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Analysis of Interatomic Separation-Pressure Relations for Alkali Halides and Periclase(MgO)*

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Abstract: A new method for the determination of interatomic separation-pressure relations is investigated and applied for alkali halides and MgO crystals. The method is developed by using Hildebrand approximation and an ionic model based on Harrison's treatment of overlap repulsive potential which takes into account the interactions up to second neighbors. The van der Waals dipole-dipole and dipole-quadrupole interactions calculated by more accurate methods are also included in the present work. It is found that the new method yield satisfactory results in agreement with the available experimental data.

Key words: Harrison's model; Hildebrand approximation; van der Waals (vdW) energies

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1 Introduction

Numerous investigators using interionic potentials[1~4], as well as phenomenological approaches[5~7] have developed various forms of interatomic separation-pressure relations for studying high-temperature and high-pressure behaviour of solids. The purpose of the present paper is to propose a simple method derived from Harrison's interionic function[8] and the Hildebrand approximation[9], applicable to alkali halides and MgO crystals, for the determination of their interatomic separation-pressure data in the wide range of temperature and pressure. The theory and method of calculation are given in Section 2. The results are discussed and compared with available experimental data in Section 3.

2 Theory and Method of Calculation

The equation of state for a solid can be derived from the Hildebrand approximation which is expressed as follows [9]

$$p = -\frac{\mathrm{d}\varphi}{\mathrm{d}V} + T\alpha B_T \tag{1}$$

where φ is the lattice potential energy and V is the volume. T is the temperature, α is the coefficient of volume thermal expansion and B_T is the isothermal bulk modulus. In Eq. (1) the first term on right hand is the pressure due to volume dependence of electronic ground state energy (static pressure) and the second term is pressure due to vibration of nuclei (thermal pressure). p is the externally applied pressure. Now using the relation $V = xr^3$, Eq. (1) can be rewritten as follows

$$p = -\frac{1}{3xr^2}\frac{\mathrm{d}\varphi}{\mathrm{d}r} + T\alpha B_T \tag{2}$$

where x is a constant which depends on the structure of solid and x equal to 2 for NaCl-type and 1.54

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for CsCl-type structures, and r is the interatomic separation.

The thermal pressure in Eq. (2), which is given by $T\alpha B_T$, is based on the Hildebrand approximation. It should be mentioned that the correct expression for thermal pressure $p_{\rm th}$ can be taken from calculus as follows

$$\left(\partial p/\partial T\right)_V = \left(\partial p_{\rm th}/\partial T\right)_V = \alpha B_T \tag{3}$$

Upon integration we get

$$p_{\rm th} = \int_0^T (\alpha B_T)\,{\rm d}T \tag{4}$$

This becomes $T\alpha B_T$ only if the product αB_T is independent of T. This is approximately true above the Debye temperature $\Theta_{\rm D}$[10]. The Debye temperature $\Theta_{\rm D}$ of solids considered in the present study, have values close to room temperature except that for MgO($\Theta_{\rm D}$=945 K)[11]. The Eq. (2) works well above the Debye temperature $\Theta_{\rm D}$; but for MgO, the above equation may not be satisfied below $\Theta_{\rm D}$.

For the calculation of φ, we use Harrison's potential form for the overlap repulsive energy and also consider van der Waals (vdW) dipole-dipole and dipole-quadrupole interactions. Within the framework of Harrison's model the total lattice potential energy φ is expressed as follows[8]

$$\varphi = -a_{\rm M}Z^2e^2/r - C/r^6 - D/r^8 + \varphi_{\rm rep} \tag{5}$$

where the first term on the right-hand side of Eq. (5) is the electrostatic Coulomb energy with $\alpha_{\rm M}$ as Madelung's constant which is equal to 1.747 6 for NaCl-type structures and 1.762 7 for CsCl-type structures, e the charge of the electron, and Z the valency. The second and third terms are van der Waals (vdW) dipole-dipole and dipole-quadrupole energies. The constants C and D are related to the dipole-dipole (c_{ij}) and dipole-quadrupole (d_{ij}) interaction coefficients as follows[12]

$$C = S_{+-}c_{+-} + S_{++}c_{++} + S_{--}c_{--} \tag{6}$$

$$D = T_{+-}d_{+-} + T_{++}d_{++} + T_{--}d_{--} \tag{7}$$

where S_{ij} and T_{ij} are lattice sums which had been given by Tosi[9]. The subscripts $+-$, $++$, $--$ represent the cation-anion, cation-cation, anion-anion interactions, respectively. The values of c_{ij} and d_{ij} are obtained from the Kirkwood-Muller formulate given below[12]

