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THERMAL PROPERTIES OF ALKALI METALS FROM STATIC AND DYNAMIC COMPRESSIBILITIES*

R. GROVER
Lawrence Radiation Laboratory, University of California, Livermore, Calif. 94550, U.S.A.

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Abstract—A detailed comparison of the isothermal compression data of Vaidya *et al.* on the alkali metals in the preceding article is made with high temperature shock compression data. The comparison provides evidence for strong electronic *d*-band effects in the equation of state of Rb at high temperatures at pressures as low as 50 kbar.

1. INTRODUCTION

IN PREVIOUS work,[1],[2] it has been shown that for most metals there is excellent agreement between recent static compressibility data up to 45 kbar and dynamic compressibility data interpolated between shock velocity measurements at high pressure ($\gtrsim 100$ kbar) and sonic velocity data at low pressures ($\lesssim 10$ kbar). Apparently, agreement between static and dynamic data can be expected when shock velocity data extrapolates at low pressure closely to the measured sound velocity for the same phase and when irreversible heating accompanying shock compression is small.

In the immediately preceding paper by Vaidya, Getting and Kennedy (hereafter referred to as I), in which compressibility data for four highly compressible alkali metals is presented, the agreement with shock compression data is uneven. The disagreement is however, considerably less than the previously noted disagreement with various sets of Bridgman data[3]. In this paper the disagreement with shock data is attributed to the unusually low values of thermal pressure in the heavier alkali metals. An explanation of this behavior in terms of the influence of electric *d*-bands in the heavier alkali metal will be discussed as well as the possibility of confirming this explanation by additional shock wave data at very low pressures. Al'tshuler and Bakanova[4] have been led to similar conclusions by a study of the systematics of shock compressibility data for the metals in the periodic table which exhibit phase transitions.

2. COMPARISON OF STATIC AND DYNAMIC DATA

A graphical comparison of static and shock compression data is given in Fig. 1. The shock Hugoniot data extends down to pressures in the vicinity of 50 kbar while static isothermal data reaches up to about the same pressure. Extensions of the static isotherm above 45 kbar according to the preferred modified Murnaghan fit given in I are shown as dashed lines. The Hugoniot data of Rice as recently renormalized by the LASL group[5] has been extended to zero pressure by dashed lines for the purposes of comparing with the static data. The Hugoniot will normally lie above the isotherm due to the higher temperatures which arise from irreversible heating during shock compression. The two sets of data for Li are seen to be close to each other as is typically the case for metals of normal compressibility when shock heating is small [2]. As noted in I, the Hugoniot data for Na and K lies above the isothermal data by a reasonable amount, due to the thermal pressure generated by shock compression.

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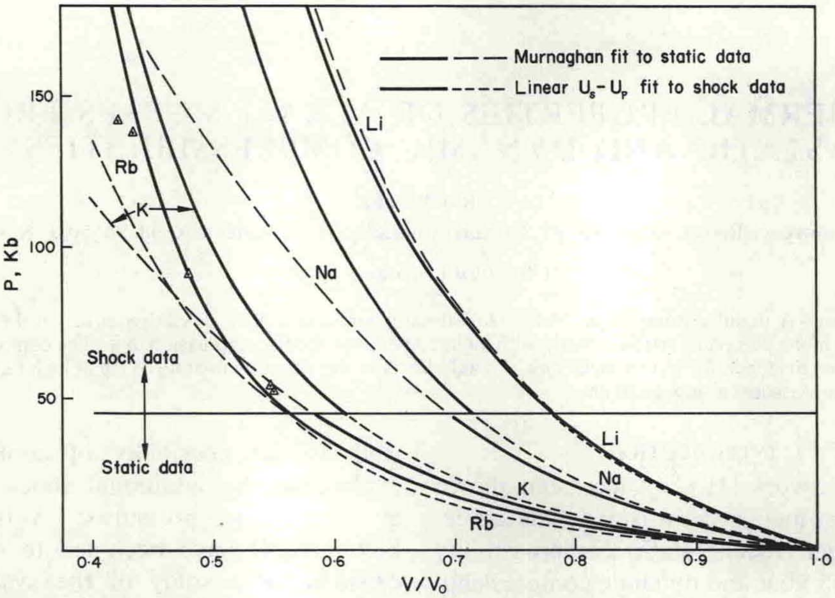

Fig. 1. Fits to static, isothermal and shock Hugoniot compression data. Δ-individual Hugoniot points for Rb.

