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TECHNICAL NOTES

Normal isotherms of alkali halides from shock data*

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RECENT static compressibility measurements on the alkali halides up to pressures of 45 kbar agree well with previous compression data by Bridgman but disagree in many cases strongly with published isothermal compressions derived from dynamic shock wave experiments [1]. In a previous comparison [2] of sonic velocity data with Bridgman static compression data on a number of alkali halides it was found that the initial bulk moduli were in good agreement, but that differences in the pressure derivatives of the bulk moduli were large. For the potassium and rubidium salts the major part of the disagreement arises from the neglect in the analysis of the shock wave data of the well-known phase transitions between the NaCl and CsCl crystal structures. In this note revised isotherms for the potassium and rubidium salts are calculated taking into account the phase transition. Revised isotherms for the Li and Na salts are also presented based both on sound velocities at zero pressure and a more extensive set of shock data points. The reduction of shock wave data to isotherms is carried out by standard phenomenological methods based on the Mie–Gruneisen equation of state for solids [3]. Similar calculations were reported in graphical form by Christian in his unpublished thesis [4]. For NaCl a very close agreement between static and dynamic data has already been found [5] on the basis of more extensive dynamic data.

Isotherms for the K and Rb salts were calculated by a method of McQueen *et al.* [6] in which the Hugoniot for the high density phase is calculated. This "metastable" Hugoniot represents pressure-volume (P–V) points along which the shock conservations relations are satisfied assuming the initial state of specific volume, V_{20}, is an extension of the high density isotherm to zero pressure. Then the difference between the pressure along the experimental Hugoniot originating at the initial specific volume V_{10} and the metastable Hugoniot P_2 at the same volume V is readily shown to be

$$\Delta P \equiv P_1 - P_2 = \frac{V^{-1}\gamma_2(V)\,[\Delta_0 E + P_1 \Delta_0 V/2]}{1 - V^{-1}\gamma_2(V)\,(V_{20} - V)/2} \quad (1)$$

$$\Delta_0 V \equiv V_{10} - V_{20}.$$

Here the Gruneisen coefficient $\gamma_2(V)$ for the high pressure phase and the volume difference between the two phases at zero pressure are initially estimated and then corrected in subsequent iterations. Initially γ/V is assumed a constant, its value in the low pressure phase, and $\Delta_0 V$, the volume change along the isotherm as reported in Ref. [1]. The internal energy difference at zero pressure, $\Delta_0 E$, is assumed to be given by $P_T \Delta_0 V$ since the temperature dependence of the transition pressures, P_T, is small [7]. The points used are the original points measured by Christian on samples within 1 per cent of crystal density and overlapping points of Russian data [4]. With these first values equation (1) is used to calculate corresponding pressure points along the metastable Hugoniot. The resultant P–V points are converted to shock–velocity points and fit by a linear relationship. A standard shock-data reduction of this Hugoniot is then done using

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the Dugdale–MacDonald formula for γ_2[3]. With the $\gamma_2(V)$ and a new value $\Delta_0 V$ from this calculation, equation (1) is solved again to obtain a corrected metastable Hugoniot. Several additional iterations of this procedure are necessary to obtain a stable isotherm and $\gamma_2(V)$ for the high density phase. The final velocity fit, γ_{20} and $\Delta_0 V$ data obtained for the K and Rb salts are listed in Table 1. The calculated 25°C isotherms are tabulated in Table 2. Corrected isotherms for RbF have not been calculated since the statically measured phase transition is small and does not significantly affect the calculated isotherm.

For the Li and Na salts, new least square fits to dynamic compression data are shown in Table 3. The dynamic measurements include the measured bulk sound speeds at zero pressure[8]. Only shock points taken on samples within 1 per cent of crystal density were used. For NaI two points from shock data by Russian experimentalist overlapping the range of

Table 1. Hugoniot parameters used to calculate isotherms of Tables 2 and 3. For the potassium and rubidium salts the parameter refer to a metastable Hugoniot for the high pressure phases (see text) and P_T is the statically measured transition pressure

Mat.	V_0(cc/g)	C(cm/μsec)	S	γ_0	P_T(kbar)†	δ‡	Mat.	C	S
KF	0·372	0·278	1·56	2·13	17·3	+0·07	LiF*	0·5063	1·429
KCl	0·441	0·283	1·44	1·88	19·3	−0·02	LiCl	0·393	1·35
KBr	0·321	0·213	1·53	2·06	17·1	−0·07	LiBr	0·272	1·33
KI	0·292	0·216	1·27	1·54	18·0	+0·07	NaF	0·424	1·184
RbCl	0·315	0·229	1·49	1·98	5·2	−0·02	NaCl*	0·3435	1·43
RbBr	0·263	0·219	1·33	1·66	4·5	+0·05	NaBr	0·256	1·36
RbI	0·250	0·176	1·44	1·88	3·4	+0·01	NaI	0·209	1·46

*From HAUVER G. E., *Bull. Am. Phys. Soc. II* **15**, 1617 (1970).
†From Ref. [1].
‡Mean fractional lowering of $1 - V/V_0$ in Table 2 from data of Ref. [1].

Table 2. Relative volumes of K and Rb salts at 25 degree C

Pressure kilobar	KF	KCl	KBr	KI	RbCl	RbBr	RbI
5	—	—	—	—	—	0·842	0·834
10	—	—	—	—	0·808	0·822	0·807
15	—	—	—	—	0·790	0·804	0·784
20	0·852	0·800	0·787	0·819	0·773	0·788	0·764
25	0·838	0·785	0·771	0·802	0·759	0·774	0·747
30	0·825	0·772	0·756	0·787	0·745	0·760	0·731
35	0·814	0·760	0·743	0·773	0·733	0·748	0·717
40	0·803	0·749	0·731	0·760	0·722	0·736	0·705
45	0·793	0·738	0·719	0·747	0·712	0·726	0·693
50	0·783	0·728	0·709	0·736	0·702	0·716	0·682
60	0·766	0·711	0·691	0·715	0·685	0·697	0·662
70	0·751	0·695	0·674	0·697	0·669	0·681	0·645
80	0·737	0·681	0·660	0·680	0·655	0·666	0·630
90	0·724	0·668	0·647	0·665	0·643	0·653	0·616
100	0·713	0·656	0·635	0·652	0·632	0·640	0·604
120	0·692	0·635	0·614	0·627	0·611	0·618	0·582
140	0·674	0·617	0·596	0·606	0·594	0·599	0·564
160	0·659	0·601	0·580	0·587	—	0·583	0·547
180	0·645	0·586	0·566	—	—	—	—
200	0·632	0·573	0·554	—	—	—	—