$$c_{ij} = -\frac{6mc^2}{N}X_iX_j\left(\frac{X_i}{a_i} + \frac{X_j}{a_j}\right)^{-1} \tag{8}$$

$$d_{ij} = -\frac{9mc^2}{Ne^2}c_{ij}\left(\frac{X_i}{n_i} + \frac{X_j}{n_j}\right)^{-1} \tag{9}$$

where c is the velocity of light, a and X are the polarisabilities and molar susceptibilities, respectively. N is the Avogadro's number. n_i and n_j are the number of outmost electrons. The values of C and D calculated from Eqs. (6)~(9) were used in the present work.

The overlap repulsive energy can be written as[8]

$$\varphi_{\rm rep} = \frac{n_0\eta^2}{2m}\left[M\bar{\mu}^3 r\cdot\exp(-k\bar{\mu}r) + \frac{1}{2}M'\mu_1^3 r'\cdot\exp(-k\mu_1 r') + \frac{1}{2}M'\mu_2^3 r'\cdot\exp(-k\mu_2 r')\right] \tag{10}$$

where η is the Planck's constant h divided by 2π, m the mass of electron. For NaCl-type structures, $M=6$ and $M'=12$ are the numbers of first and second neighbor ions. Similarly, r and $r'=\sqrt{2}\,r$ are the first and second nearest neighbor distances. For CsCl-type structures $M=8$, $M'=6$, and $r'=(2/\sqrt{3})r$. $\bar{\mu}$ is the arithmetic average of μ_1 and μ_2 for the cation and anion. The values of μ_1 and μ_2 can be calculated from the following relation

$$\mu_i^2 = -2m\Sigma_i/\eta^2 \tag{11}$$

where Σ_i is the valence state energy of ions. In order to calculate lattice potential energy φ from Eq. (5), there remain only two unknown parameters, viz. n_0 and k which are obtained from the equilib-

rium condition and the following relations

$$\left(\mathrm{d}\varphi/\mathrm{d}r\right)_{r=r_0}=0 \tag{12}$$

$$\left(\mathrm{d}^2\varphi/\mathrm{d}r^2\right)_{r=r_0}=9xr_0B_{T_0} \tag{13}$$

The potential parameters thus calculated from Eq. (12) and Eq. (13) are assumed to be independent of pressure. The values of $\mathrm{d}\varphi/\mathrm{d}r$ are now computed by decreasing r and finally the pressure p is obtained from Eq. (2). The method is repeated along different isotherms from room temperature up to higher temperature. The input data required are given in Table 1. The results obtained are reported in Table 2 ~Table 5 along with the available experimental data.

Table 1　Values of input parameters used in the present work

Crystal	r_0 /(nm)	α_0 /(10^{-4}K^{-1})	B_{T_0} /(GPa)	μ_1 /(nm^{-1})	μ_2 /(nm^{-1})	C /(10^{-67}J·cm^6)	D /(10^{-83}J·cm^8)	n_0	k
LiF	0.201 3[13]	0.999[13]	66.5[13]	39.62[15]	21.12[15]	46	26	3	1.34
NaF	0.231 7[13]	0.96[13]	46.5[13]	30.87[15]	21.12[15]	139	98	11.5	1.54
CsCl	0.357 1[14]	1.37[14]	18.0[14]	21.16[15]	17.99[15]	333	357	974	2.08
MgO	0.210 5[14]	0.312[14]	173.0[14]	38.38[15]	19.23[15]	170	79	7.00	1.2

Table 2　Values of pressure versus interatomic separation for LiF crystal at different temperatures (The available experimental data[16] are given within parentheses)

