

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-Grüneisen 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 Similar calculations were reported in graphical form by Christian in his unpublished thesis[4].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.

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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 conservation 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 Grüneisen 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

the Dugdale-MacDonald formula for γ_2 [3]. With the $\gamma_2(V)$ and a new value Δ_0V 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 Δ_0V 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.	$V_0(\text{cc/g})$	$C(\text{cm}/\mu\text{sec})$	S	γ_0	$P_T(\text{kbar})^\dagger$	δ^\ddagger	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	—	—	—	—

Table 3. Relative volumes of Li and Na Salts at 25 degree C

Pressure kilobars	LiF	LiCl	LiBr	NaF	NaCl	NaBr	NaI
5	—	—	—	—	—	—	—
10	—	0.970	0.964	0.981	0.964	0.956	0.945
15	0.979	0.957	0.947	0.972	0.947	0.937	0.922
20	0.972	0.944	0.932	0.963	0.933	0.920	0.902
25	0.965	0.933	0.919	0.954	0.919	0.905	0.885
30	0.959	0.922	0.906	0.946	0.907	0.890	0.869
35	0.953	0.911	0.894	0.939	0.895	0.877	0.854
40	0.947	0.901	0.883	0.931	0.884	0.865	0.841
45	0.942	0.892	0.872	0.924	0.874	0.853	0.828
50	0.936	0.883	0.862	0.917	0.864	0.843	0.817
60	0.926	0.867	0.844	0.904	0.846	0.823	0.796
70	0.916	0.852	0.827	0.891	0.830	0.805	0.778
80	0.906	0.838	0.812	0.879	0.816	0.789	0.761
90	0.898	0.825	0.798	0.868	0.802	0.774	0.746
100	0.889	0.813	0.785	0.858	0.790	0.760	0.732
120	0.874	0.791	0.761	0.838	0.767	0.736	0.708
140	0.859	0.772	0.740	0.820	0.747	0.715	0.687
160	0.846	0.754	0.722	—	0.730	0.696	0.669
180	0.834	0.738	0.705	—	0.714	0.679	0.653
200	0.823	0.724	0.690	—	0.700	0.664	0.638
220	0.812	0.711	0.676	—	—	0.650	—

the Christian[4] data are also used. A revised fit for LiI is not shown in Table 1 because of a lack of sonic data.

The calculated isotherms for these salts are shown in Table 1 up to pressures of 200 kbar. They are now in reasonable agreement with the 45 kbar static measurements[1]. However, for a number of these materials (LiCl, LiI, KI, RbCl, RbBr, RbI), the number of shock points is small (≤ 4). For a more detailed data comparison such as has been carried out on NaCl [5] more shock data in this pressure range is desirable.

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REFERENCES

1. VAIDYA S. N. and KENNEDY G. C., *J. Phys. Chem. Solids* **32**, 951 (1971); Also KENNEDY G. C. and KEELER R. N. in *American Institute of Physics Handbook*, 3rd Ed, pp. 4-38 (1972).
2. BARSCH G. R. and CHANG Z. P., *Phys. Status Solidi* **19**, 139 (1967).
3. RICE M. H., McQUEEN R. G. and WALSH J. M., *Solid St. Phys.* **6**, 1 (1958).
4. CHRISTIAN R. H., (UCRL-4900, unpublished). See

Compendium of Shock Wave Data, Vols. 1 and 2 (UCRL-50108, 1966 plus Supplement 1967), (Edited by M. van Thiel). Available from NBS, Springfield, VA.

5. FRITZ J. N., MARSH S. P., CARTER W. J. and McQUEEN R. G., in *Symposium on the Accurate Characterization of the High Pressure Environment*, 14-18 Oct. (1968) U.S. Dept. of Commerce, National Bureau of Standards, Gaithersburg, Maryland.
6. McQUEEN R. G., MARSH S. P., CARTER W. J., FRITZ J. N. and TAYLOR J. N., in *High Velocity Impact Phenomena*, (Edited by R. Kinslow), Chap. 7, Academic Press, New York (1970).
7. PISTORIUS C. W. F. T., *J. Phys. Chem. Solids* **26**, 1003 (1965).
8. HEARMON R. F. S. in *Zahlenwerte und Funktionen*, Nov. Series Group III (Edited by H. Landolt and R. Bornstein), p. 1, Springer-Verlag, Berlin (1966).