Table 1. Summary comparison of metal bulk modulus data and Gruneisen γ. (st) indicates quantities derived from static data, (so) from sonic velocity data and (sh) from shock data. Listed moduli are in units of kilobars. $B' \equiv \mathrm{d}B/\mathrm{d}P$

Metal	γ_G^*	B_T	$B_s(st)$	$B_s(so)$	$B_s(sh)$	$B'_T(st)$	$B'_s(so)$	$B'_s(sh)$
Li	0·91	118·4	123·0	117·0	112·0	3·33	–	3·62
Na	1·16	61·2† (59·9)	64·3	65–69	63·6	3·68† (3·97)	3·6–3·7	3·97
K	1·32	31·4	34·4	33·8	32·0	3·63	3·98	3·75
Rb	1·42	26·2	29·2	(24–26)‡	21·4	3·39	(3·63)‡	3·93

*Calculated from tabulations of thermal expansion data in Handbook of Physics (American Institute of Physics, 1963) and specific heat data in *Selected Thermodynamic Properties of Metals and Alloys*, R. Hultgren, R. L. Orr, P. D. Anderson and K. K. Kelly (J. Wiley, New York, 1963) and Supplements.

†For Na, an average of two MME fits listed in Table 9 of I have been used instead of the combined fit shown in parentheses.

‡Extrapolated from data below 200°K.

In contrast, however, the extrapolated Hugoniot of Rb is considerably below the static isotherm below 45 kbar.

In order to evaluate this comparison, various sets of data on the initial adiabatic compressibility of these alkali metals are summarized in Table 1. The isothermal compressibility determined from best fits to static data are listed and converted to adiabatic bulk moduli with the use of the listed values of Gruneisen's γ_G. The listed value of γ_G, in turn, were made consistent with the static isothermal modulus, since these isothermal moduli are probably the most reliable of the available data. The listed bulk moduli obtained from room-temperature sonic velocity measurements in the alkali metal show a larger spread of values than is usual in metals, presumably because of the difficulty in measuring shear wave velocities near the melting temperature of a metal (see I for reference to sonic data). This problem is particularly severe for Rb in which shear wave have only been measured below 200°K. The shock data listed is obtained in the usual way[2] from a linear fit to shock velocity measurements.

For Na and K there is an acceptable, if somewhat poorer, agreement between sonic and shock moduli in view of the spread of the sonic data for Na. The static moduli reported in I are also consistent. In Li there is a larger discrepancy between shock and sonic data and a comparable spread between the shock data listed and two other available sets of shock wave data[6]. However, because of the smallness of the thermal corrections and the larger uncertainty in this low pressure data on Li, we shall not attempt to resolve these discrepancies. A much larger discrepancy exists between the extrapolation adiabatic modulus of Rb from shock data and the statically measured value. The sonic values extrapolated from low temperature data also indicate that the shock modulus is too small. In as much as the static modulus was measured to be the same in two very different static apparati in I, and is the only one of the three types directly measured, we must assume the static modulus to be correct. The larger disagreements between various measured values of the pressure derivatives of the bulk modulus, the B' in Table 1, are typical of the differences for normal metals[2].

The implication of the Rb discrepancy is that the extrapolation of shock data to zero pressure is incorrect in this case. The lowest shock data points for Rb which are shown in Fig. 1 also appear to deviate systematically from the single linear fit which is made to the entire range of the Rb shock data. For this reason, the initial compressibility data of I has been transformed into the shock-particle velocity plane (i.e., the $U_s - U_p$ plane) and is shown together with shock data points in Fig. 2. A best fit to this data is clearly a non-linear $U_s - U_p$ relation. It would be desirable to confirm this non-linearity by further shock velocity measurements at low pressure.

