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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