J. Phys. Chem. Solids, 1971, Vol. 32, pp. 2539–2544. Pergamon Press. Printed in Great Britain

THERMAL PROPERTIES OF ALKALI METALS FROM STATIC AND DYNAMIC COMPRESSIBILITIES*

R. GROVER

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

(*Received* 1 *February* 1971)

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.

*Work performed under the auspices of the U.S. Atomic Energy Commission.

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.

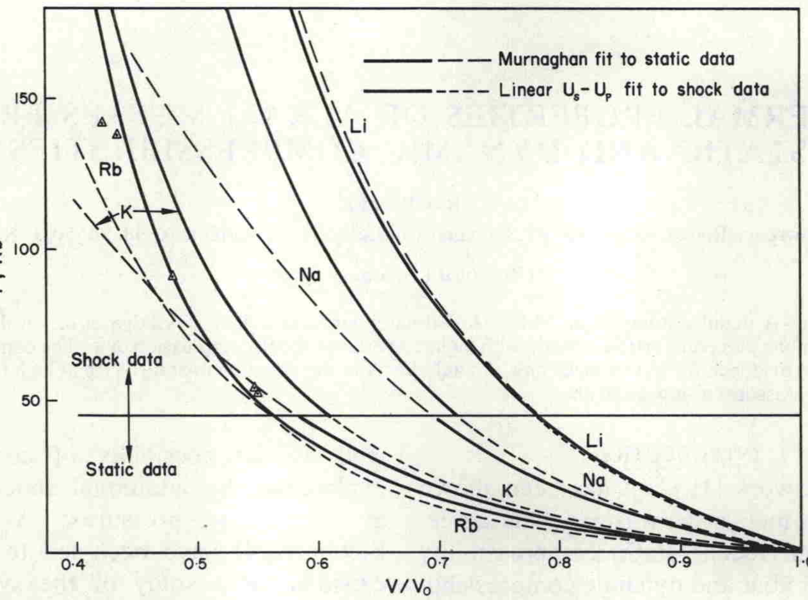

Fig. 1. Fits to static, isothermal and shock Hugoniot compression data. Δ-individual Hugoniot points for Rb.

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. $B' \equiv dB/dP$

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