The upward curvature of the $U_s - U_p$ relation is only observed for metals in which there is a presumed change in electronic band structure. These effects have been discussed by Royce[7] as well as in [4]. In the latter reference, the authors actually included Rb in their collection of metals exhibiting electronic phase changes along the Hugoniot on the basis of an indication of a small amount of curvature in the original $U_s - U_p$ data on Rb.

3. DETERMINATION OF GRUNEISEN γ_G, FROM COMPRESSION DATA

By a simple subtraction at fixed volume it is possible to obtain an approximate average Gruneisen coefficient, $\bar{\gamma}_G$ between the

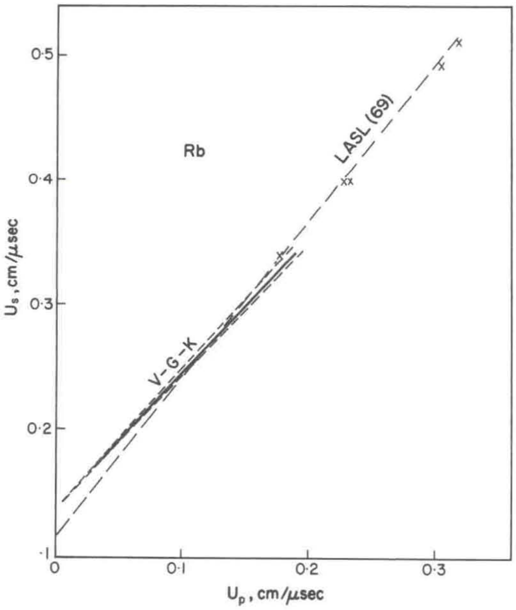

Fig. 2. Compression data in the shock velocity U-particle velocity U_p plane for Rb. x-individual shock points and fit from Ref.[5]. V-G-K-fits to static data from I.

Hugoniot and the static isotherm. The average $\bar{\gamma}_G$ is determined from Hugoniot and isothermal pressures, P_H and P_{T_0}, and internal energies, E_H and E_{T_0} according to

$$\bar{\gamma}_G(V) \equiv \frac{V[P_H(V)-P_{T_0}(V)]}{E_H(V)-E_{T_0}(V)}. \qquad (1)$$

$P_H(V)$ and $E_H(V)$ can be calculated directly from measured shock velocities by standard conservation equations. $E_{T_0}(V)$ can be calculated from $P_{T_0}(V)$ if the Mie-Gruneisen equation-of-state is assumed for the solid.

$$E_{T_0}(V) = \int_V^{V_0} P_0(V)\,dV - 3RT_0\int_V^{V_0} \gamma_G(V)\frac{dV}{V}. \qquad (2)$$

In principle $\gamma_G(V)$ can be calculated from compressibility data in the solid phase by an iterative solution of equations (2) and (1). However, at larger compressions the contribution of the second term in the right hand side of (2) becomes small and the solution is considerably simplified by making an approximate guess for $\gamma_G(V)$ in the integral. On the other hand at small compressions equations (1) and (2) are equivalent to determining $\gamma_G(V)$ from the difference between the initial adiabatic and isothermal bulk moduli. Clearly the moduli in Table 1 are not sufficiently reliable. For this reason we have used, as a first guess, a γ_G equal to its initial value (see Table 1) in equation (2) in order to calculate a γ_G at maximum compression from equation (1). A constant γ equal to the average of these two was then used in (2) to evaluate the final $\gamma_G(V)$ by equation (1). The resulting $\gamma_G(V)$ for Na and K over a restricted range of high densities is shown in Fig. 3. For Rb the necessary shock data below 45 kbar is unavailable as argued above. Therefore, a calculation of γ_G at the lowest shock points around 54 kbar (see Fig. 1) was done ignoring the second term of equation (2) giving a $\gamma_G \sim 0{\cdot}25$. The uncertainty even at large compression in the calculated γ_G for Na and K are large, $\sim \pm 20$ per cent, due to the subtraction of pressure and energy data in equation (1).

