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LETTER TO THE EDITOR

A calculation of the pressure dependence of the superconducting transition temperature T_c in niobium and vanadium

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Abstract. The electronic part, η, of the electron–phonon mass enhancement is calculated at normal and reduced volumes for Nb and V. We find that η increases rapidly with decreasing volume and the coefficients $d\ln\eta/d\ln V$ are in good agreement with empirical analyses of the pressure dependence of T_c in these transition metals.

Unlike superconducting simple metals where the pressure derivative dT_c/dp is, in general, negative, this derivative varies in sign as well as magnitude between different transition metals (for a comprehensive review see Smith 1972a). Recently, Hopfield (1971) has analysed some of the experimental results for transition metals using the McMillan (1968) equation for T_c:

$$T_c = \frac{\theta_D}{1{\cdot}45} \exp\left(\frac{-1{\cdot}04\,(1+\lambda)}{\lambda - \mu^*(1+0{\cdot}62\lambda)}\right) \tag{1}$$

where θ_D is the Debye temperature and μ^* is the electron–electron interaction parameter. The electron–phonon enhancement λ can be written as:

$$\lambda = \frac{n(E_F)\langle I^2\rangle}{M\langle\omega^2\rangle} = \frac{\eta}{M\langle\omega^2\rangle} \tag{2}$$

where M is the atomic mass, $\langle\omega^2\rangle^{1/2}$ is an appropriate average phonon frequency, $n(E_F)$ is the electronic density of states at the Fermi energy E_F and $\langle I^2\rangle$ is the square of the electron–phonon matrix element averaged over the Fermi surface. Neglecting the variation of μ^* with volume Hopfield obtained from equation (1):

$$\frac{d\ln T_c}{dp} = \frac{1}{B}\left[\gamma_g + \left(\frac{1{\cdot}04\lambda}{\lambda-\mu^*(1+0{\cdot}62\lambda)} - \frac{1{\cdot}04\lambda(1+\lambda)(1-0{\cdot}62\mu^*)}{[\lambda-\mu^*(1+0{\cdot}62\lambda)]^2}\right)\left(2\gamma_g + \frac{d\ln\eta}{d\ln V}\right)\right] \tag{3}$$

where B is the bulk modulus, γ_g is the *effective* Gruneisen $\gamma = -d\ln\langle\omega^2\rangle^{1/2}/d\ln V$ and $\theta_D/1{\cdot}45$ has been replaced by $\langle\omega^2\rangle^{1/2}$.

Since the first large parentheses in equation (3) is $-2{\cdot}0$ or less the sign of dT_c/dp is determined *mainly* by the magnitude of γ_g. Roughly speaking for $\gamma_g > 1{\cdot}7$ this sign is negative and is positive for smaller values of γ_g. Taking experimental values of dT_c/dp and B and estimates of γ_g from Gschneider (1964) Hopfield inverted equation (3) to obtain

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d ln η/d ln V for several transition metal superconductors. He found this quantity was fairly constant; a typical value being $-3{\cdot}5$. This is in contrast to simple metals for which d ln η/d ln $V \sim -1{\cdot}0$ and dT_c/dp can be well understood using pseudopotential theory, eg Trofimenkoff and Carbotte (1970), Carbotte and Vashishta (1971) and Coulthard (1971).

In this letter we present *ab initio* calculations of d ln η/d ln V for Nb and V using the theory of Gaspari and Gyorffy (1972). This model gives a simple expression for the electronic parameter η in terms of quantities which can be obtained from band theory:

$$\eta = \frac{2mE_F}{\hbar^2\pi^2}\left(\frac{2\sin^2(\delta_1-\delta_0)}{n(E_F)} + \frac{[4\sin^2(\delta_2-\delta_1)+6\sin^2\delta_2]n_2(E_F)}{n_2^{(1)}n(E_F)}\right) \tag{4}$$

where δ_0, δ_1, δ_2 are the angular momentum phase shifts of the appropriate muffin-tin potential evaluated at E_F, n_2 is the d component of the density of states and $n_2^{(1)}$ is the d component of the 'single scatterer' density of states (see Evans *et al* 1973):

$$n_2^{(1)} \simeq \frac{5}{\pi}\frac{d\delta_2}{dE}(E_F). \tag{5}$$

Calculations based on equation (4) have been carried out by Evans *et al* (1973) for several transition metals and the results for η are in qualitative agreement with the empirical estimates obtained by McMillan (1968) from the inversion of equation (1). Evans *et al* have also discussed the approximations and assumptions involved in the Gaspari–Gyorffy scheme.

In order to apply this theory to the calculation of d ln η/d ln V we require muffin-tin potentials, densities of states and Fermi energies for metals at different lattice spacings. A few non self-consistent band structure calculations have been carried out at reduced lattice spacings eg Davis *et al* (1968) on Cu, O'Sullivan *et al* (1971) on the noble metals and Das *et al* (1973) on Pd. These calculations are based on the Mattheiss (1964) prescription for the lattice potential and give successful descriptions of the pressure variation of the Fermi surface and electronic specific heat. Similar self-consistent calculations are reported by Kmetko (1971) and recently by Papaconstantopoulos *et al* (1972) for V and by Anderson *et al* (1973) for Nb.

We have used the self-consistent muffin-tin potentials of these latter authors to calculate the phase shifts δ_l at normal and reduced lattice spacings for Nb and V. This procedure is the same as that used by Stocks *et al* (1972) in their calculation of T_c for Cs under pressure. The phase shifts are given in Table 1 along with the densities of states calculated by Papaconstantopoulos *et al* and Anderson *et al*.

