\,,$$

and take its value from Ref. 19. In calculating $d\ln J^2/d\ln V$ we use the model developed in Sec. II assuming that the atomic quantities B and Q are not changing too much under pressure (this assumption will be discussed below). By differentiating (6) we get

$$\frac{d\ln J^2}{d\ln V} = -\frac{2}{3}\,(4+x) + \frac{32}{9}\,\frac{x}{J^2}\,(5C_1 d_1 + 2C_2 d_2 + 2C_3 d_3)\,, \tag{13}$$

where

$$d_1 = A(8 + 4x + x^2)\,;$$

$$d_2 = Ax^2\,;$$

$$d_3 = A(-2 + 2x + x^2)\,,$$

and the other quantities are defined in Eq. (6).

The resulting values of $d\ln\eta/d\ln V$ are also listed in Table III and we see that they differ from $(d\ln\eta/d\ln V)^{\text{emp}}$ by less than 30%.

In order to check the assumption of constant values of B and Q that was made in getting Eq. (13), we calculated J^2 explicitly using a self-consistent augmented-plane-wave band-structure calculation, with reduced and normal lattice spacings for [23]V and [24]Nb. γ_{el} was calculated directly from the density-of-states curves for the different lattice spacings. These results together with the total directly calculated $d\ln\eta/d\ln V$ are also listed in Table III (indicated by "dir").

Despite the fact that the details of the calculation show some changes in B and Q with volume, the over-all values for $(d\ln\eta/d\ln V)^{\text{dir}}$ are very similar to those of the model calculation.

We point out that this consistency between the two calculations and the agreement with experiment were achieved without any adjustable parameter.

Analyzing the results we conclude that the anomalous large negative values of $d\ln\eta/d\ln V$ in transition metals are a consequence of the large negative value of $d\ln J^2/d\ln V$, i.e., broadening of the band by reducing the volume. This strong effect is partially cancelled by the resulting decrease in the density of states ($\gamma_{\text{el}} > 0$). This result is in accord with the conclusions of Ratti *et al.*[25] that the large value of $|d\ln\eta/d\ln V|$ is governed by the broadening of the resonances under pressure. However, their over-all value of $|d\ln\eta/d\ln V|$ is somewhat larger, as they supress changes arising from the density of states by using the single-scatterer approximation.

IV. PRESSURE EFFECT IN ALLOYS

The only system on which continuous measurements of the pressure induced changes in T_c were performed, is the Zr-Nb-Mo family.[22] This system is particularly interesting as dT_c/dP changes sign within the row. The ideal situation would be

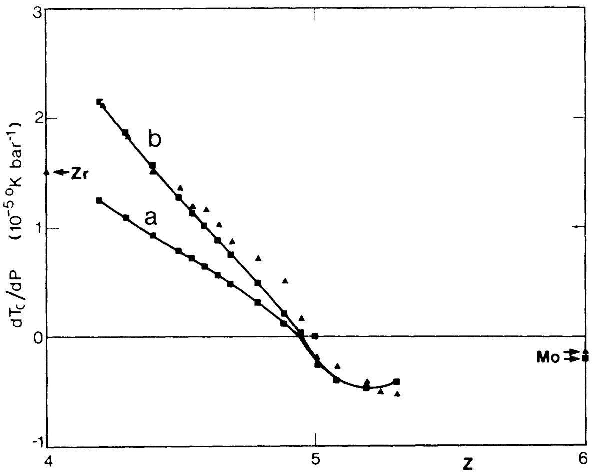

FIG. 4. Experimental (triangles) and calculated (squares) values of dT_c/dP vs the number of electrons per atom in the Zr-Nb-Mo system. The two calculated curves represent different choices of the lattice Grüneisen parameter for Zr. The arrows indicate the corresponding values for Zr and Mo.

