

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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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 $\pm M' z_d \hat{t}_{1d}/t_{1d}^2$ and $M'_{\pm} z_d \hat{t}_{1d}/t_{1d}^2$; in evaluating M' and $M'_{\pm}$ TKS polarizabilities[10] have been used. The total relaxation energy can now be computed from,

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

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'_+ and n'_- 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, $\mathbf{r}_{kl} = \mathbf{t}_{kl} + \xi_k - (\pm M' z_d \hat{t}_{1d}/t_{1d}^2)$. The terms

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