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THERMOPHYSICAL PROPERTIES OF MATERIALS

Phase Transitions in Alkali Halide Crystals

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Abstract—The paper is devoted to the study of the characteristics of structural phase transitions occurring in ionic crystals under an extremely high pressure. The calculations are made for crystals of infinite size at absolute zero temperature. The pressure of $B1$–$B2$ polymorphic transformation is calculated for a number of alkali halide crystals using pair interaction potentials obtained self-consistently within the framework of inhomogeneous electron gas theory. In so doing, the effects of seven coordination spheres are taken into account in the thermodynamic potential. The changes of the cohesion characteristics of crystals (cohesion energy, lattice constant) are calculated for the transition from the $B1$ structure (NaCl type) to the $B2$ structure (CsCl type). Based on the obtained results, conclusions are made on the stability of one or another crystal structure in the given range of external pressure. For crystals in the $B1$ phase, the moduli of elasticity and relative changes of the volume at the phase transition pressure are calculated. It is shown that the inclusion of the effect of higher coordination spheres affects considerably the values of the elastic characteristics of ionic crystals.

INTRODUCTION

The choice of the type of lattice of ionic crystals is defined by the ratio of ionic radii. In so doing, the cations usually have a smaller size than the anions; therefore, the cations in ionic crystals are located in voids formed due to close packing of the larger anions. If the cations are so large that they do not fit the voids, they spread the anions apart and loosen their close packing. For example, sodium chloride crystals have a structure of face-centered cubic lattice because the size of a chlorine ion (r_{Cl} = 1.81 Å) is almost twice the size of a sodium ion (r_{Na} = 0.98 Å). With such a ratio of the ionic radii, the free space at the center of the cubic cell of sodium chloride turns out to be insufficient to accommodate one more ion. The situation is different with a cesium chloride crystal. The sizes of chlorine and cesium ions are close (1.81 and 1.65 Å), and the space at the center of an elementary cube is sufficient to accommodate one more ion, and a closer packed structure; i.e., a body-centered cube, proves to be more convenient from the energy point of view. The decisive importance of the ratio of ionic radii in the selection of the type of ionic crystal lattice is illustrated by the fact that, if this ratio changes under the effect of external factors (temperature, pressure), the crystal structure of this ionic compound will also change [1].

The anion radius increases faster with increasing temperature than the cation radius, this resulting in an increase of the difference in the size of ionic radii. Therefore, some crystals (e.g., cesium chloride and rubidium chloride) change their structure with an increase in temperature: they rearrange from a body-centered cube into an elementary cube. An inverse rearrangement is observed with an increase in pressure, when the anion radius decreases faster than the cation radius: the ionic radii become closer in size, and this may result in the transition of the crystal from a primitive cubic lattice into a body-centered one. Such rearrangements of the crystal lattice with increasing pressure bring the crystal to a state with a lattice of the CsCl type. A further pressure increase may cause the crystal to change to a metallized state [2, 3]. This paper is devoted to the study of polymorphic transformations of alkali halide crystals of an infinitely large size at a temperature T = 0 K within inhomogeneous electron gas theory.

CALCULATION OF THE PRESSURE OF POLYMORPHIC TRANSFORMATION OF ALKALI HALIDE CRYSTALS

The thermodynamic potential of a crystal under an external pressure (at T = 0 K) may be represented in the form

$$H_i(R) = NU_i + pV_i - \alpha_\mu/R. \qquad (1)$$

Here, N is the coordination number of the structure; V_i is the elementary cell volume; U_i is the short-range potential of pair interaction; α_μ is the Madelung constant of the given crystal structure; the subscript i numbers both phases. During the calculations, the ion surroundings were taken into account up to the seventh order inclusive. Therefore, the product NU_i entering (1) may be represented as the sum over seven coordination spheres, i.e.,

$$H_i(R) = \sum_{k=1}^{7} N_k U_k^i(\alpha_k R) + pV_i - \alpha_\mu/R, \qquad (2)$$

where $\alpha_k = R_k/R_0$ is the ratio of the radius of the kth coordination sphere to the radius of the first coordination sphere. At $T = 0$ K, the pressure is related to the energy U_i by the relation

$$p = -(\partial U_i/\partial V_i). \qquad (3)$$

Therefore, the expression for the thermodynamic potential finally assumes the form

$$H_i(R) = \sum_{k=1}^{7} N_k U_k^i - V_i \frac{\partial U_i}{\partial V_i} - \frac{\alpha_\mu}{R}. \qquad (4)$$