if we had a continuum of values of γ_{el} and ξ, so that the prescription of Sec. III might be used. As this data is lacking we proceed as follows: we interpolate linearly the values of Θ_D and Γ between those given in Table II. $d\ln J^2/d\ln V$ is calculated in the same manner of Sec. III. As the Grüneisen parameter of Zr is not given by Collins and White[19] we assume that the ratio ξ_{Zr}/ξ_{Nb} remains the same as that given by Gschneidner[21] and thus get $\xi_{Zr} \simeq 0.75$. The values of ξ are then linearly interpolated. The difference between the empirical and calculated values of $d\ln\eta/d\ln V$ for Nb, brings about a shift in the dT_c/dP curve, which is corrected by adding a constant to the calculated $d\ln\eta/d\ln V$. There remains the problem of γ_{el} which is a complicated quantity that contains an admixture of contributions from band shifting, stretching, and twisting.[15] The effect of band structure on γ_{el} was discussed by Varley.[26] The complications involved may be illustrated by the fact that Mo and Nb have the same value of γ_{el},[19] in spite of the fact that their location on the rigid-band model density-of-states curve differs both in the magnitude of $N(0)$ and in the sign of the slope of the curve. Indeed, one can qualitatively show, using Varley's formula, that there is a trend of cancellation of the different changes in the quantities determining γ_{el}, keeping it roughly constant between Nb and Mo. Having no better information we thus choose $\gamma_{el} = 1.5$ in the whole Zr-Nb-Mo system.

We have calculated dT_c/dP along these lines by inverting Eq. (12). The values of λ were obtained by inverting Eq. (4) using the experimental values of T_c given by Smith[22] with the convention described in Sec. II for μ^*. The results are shown in Fig. 4 (line a). The change of sign of dT_c/dP occurs in the vicinity of Nb as for the experimental points. However, the slope of the curve in its positive region is too small. From the calculation one sees that the dominant quantity in determining dT_c/dP is the lattice Grüneisen parameter ξ. The shape of our curve in the positive region depends on our value of ξ_{Zr} and the linear interpolation performed. Indeed, extrapolating up to (the hcp) Zr yields quite accurately the experimental value for dT_c/dP (indicated by an arrow). In order to get better agreement with experiment one has to decrease the values of ξ in that region. It seems that there is an excess reduction in ξ for $4.2 \leq Z \leq 5$ (relative to the interpolation between Nb and hcp Zr) as we approach the instability[27] connected with the change of structure near $Z = 4.2$. Such an increase in dT_c/dp was recently observed[28,29] in V_3Si samples near the martensitic transformation, and indeed in some of the samples Smith *et al.*[28] even measured a big negative Grüneisen parameter. If for example we use for $Zr_{0.2}Nb_{0.8}$, $\xi = 0.43$ and interpolate ξ linearly up to Nb, we get the curve *b* in Fig. 4. The "excess" dT_c/dP observed by Smith may be a consequence of the (reasonable) nonlinear dependence of ξ on Z, or from electronic effects like important changes in γ_{el} that might occur near the structure instability.

In the region $Z \geq 5$, ξ is almost constant and the curve is determined by the other quantities appearing in Eq. (12). Here the agreement with experiment is reasonable, including the value for Mo (indicated by an arrow).

V. DISCUSSION

In this paper we dealt with two aspects of superconductivity in transition metals. In the first part we discussed the systematic variation of T_c along the rows of the Periodic Table. We built a model that predicts T_c from a knowledte of the Debye temperature Θ_D, the lattice spacing, and the specific-heat coefficient Γ. It is clear that these quantities are not independent as a large electron density near the Fermi energy enhances screening, thus decreasing the interionic forces. This general idea had been used by Allen and Dynes,[30] who expressed the electronic factors appearing in λ by phonon properties. However, as they need a detailed knowledge of the bare phonon frequencies, their calculation is limited at present to "pseudopotential" metals. Using the same ideas Gomersall and Gyorffy[31] followed the opposite procedure and expressed λ only by electronic properties getting a nice qualitative agreement with Matthias's rules.[14] As a model calculation for $\Gamma(Z)$ was developed by Miedema[32] it seems that we are able to get continuous lines of $T_c(Z)$ without the use of experimental data at discrete points. Work in this direction is now performed.