298 K		573 K		873 K		1 073 K	
r/(nm)	p/(GPa)	r/(nm)	p/(GPa)	r/(nm)	p/(GPa)	r/(nm)	p/(GPa)
0.201 3	0(0)	0.203 5	0(0)	0.206 6	0(0)	0.209 3	0(0)
0.200 3	0.995(1.0)	0.202 4	0.996(1.0)	0.205 3	0.998(1.0)	0.207 7	1.003(1.0)
0.199 4	1.974(2.0)	0.201 4	1.984(2.0)	0.204 1	1.988(2.0)	0.206 3	1.997(2.0)
0.198 5	2.952(3.0)	0.200 4	2.967(3.0)	0.203 0	2.984(3.0)	0.205 0	3.007(3.0)
0.197 7	3.954(4.0)	0.199 5	3.957(4.0)	0.201 9	3.962(4.0)	0.2037	3.984(4.0)
0.196 9	4.938(5.0)	0.198 6	4.941(5.0)	0.200 9	4.967(5.0)	0.202 6	4.977(5.0)
0.196 1	5.909(6.0)	0.197 7	5.922(6.0)	0.199 9	5.953(6.0)	0.201 5	5.983(6.0)
0.195 4	6.875(7.0)	0.196 9	6.894(7.0)	0.194 4	6.915(7.0)	0.200 4	6.955(7.0)
0.194 6	7.846(8.0)	0.196 1	7.877(8.0)	0.198 2	7.938(8.0)	0.199 4	7.958(8.0)
0.194 0	8.816(9.0)	0.195 3	8.843(9.0)	0.197 3	8.884(9.0)	0.198 5	8.929(9.0)

Table 3　Values of pressure versus interatomic separation for NaF crystal at different temperature (The available experimental data[16] are given within parentheses)

298 K		473 K		673 K		873 K		1 073 K	
r/(nm)	p/(GPa)	r/(nm)	p/(GPa)	r/(nm)	p/(GPa)	r/(nm)	p/(GPa)	r/(nm)	p/(GPa)
0.231 7	0(0)	0.233 1	0(0)	0.234 9	0(0)	0.236 9	0(0)	0.239 2	0(0)
0.230 1	1.014(1.0)	0.231 4	1.005(1.0)	0.233 1	0.997(1.0)	0.234 8	0.998(1.0)	0.237 0	1.002(1.0)
0.228 6	1.987(2.0)	0.229 9	1.991(2.0)	0.231 4	1.995(2.0)	0.233 0	1.995(2.0)	0.234 9	1.998(2.0)
0.227 3	2.981(3.0)	0.228 5	2.988(3.0)	0.229 9	2.991(3.0)	0.231 4	2.993(3.0)	0.233 1	3.004(3.0)
0.226 0	3.974(4.0)	0.227 2	3.981(4.0)	0.228 5	3.987(4.0)	0.229 9	3.990(4.0)	0.231 5	3.993(4.0)
0.224 9	4.955(5.0)	0.225 9	4.961(5.0)	0.227 2	4.979(5.0)	0.228 5	4.983(5.0)	0.230 0	4.989(5.0)
0.223 8	5.926(6.0)	0.224 8	5.942(6.0)	0.226 0	5.952(6.0)	0.227 3	5.966(6.0)	0.228 6	5.973(6.0)
0.222 8	6.908(7.0)	0.223 7	6.913(7.0)	0.224 9	6.931(7.0)	0.226 1	6.958(7.0)	0.227 3	6.962(7.0)
0.221 8	7.863(8.0)	0.222 6	7.892(8.0)	0.223 8	7.905(8.0)	0.225 0	7.924(8.0)	0.226 1	7.937(8.0)
0.221 0	8.847(9.0)	0.221 7	8.864(9.0)	0.222 8	8.894(9.0)	0.224 0	8.912(9.0)	0.224 9	8.935(9.0)

Table 4 Values of pressure versus interatomic separation for CsCl crystal at different temperatures (The available experimental data[16] are given within parenthesestures)

298 K		473 K		673 K		873 K	
r/(nm)	p/(GPa)	r/(nm)	p/(GPa)	r/(nm)	p/(GPa)	r/(nm)	p/(GPa)
0.357 1	0(0)	0.360 3	0(0)	0.364 6	0(0)	0.369 6	0(0)
0.351 4	0.995(1.0)	0.353 7	0.997(1.0)	0.356 8	0.998(1.0)	0.360 0	1.001(1.0)
0.346 8	1.984(2.0)	0.348 5	1.987(2.0)	0.350 9	1.901(2.0)	0.353 2	1.921(2.0)
0.343 0	2.913(3.0)	0.344 3	2.923(3.0)	0.346 2	2.927(3.0)	0.347 9	2.938(3.0)
0.339 7	3.894(4.0)	0.340 7	3.902(4.0)	0.342 2	3.924(4.0)	0.343 5	3.947(4.0)
0.336 8	4.877(5.0)	0.337 6	4.896(5.0)	0.338 8	4.903(5.0)	0.339 8	4.927(5.0)
0.334 3	5.853(6.0)	0.334 8	6.871(6.0)	0.335 8	6.892(6.0)	0.336 6	6.905(6.0)
0.331 9	6.817(7.0)	0.332 3	6.834(7.0)	0.333 2	6.859(7.0)	0.333 7	6.874(7.0)
0.329 8	7.802(8.0)	0.330 1	7.829(8.0)	0.330 7	7.844(8.0)	0.331 1	7.856(8.0)
0.327 9	8.756(9.0)	0.328 0	8.772(9.0)	0.328 4	8.795(9.0)	0.328 7	8.810(9.0)

