TABLE II. Parameters of fusion curves.

	μ Eq. (15)	η Eq. (21)	η	$\gamma_{m,Av}$ Eq. (23)	$\gamma_{m,Av}$ Eq. (39)	η Eq. (40)	B Eq. (21)
Cs	3.5[a]	2.3	···	1.0	1.1_0	2.6	3.8
Rb	4.7	3.1	···	1.4	1.4_2	3.2	3.6
K	2.8	2.2	···	0.9_5	0.9_5	2.3	3.9
Na	(2.6)	(2.7)	3.79[b] (50–60 kilobars) 2.86 (90–100 kilobars)	(1.2)	(1.0)	(2.3)	(3.8)

[a] Values at the origin of d^2T_m/dP_m^2 in Eq. (15) were computed from second differences of T_m *vs* P_m from Bridgman's data (reference 17). It was necessary to smooth the values of Δ^2T_m near the origin for K. For Na, the values of Δ^2T_m were too erratic to permit smoothing, and the value at the origin was taken as the average of values corresponding to the first four intervals of P_m.

[b] See reference 14. Parenthetic pressure ranges correspond to direct fit.

which enters B, must be obtained indirectly. Values of the parameter μ corresponding to the volume variation of $\gamma_m-\frac{1}{3}$ are shown in Table II, as determined by Eq. (15) from quantities evaluated at the origin; values of d^2T_m/dP_m^2 were computed by numerical differentiation of the fusion temperature with respect to pressure. As noted, the value for Na is somewhat doubtful, as is that for K to a less extent. These values of μ and the values of the fourth column of Table I for B yield the tabulated values of η in the second column of Table II, from Eqs. (21). It is seen that the values of η are reasonably concordant with the listed values obtained by Murnaghan from direct fit, over ten-kilobar intervals of pressure, of the pressure-volume curve for Na at normal temperature.

A severer test of the assumptions underlying the theory can be obtained by noting that the average value $\gamma_{m,Av}$ of the Grüneisen parameter along the fusion curve, defined by Eq. (23) in terms of η, should be approximately equal to the average value defined implicitly by Eq. (18) for the variation of $\gamma_m-\frac{1}{3}$ with fusion temperature. The latter average is given by

$$\frac{\gamma_{m,Av}-\frac{1}{3}}{\gamma_{m,0}-\frac{1}{3}}=\frac{1-(T_{m,0}/T_{m,\max})^{\beta-1}}{(\beta-1)(T_{m,\max}/T_{m,0}-1)}, \tag{39}$$

where $T_{m,\max}$ is the maximum temperature on an observed fusion curve. It is seen that agreement is reasonable for tabulated values of $\gamma_{m,Av}$ in Table II, as obtained by means of Eq. (23) from the values of η in the second column, and as obtained by means of Eq. (39) from the values of μ and η in the first and second columns, respectively. One should not expect identity necessarily, since the two evaluations of $\gamma_{m,Av}$ correspond to different methods of averaging. Finally, one notes that $d\gamma_m/dT_m$ is negative, from Eq. (18); the sign of the derivative agrees with the relation $\gamma_{m,Av}<\gamma_{m,0}$, which holds for the values of $\gamma_{m,Av}$ in Table II except for one instance in the doubtful case of Na.

The approximate equality of these two evaluations of $\gamma_{m,Av}$ yields a method of inferring the value of η from knowledge of the values of $\gamma_{m,0}$ and μ. If Eq. (39) is rewritten, by means of Eqs. (23) and (24), as

$$\frac{\eta-1}{\eta_0-1}=\frac{1-(T_{m,0}/T_{m,\max})^{\beta-1}}{(\beta-1)(T_{m,\max}/T_{m,0}-1)}, \tag{40}$$

the definition $\beta=\mu/(\eta-1)$ permits one to solve the equation for η by trial, if η_0 and μ are known. Values of η obtained in this manner, with use of values of $\gamma_{m,0}$ and μ from Tables I and II, respectively, are shown in the sixth column of Table II; the agreement with the values of the second column is satisfactory. Values of B from Eq. (21) corresponding to values of μ and η from the first and sixth columns, respectively, are tabulated in the last column of Table II; the agreement with the values of the fourth column of Table I is good for Rb and K, but the differences in the cases of Cs and Na reflect the sensitivity of $B=(\eta+\mu)/(\eta-1)$ to the value of $\eta-1$ in the denominator. Thus, the theory given is able to predict an approximate value of the Simon exponent for the alkali metals; by way of contrast with the values of the last column of Table II, note that Salter's evaluation (27) of the Simon exponent yields numbers of the order of 1.5.

By use of a Taylor expansion of Eq. (18) to obtain an evaluation of $\gamma_{m,Av}$, one finds the explicit expression

$$\eta\sim\tfrac{1}{2}\{\eta_0+1+[(\eta_0-1)^2-4\mu(T_{m,\max}/T_{m,0}-1)]^{1/2}\}, \tag{41}$$

valid as an approximation provided $T_{m,\max}/T_{m,0}$ is sufficiently small. This equation yields values of η differing from those corresponding to Eq. (40) by about 6% on the average for Cs, Rb, and Na; it fails for K, where the large value of $T_{m,\max}/T_{m,0}-1$ (in this case about $\frac{1}{3}$) makes the radical imaginary.

On the assumption that the heat capacity of the solid at fusion has the Dulong and Petit value, Eqs. (36) and (34) of I yield the approximation

$$q=1+2\gamma_m(3\gamma_m-1)\Omega, \tag{42}$$

in which Ω is the parameter appearing in Eq. (7). Use of Eq. (18) in this expression for q with values of μ and η from Table II, permits one to evaluate the minimum value $q_{\min}$ of q corresponding to the temperature $T_{m,\max}$ on a fusion curve. The relative difference $(q_0-q_{\min})/q_0$ is largest for the elements K and Cs showing the largest ordinates in Fig. 2, in which cases it amounts to about 10%. Since this value probably exceeds the experimental error in the fusion data, Eqs. (20) and (31) are valid only as first-order approximations; a more refined analysis should take the variation of q into account.

IV. CONCLUSION

The successful comparison of theory with experiment for the alkali metals permits one to assess tentatively the significance of the Simon equation for elements of