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Formation energies of Schottky and Frenkel defects in thallium halides

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UNLIKE in alkali halides where only Schottky defects are present, there is some speculation regarding the type of intrinsic defects in

thallium halides[1-4]. We have calculated the formation energies of Schottky as well as Frenkel defects in thallium halides, by employing a procedure analogous to that of Tosi and Doyama[5] in order to throw light on the nature of defects in these solids.

As in the quasi-continuum model of Mott and Littleton[6], we divide the crystal into two regions, region I containing the defect and the nearest neighbour ions (referred to by suffix d and k respectively) and region II, describing the rest of the lattice (denoted by l). We express the energy of a given defect configuration relative to the perfect crystal

Here z_d is the effective charge and V_d is the Madelung potential at the defect site; \mathbf{t}_{ij} is the position vector from the site j to the site i in the rigid lattice; ϕ_{ij} is the short range interaction energy of the two ions in the defect crystal and $\bar{\phi}_{di}$ is the shortrange interaction energy of the i^{th} ion and the ion replaced by the defect d . The displacement dipole and the displacement + electronic dipole of a positive and negative far ion are denoted by $\pm M' z_d \hat{t}_{id} / t_{id}^2$ and $M'_{\pm} z_d \hat{t}_{id} / t_{id}^2$; in evaluating M' and M'_{\pm} TKS polarizabilities[10] have been used. The total relaxation energy can now be computed from,

$$\begin{aligned}
 U_{\text{relax}} = & (e^2/a_0) \left\{ \frac{1}{2} \sum'_{kk'} z_k z_{k'} (1/r_{kk'} - 1/t_{kk'}) \right. \\
 & - \sum'_{kk'} z_k z_{k'} (1/s_{kk'} - 1/t_{kk'}) + \sum_k z_d z_k (1/s_{dk} - 1/t_{dk}) + \sum'_{kk'} z_k (\mathbf{m}_{k'} \cdot \hat{r}_{kk'} / r_{kk'}^2) \\
 & - \sum'_{kk'} z_k (\mathbf{m}_{k'} \cdot \hat{s}_{kk'} / s_{kk'}^2) + \sum_k z_d (\mathbf{m}_k \cdot \hat{s}_{dk} / s_{dk}^2) \\
 & + \frac{1}{2} \sum'_{kk'} [\mathbf{m}_k \cdot \mathbf{m}_{k'} - 3(\mathbf{m}_k \cdot \hat{r}_{kk'}) (\mathbf{m}_{k'} \cdot \hat{r}_{kk'})] / r_{kk'}^3 \\
 & + \frac{1}{2} a_0^3 \sum_k m_k^2 / \alpha_k + \frac{1}{2} \sum_k z_d (z_k \xi_k + \mathbf{m}_k) \cdot (\mathbf{n}'_+ M'_+ + \mathbf{n}'_- M'_-) \\
 & \left. - \frac{1}{2} (n''_+ M'_+ + n''_- M'_-) \right\} + \frac{1}{2} \sum'_{kk'} [\phi_{kk'}(r_{kk'}) - \phi_{kk'}(t_{kk'})] \\
 & + \sum_k [\phi_{dk}(r_{dk}) - \phi_{dk}(t_{dk})] + \sum_{kl} [\phi_{kl}(r_{kl}) - \phi_{kl}(t_{kl})]. \quad (2)
 \end{aligned}$$

as the sum of the energy required to create the defects in the rigid lattice and the relaxation energy. The latter is minimized with respect to all the relaxation parameters using the steepest descent method of Rosenbrock [7]. A concise form of the mathematical algorithm used in the present calculations is given below.

The rigid lattice energy change in creating the defects is written as,

Here, the terms due to $i = j$ are excluded from the primed sums, ξ and m are the displacements and moments of Region I ions, $\mathbf{r}_{ij} = \mathbf{t}_{ij} + \xi_i - \xi_j$, $\mathbf{s}_{ij} = \mathbf{t}_{ij} - \xi_j$, α is the electronic polarizability while n''_{\pm} and \mathbf{n}'_{\pm} are the lattice summations[8, 9] for the long-range polarization potentials and fields (see opposite page). In equation (2) the relaxations of the far ions are approximated to ion displacement dipoles; thus, $\mathbf{r}_{kl} = \mathbf{t}_{kl} + \xi_k - (\pm M' z_d \hat{t}_{id} / t_{id}^2)$. The terms

$$U_{rl} = z_d V_d e^2 / a_0 + \sum_k [\phi_{dk}(t_{dk}) - \bar{\phi}_{dk}(t_{dk})] + \sum_l [\phi_{al}(t_{al}) - \bar{\phi}_{al}(t_{al})] \quad (1)$$