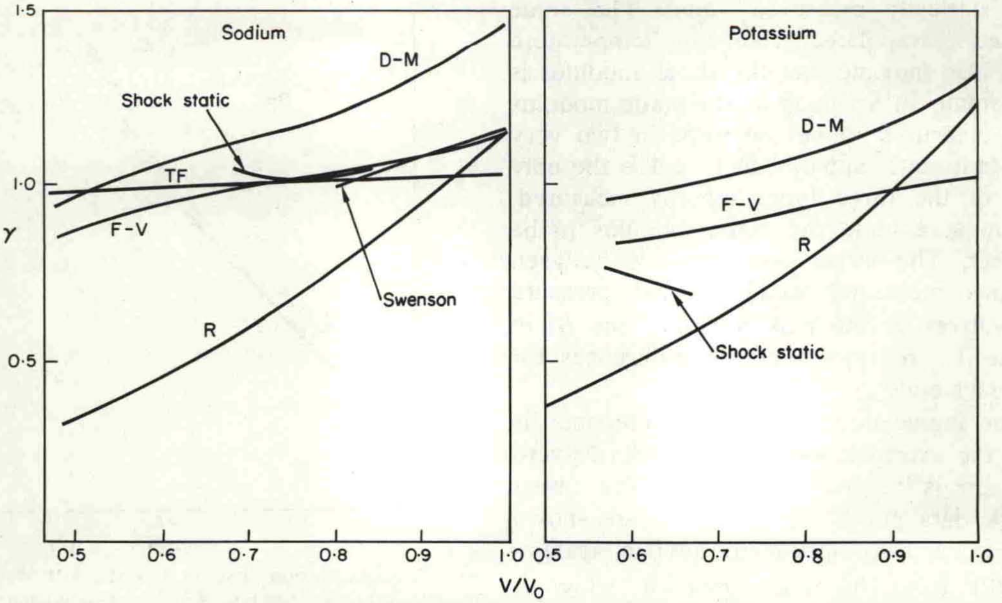

Fig. 3. Comparison of shock-static values of the Gruneisen coefficient with theoretical estimates discussed in Ref. [3].

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 $5d$-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 $6s$-electron to an inner $5d$-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 $6s$-band energy level and the broadening of the $5d$-band with compression. This transition is anticipated at a lower pressure (~ 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 ~ 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, $d\sigma_E/dV$, at the Fermi level. When the temperature is high enough to excite an appreciable number of electrons into the d-band $d\sigma_E/dV$ 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 ~ 50 per cent hotter than K at shock pressures ~ 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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REFERENCES

1. VAIDYA S. N. and KENNEDY G. C., *J. Phys. Chem. Solids* **31**, 2329 (1970).
2. GROVER R., *J. Phys. Chem. Solids* **31**, 2347 (1970).
3. GROVER R., KEELER R. N., ROGERS F. J. and KENNEDY G. C., *J. Phys. Chem. Solids* **30**, 2091 (1969).
4. AL'TSHULER L. V. and BAKANOVA A. A., *Soviet Phys. Usp.* **11**, 678 (1969).
5. GMX-6 Group, Los Alamos Sci. Lab., LA-4167-MS (1969) unpublished.
6. *Compendium of Shock Wave Data* Vols. 1 and 2 (UCRL-50108, 1966, plus Supplement 1967). (Edited by M. van Thiel and A. S. Kusubov.) Available from Clearinghouse for Federal and Technical Information, NBS, U.S. Dept. of Commerce, Springfield, Va. 22151.
7. ROYCE E. B. in *XLVII Course on Physics of High Energy Density* at International School of Physics "Enrico Fermi", Varenna, Italy 1969 (to be published) (also UCRL-71846 unpublished).
8. STERNHEIMER R., *Phys. Rev.* **78**, 235 (1950). ROSS, M. private communication.
9. LUEDEMANN H. D. and KENNEDY G. C., *J. geophys. Res.* **73**, 2795 (1968).
10. ROSS M., *Phys. Rev.* **171**, 777 (1968).