For Rb the uncertainty of the estimated γ_G is even larger because of the closeness of the Hugoniot point to the static isotherm.

The average values of γ_G calculated above are averages at a fixed density over a range of temperatures in the solid, solid–liquid two phase and a portion of the liquid phase. For the simpler metals in which the electronic contributions to thermal properties are not too large, this averaged γ is not expected to differ by more than 20 per cent from the value of γ_G in the solid phase of the same density. However, the large and temperature dependent electronic effects which appear to be responsible for the small Gruneisen coefficient in the Rb data at high temperature do not permit us to determine γ_G for *solid* Rb.

The calculation values of γ_G for Na are seen in Fig. 3 to be reasonable agreement with other theoretical estimates (see Ref. [3] for review of these) and the data of Swenson. The calculated values for K and Rb at higher compressions are increasingly smaller than conventional estimates which deal primarily with the contributions of the motions of the atomic centers to the thermal equation of state.

4. *d*-BAND ELECTRONIC EXCITATIONS IN Rb AND K

The 5*d*-electron band has well-known effects in the heaviest alkali metal, Cs. An electronic phase transition which occurs around 45 kbar without a change in crystal structure has been shown by Sternheimer [8] to be due to the transfer of the outer 6*s*-electron to an inner 5*d*-electron shell. The corresponding transition in Rb should occur above 100 kbar according to theoretical estimates [8]. In Cs the transition occurs in the solid at high compression because of the elevation of the 6*s*-band energy level and the broadening of the 5*d*-band with compression. This transition is anticipated at a lower pressure ($\sim$ 25 kbar) by a maximum in the pressure dependence of the melting temperature. A similar maximum in the melting temperature curve of K and Rb has apparently been observed by Ref. [9] in the vicinity of 80 kbar. Scaling the phase transition to the maximum of the melting curve as in Cs results in a solid phase transition $\sim$ 150 kbar for Rb and K.

Although the pressures are considerably less in the region under discussion, the proximity of inner *d*-band energy levels to the valence *s*-band can strongly affect the thermal properties at lower pressures. For instance, there are several ways in which the thermal excitation energy of electrons E_e can produce an abnormally small electron pressure P_e, i.e., the effective electronic Gruneisen coefficient, $\gamma_e = V(\partial P_e/dE_e)_V$ will be small. First of all, a part of this coefficient is proportional to the rate of change with specific volume of the density of electronic states in energy, $\mathrm{d}\sigma_E/\mathrm{d}V$, at the Fermi level. When the temperature is high enough to excite an appreciable number of electrons into the *d*-band $\mathrm{d}\sigma_E/\mathrm{d}V$ becomes negative reducing γ_e in magnitude. A second, related effect discovered by Ross [10] in the high temperature properties of X_e may be also operative here. Ross found that from simple thermodynamic arguments, that if the bottom of the excited bands decrease in energy with compression, the electronic pressure can also be considerably reduced at high temperature. Finally, a self-consistent, Hartree–Fock solution for electron-energy levels at high temperature may lead to a considerable rearrangement of the *d*- and *s*-band energy levels making a Cs-like transition possible at lower densities. This possibility arises from the fact that when excited *s*-electrons transfer to an inner *d* level they increase the shielding of the valence outer *s* band and thus raise its energy levels which in turn makes more likely the further transfer of electrons to the *d* band. This effect must make the metal softer at higher temperatures since the *d*-bands are smaller in radius and therefore effectively reduce the Gruneisen coefficient. If this effect occurs in the liquid phase the 'transition' can

be expected to be smeared over a range of temperature and densities.

The reduction of γ_G with increasing temperature by any of the above mechanisms can explain the different behavior of γ in Rb and K. Rough estimates of the shock heating in [3] indicate that Rb is $\sim$ 50 per cent hotter than K at shock pressures $\sim$ 50 kbar. This large a difference in shock heating arises from the larger compressibility of Rb and its smaller specific heat. The apparent similarity of the $U_s - U_p$ data on Rb with the shock data in the rare earths [4] suggests furthermore, that the third, Hartree–Fock explanation above for a low γ is most correct. A more definite answer would be given by a detailed band theory calculation.

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