Table 5 Values of pressure versus interatomic separation for MgO crystal at different temperatures (The available experimental data[17] are given within parentheses)

300 K		500 K		1 000 K		1 500 K		2 000 K	
r/(nm)	p/(GPa)	r/(nm)	p/(GPa)	r/(nm)	p/(GPa)	r/(nm)	p/(GPa)	r/(nm)	p/(GPa)
0.210 5	0(0)	0.211 0	0(0)	0.212 5	0(0)	0.214 1	0(0)	0.216 0	0(0)
0.206 9	1.028(1.03)	0.207 4	1.001(1.00)	0.208 9	0.917(0.92)	0.210 5	0.829(0.83)	0.212 3	0.741(0.74)
0.203 2	2.361(2.4)	0.203 7	2.296(2.3)	0.205 1	2.124(2.1)	0.206 8	1.921(1.9)	0.208 5	1.737(1.7)
0.199 4	4.083(4.1)	0.199 9	3.982(4.0)	0.201 3	3.691(3.7)	0.202 9	3.367(3.4)	0.204 6	3.046(3.0)
0.195 4	6.322(6.4)	0.195 9	6.183(6.2)	0.197 2	5.742(5.8)	0.198 8	5.273(5.3)	0.200 5	4.793(4.8)
0.191 3	9.247(9.4)	0.191 7	9.067(9.1)	0.193 0	8.467(8.5)	0.194 6	7.798(7.9)	0.196 2	7.132(7.2)
0.186 9	13.102(13.3)	0.187 4	12.815(13.0)	0.188 7	12.001(12.2)	0.190 1	11.224(11.3)	0.191 8	10.307(10.3)
0.182 3	18.273(18.7)	0.182 8	17.948(18.3)	0.184 1	16.848(17.2)	0.185 5	15.735(16.0)	0.187 1	14.609(14.7)
0.177 5	25.058(26.0)	0.178 0	24.664(25.5)	0.179 2	23.322(24.0)	0.180 6	21.837(22.4)	0.182 2	20.434(20.7)

3 Results and Discussions

We have investigated the interatomic separation-pressure relationship in the wide range of temperatures and pressures using Harrison's interionic function[8] and Hildebrand approximation[9]. We have performed calculations for four crystals, viz. LiF, NaF, CsCl and MgO. The corresponding experimental data have been reported by Yagi[16] and O. L. Anderson[17]. It is clear from the calculated values for all three alkali halides are in good agreement with the experimental values[16]. For MgO, it is found that the calculated results at $T=300$ K and $T=500$ K deviate slightly from the experimental data[17]. The discrepancy may be due to the assumption $\alpha B_T=$constant, which holds well for $T\geqslant\Theta_D$. By increasing temperature, the deviations are found to decrease (Table 5) and a very good agreement is obtained at higher temperature $T\geqslant\Theta_D$. To summarize, from the new interatomic separation-pressure relationship, we can predict adequately the variations of pressure with interatomic separation at different temperature for LiF, NaF, CsCl and MgO crystals in agreement with experimental data. Thus, the results obtained in the present study clearly demonstrate that the formulations originally due to Harrison's potential model and Hildebrand approximation provide a useful method for studying the interatomic separation-pressure relationship in the case of alkali halides and MgO crystals.

Finally, it should also be mentioned that the interatomic separation-pressure relationship proposed in the present study is of general nature and therefore its application may be extended to different classes of solids of geophysical importance. The results of the present investigation also lead to the understanding of the equation of state based on the microscopic details of the theory of interionic potentials.

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碱卤化合物和 MgO 的离子间距-压强关系分析

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摘要: 给出了一种新的方法来决定固体的离子间距与压强的关系,并将这种方法应用到碱卤化合物和 MgO 晶体。这种新方法的理论基础是利用 Hildebrand 近似、并运用 Harrison 的处理方法来考虑排斥能,即考虑离子间的相互作用直到次临近离子。还利用了更精确的方法来计算偶极子-偶极子和偶极子-四极子之间的相互作用。利用这种新方法得到的结果和实验结果吻合得很好。

关键词: Harrison 模型;Hildebrand 近似;van der Waals (vdW)能量

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