Returning to the present work we conclude that the agreement of the experimental with the calculated $T_c(Z)$ curves is satisfactory. The results depend explicitly on our choice for μ^*, assuming it to be proportional to $N(0)$. The conventional way to estimate μ^* is by using the isotope effect $\alpha = -d\ln T_c/d\ln M$, and in our case one gets

$$\mu^* = 2.925b + [(2.925b)^2 + 2b]^{1/2},$$

where

$$b = 0.43\frac{(1-2\alpha)K}{K^{-1} - 2.543}, \quad K = \left(\ln\frac{1.83\,\Theta_D}{T_c}\right)^{-1}.$$

Unfortunately, in our materials only Mo was measured and using $\alpha = 0.37$ we get $\mu^*_{\mathrm{Mo}} = 0.10$, which is similar to the value obtained by McMillan.[6] If we assume a constant μ^* with this relatively small value, the calculated line in Fig. 1 would still be far below the limits of the figure near $Z \simeq 5.7$, destroying the agreement with experiment. In the model we used for μ^* this value for Mo gives rise to $\mu^*_{\mathrm{Nb}} = 0.239$. Though the use of this number would maintain the general shape of the $T_c(Z)$ curve we choose the more commonly used value $\mu^*_{\mathrm{Nb}} = 0.149$. In any case, our results prefer $\mu^* = N(0)\,U_c$ over a constant μ^*.

The extension of this theory to hcp and fcc lattice structures is now in progress and we hope to be able to explain the behavior of the superconducting transition temperature along the whole rows of the Periodic Table. Also, it would be desirable to develop a similar model for other structures such as the β-W's that are more interesting because of their high T_c and the peculiarities in their band structure.[33]

In the second part of this paper we considered the pressure effect. We developed a model for calculating $d\ln\eta/d\ln V$—the dependence of the electronic part of λ on volume, the agreement with experiment being of about 30%. A calculation of this quantity directly, using band structures of normal and reduced lattice spacings agrees with that of the model. We want to note that the reduced lattice used, had a lattice constant of 95 at.% of the normal one, a fact that corresponds to a very high pressure (240 kbar for ^{23}V), and it is not clear at all that the behavior is linear on such a broad range.

In attempting to explain the $dT_c/dP(Z)$ curve obtained by Smith[22] for Zr-Nb-Mo alloys we used several assumptions because of the lack of experimental data. We want to point out, that the agreement obtained with experiment, cannot justify (in this case) our model for $d\ln\eta/d\ln V$ because of the fact that the calculated line in the range $Z < 5$ depends mainly on the choice of the Grüneisen parameter ξ. This is a consequence of the assumptions made in this section, especially that of a constant γ_{el}, and of the fact that the transition temperature in this range is roughly constant, leading to an approximately constant value for the factor $f(\lambda, \mu^*)\ln(1.83\,\Theta_D/T_c)$ appearing in Eq. (12). A deviation from the linear curve in the region where ξ is still (assumed to be) linear, appears only close to Nb, where the decrease in T_c changes this factor. Thus, the conclusion of this section has to be that dT_c/dP in this family can be explained using changes in ξ only, though it is not the only possible explanation.

A short glance on Smith's line reveals the correlation between the change of sign in $dT_c/dP(Z)$ and the change of sign of the slope in the $T_c(Z)$ curve, that is connected with the $\Gamma(Z)$ curve as was shown in Sec. II. This suggests that another explanation for this line may be found by correlating the applied pressure with shifts of the Fermi level that will bring about changes in T_c as a result of the changes in $N(0)$.[34] As was mentioned in Sec. IV the translation of this idea to a numeric form may be complicated. This will be discussed elsewhere.

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