The improved formulas are similar in structure with the original BCS-formula, i.e.

$$T_c \propto \theta \exp(-1/g). \tag{5}$$

Modifications concern first of all the quantity g, which in the case of BCS is simply

$$g_{\mathrm{BCS}} = N V_{\mathrm{BCS}} = N(V_{\mathrm{Ph}} - V_{\mathrm{C}}). \tag{6}$$

V_{Ph} is the attractive electron-phonon interaction and V_{C} the repulsive Coulomb interaction. We have used this expression above, with $N = 3/2\pi^{-2} k_B^{-2} \gamma$, i.e. with the "dressed" density of states.

Jensen and Maita[15] obtain

$$g_{\mathrm{JM}} = \frac{N_0(V_{\mathrm{Ph}} - U_{\mathrm{C}})}{1 + N_0 V_{\mathrm{Ph}}} \tag{7}$$

where N_0 is the "bare" density of states given by

$$N = N_0(1 + N_0 V_{\mathrm{Ph}}) \tag{8}$$

and U_{C} is a modified Coulomb interaction parameter. Jensen and Maita find good agreement with experiment for alloys with $4 \leqq n \leqq 6$ when both interactions V_{Ph} and U_{C} are assumed to be very nearly constant, with $V_{\mathrm{Ph}} \sim 0.85$ eV atom and $U_{\mathrm{C}} \sim 0.27$ eV atom, respectively. Since our alloys fall in this region we have investigated our data in this respect and find indeed a much better constancy of $V_{\mathrm{Ph}} - U_{\mathrm{C}}$ than previously for V_{BCS}, V_{Ph} and U_{C} being 0.90 eV atom and 0.27 eV atom, respectively. With the assumption that V_{Ph} and U_{C} are also independent of pressure, which seems now even more justified than for V_{BCS}, we obtain, proceeding in the above manner

$$N_0 = f(a\,p + n) \tag{9}$$

which implies that the "bare" d-band would be rigid with respect to pressure.

As stated above, we do not feel that the experimental accuracy permits any preference for either equation (4) or (9) at present. We merely wish to show that with a more elaborate expression for T_c a reasonably simple interpretation for the effect of pressure on T_c in transition metals can also be made.

An analogous use of McMillan's[9] expression for T_c which had proved to be helpful in the case of non-transition metals appears to be less favourable for the alloy system investigated here. Although McMillan's formula

$$g_{\mathrm{MM}} = \frac{\lambda - \mu(1 + 0.62\lambda)}{1.04(1 + \lambda)} \tag{10}$$

very closely resembles equation (7) of Jensen and Maita (λ corresponding to $N_0 V_{Ph}$ and $\mu(1+0.62\,\lambda)$ to $N_0 U_C$), the empirical observation which McMillan has made for λ by analyzing the data of five transition metals (V, Nb, Ta, Mo, W) is not in accord with the detailed dependence of T_c and θ on both the number n of valence electrons and on pressure. McMillan obtains empirically

$$\lambda = \frac{c}{M\theta^2} \tag{11}$$

c=constant "for a given class (bcc) of transition metals", M=ionic mass. Using (10) and (11) and assuming $d\mu=0$, one has by differentiation

$$d\ln T_c \sim d\ln\theta \left\{1 - \frac{2.18\,\lambda}{(\lambda - 0.62\,\lambda\,\mu - \mu)^2}\right\}. \tag{12}$$

Insertion of the appropriate values for niobium, $\lambda=0.82$ and $\mu=0.13$, yields

$$d\ln T_c = -3.7\, d\ln\theta\,. \tag{13}$$

Inspection of the shapes of both $T_c(n)$ and $\theta(n)$ near $n=5$ show that Eq. (13) is not satisfied; thus the validity of Eq. (11) is put into doubt from this point of view. The pressure data likewise suggest that McMillan's additional condition $\lambda=c/M\theta^2$ is not applicable to our metals: For $n<5.0$ the measured slopes $d\ln T_c/dp$ are definitely positive and $\lambda\sim 0.9$. Unless the constant c is assumed to be strongly pressure dependent, Eq. (12) requires the slope $d\ln\theta/dp=\gamma_G\cdot\kappa$ to be negative, which has never been observed for any material. Thus we conclude that c indeed depends on pressure and that presumably the moderate constancy of this quantity for the five bcc transition metals is accidental. We note that McMillan was able to give a theoretical proof of Eq. (11) only for the simple metals; i.e., the non-transition metals, for which, as mentioned above, the pressure effect on T_c can be semiquantitatively calculated when Eq. (11) is accepted.

The anomalous pressure dependence of T_c for the niobium-rich alloys at pressures below 20 kbar cannot be explained unambigously at present. The supposition that a small deformation of the d-band arises under pressure up to 20 kbar (as indicated by the thin line on the γ curve) is very hard to check. Alternatively it might be possible that the pressure is not fully hydrostatic and that small shear stresses σ via large shear coefficients $dT_c/d\sigma$ might increase T_c up to the yield stress, i.e., the kink. However, shear should only contribute second order effects[27], whereas the initial parts of our curves seem to be linear. There is also a

27 Pippard, A. B.: Phil. Mag. **46**, 1115 (1955).