Table 1. Phase shifts δ_l and energy derivative δ_2' evaluated at the Fermi energy E_F. $n(E_F)$ is the density of states and R_s is the Wigner–Seitz radius

	R_s (au)	E_F (Ryd)	δ_0	δ_1	δ_2	δ_2' (Ryd^{-1})	$n(E_F)$ (spin states/atom/eV)
Nb (normal)	3·071	0·75	−1·0437	−0·4403	1·0336	4·551	1·037
Nb (reduced)	2·918	0·935	−1·254	−0·584	1·0483	3·147	0·853
V (normal)	2·813	0·76	−0·7978	−0·232	0·8945	7·062	0·978
V (reduced)	2·672	0·92	−0·961	−0·325	0·9606	5·552	0·794

The major contributions to η in equation (4) comes from the d phase shifts δ_2. In normal Nb δ_2 is broader in energy than the corresponding curve for Nb shown in Evans *et al* (1973). The difference is probably due to the change in exchange parameter from full Slater to the present $\frac{2}{3}$ Slater (see Anderson *et al* 1973 for a detailed comparison of energy bands in Nb). In normal V δ_2 is somewhat sharper than that for Nb but in both metals δ_2 is significantly broadened on reducing the volume. Such an effect has been noted previously by Evans and Jain (1972) on their work on liquid Fe at megabar pressures in the earth's core and also by Stocks *et al* (1972) and Ratti and Jain (1973) who studied electronic properties of Cs under pressure. It was emphasized in these papers that the effect of compression on the metal was to greatly increase the effective width of the 'd resonance'.

In table 2 we list the values of η calculated using equation (4) at each volume. As in Gaspari and Gyorffy (1972) and Evans *et al* (1973) we have set $n_2/n = 1$.

Table 2. Comparison of calculated and empirical values of η

	η(M) (eV Å^{-2})	η (normal) (eV Å^{-2})	η (reduced) (eV Å^{-2})	$n' = \frac{\mathrm{d}\ln\gamma}{\mathrm{d}\ln V}$	$\frac{\mathrm{d}\ln\eta(\mathrm{H})}{\mathrm{d}\ln V}$	$\frac{\mathrm{d}\ln\eta(\mathrm{GB})}{\mathrm{d}\ln V}$
Nb	7·2	3·8	6·3	−3·3	−3·0	−2·6
V	4·6	2·4	4·0	−3·3	−3·5	−3·2

M McMillan (1968); H Hopfield (1971; GB Garland and Bennemann 1972.

The present value of η for normal Nb is larger than the previous calculated value of 3·0 eV Å^{-2} and this results from the smaller value of δ_2'. If we write $\eta \propto V^{n'}$ we can estimate $\mathrm{d}\ln\eta/\mathrm{d}\ln V = n'$ and we find that these coefficients are in good agreement with Hopfield's empirical estimates. Garland and Bennemann (1972) have also estimated $\mathrm{d}\ln\eta/\mathrm{d}\ln V$ in an analysis equivalent to that of Hopfield but these authors start with a modified form of the McMillan equation and use more recent input data for $\mathrm{d}T_c/\mathrm{d}p$. Their estimates are fairly close to those of Hopfield for most of the superconductors. Both sets of empirical values are listed in table 2 but such estimates are made uncertain because of lack of information about γ_g. The latter is not directly available from experiment, see Garland and Bennemann (1972).

We suggest that the large negative values of $\mathrm{d}\ln\eta/\mathrm{d}\ln V$ in transition metals, which are ultimately responsible for positive values of $\mathrm{d}T_c/\mathrm{d}p$, result *primarily* from the broadening of the d phase shift under compression, ie from the reduction of $\delta_2'(E_F)$. This is essentially a local effect which is dependent on the variation of the electron–ion potential with volume. A more sophisticated calculation using the full Gaspari–Gyorffy theory for η would include 'band structure' effects, ie changes in the partial densities of states n_l and total densities of states n with volume. We are assuming $n_2 = n$ at each lattice spacing so that the density of states has no large influence in equation (4). This is an essential part of the argument for although η increases with pressure, in both V and Nb, $n(E_F)$ decreases (see table 1). Garland and Bennemann (1972) have discussed possible mechanisms for the increase of η with pressure using a tight binding picture but they also take into account some effects of screening on the electron–ion potential. They suggest that the volume dependence of the latter is important since a straightforward tight binding calculation (Barišić 1971) gives values of $\mathrm{d}\ln\eta/\mathrm{d}\ln V$ which are not as negative as the empirical ones and thus cannot give rise to positive $\mathrm{d}T_c/\mathrm{d}p$ via equation

(3). Smith (1972b) has discussed this point for V, in particular, where dT_c/dp is large and positive.

In a later publication we will show that Hopfield's observation on the relative constancy of $d \ln \eta / d \ln V$ and its value of about $-3{\cdot}5$, across the transition metal series, can be understood from a simple 'single scatterer approach' and we will discuss in detail the behaviour of the electron–ion potential and 'd resonance' as a function of volume.

In conclusion we mentioned that in Cs the increase in η with pressure arises from a fourfold increase in $\delta_2(E_F)$ as the volume decreases to 39 % of its normal volume rather than any decrease in $\delta_2'(E_F)$ (Stocks *et al* 1972 and Ratti and Jain 1973). Barium also goes superconducting under high pressure (Wittig and Matthias 1969) and we suggest that the volume dependence of $\delta_2(E_F)$ in this metal will be intermediate between that of Cs and the early transition metals since even at normal densities Ba has considerable d character in its wavefunctions at the Fermi energy (eg Kmetko 1971).

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