The pressure of polymorphic transformation can be found from the relation

$$H_1(p_0) = H_2(p_0), \qquad (5)$$

in which p_0 is the pressure of polymorphic transformation. The pressure p_0 was calculated using a computer by constructing the dependences of the thermodynamic potential on the pressure $H(p)$ for a crystal having a structure of the NaCl and CsCl types. The phase transition point was determined with a preset accuracy by the equation

$$|H_1(p_0) - H_2(p_0)| < \varepsilon, \qquad (6)$$

where ε is the preassigned calculation accuracy. The value of ε was selected so that the transition pressure could be determined with an accuracy of up to 1 kbar.

As follows from the relation (4), the accuracy of calculation of the crystal potential and transition pressure depends on how close the used pair interaction potential U_i is to the experimental data. In this study, we used numerical pair potentials obtained self-consistently within the framework of inhomogeneous electron gas theory [4]. In so doing, the potentials were approximated using a smooth function that was continuous together with its derivatives. Table 1 gives the values of the cohesion energy U_0 and equilibrium distances R_0 between ions in the lattice, obtained during the approximation of potentials [4], for crystals with a lattice of the NaCl type ($B1$ structure) and CsCl type ($B2$ structure). A comparison of the results given in Table 1 leads to some conclusions. In general, all data of the theoretical calculation are in good agreement with each other and with the experimental data. However, in the calculations of the characteristics of crystals, when estimating the first addend in formula (4), Cohen and Gordon [6] included only the interaction of the ions of the first coordination sphere, this providing for good agreement of the properties of ionic structures with the experimental data. Kim and Gordon [5] allowed for the contribution by the second neighbors to the energy of interac-

Table 1. Cohesion characteristics of alkali halide crystals at $T = 0$ K

Crystal	$B1$ phase				$B2$ phase	
	R_0, au		U_0, au			
	theoretical	experimental data [7]	theoretical	experimental data [7]	R_0, au	U_0, au
LiF 1	3.65		0.4147		3.83	0.4007
2	3.80	3.81	0.3975	0.3933	3.98	0.3837
3	3.76		0.4144		3.90	0.3901
LiCl 1	4.67		0.3285		4.87	0.3187
2	4.76	4.91	0.3203	0.3216	4.99	0.3107
3	4.79		0.3264		4.84	0.3181
LiBr 1	5.03		0.3065		5.24	0.2978
2	5.06	5.16	0.3020	–	5.30	0.2932
3	5.09		0.3060		5.29	0.2961
NaF 1	4.37		0.3543		4.56	0.3449
2	4.57	4.61	0.3387	0.3473	4.75	0.3295
3	4.44		0.3544		4.51	0.3398
NaCl 1	5.40		0.2912		5.61	0.2847
2	5.54	5.54	0.2816	0.2953	5.75	0.2749
3	5.51		0.2911		5.63	0.2806
NaBr 1	5.74		0.2751		5.92	0.2690
2	5.82	5.76	0.2684	0.2778	6.05	0.2621
3	5.77		0.2750		6.00	0.2680
KF 1	4.91		0.3253		5.07	0.3197
2	5.12	5.12	0.3092	0.3099	5.29	0.3030
3	5.11		0.3116		5.18	0.3096
KCl 1	5.76		0.2794		5.95	0.2753
2	5.97	5.93	0.2668	0.2701	6.16	0.2620
3	5.88		0.2776		6.02	0.2687
KBr 1	6.05		0.2665		6.22	0.2626
2	6.22	6.14	0.2566	0.2539	6.42	0.2522
3	6.10		0.2648		6.34	0.2572
RbF 1	5.23		0.3092		5.37	0.3050
2	5.37	5.35	0.2983	–	5.54	0.2935
3	5.29		0.2998		5.42	0.3011
RbCl 1	6.03		0.2699		6.18	0.2668
2	6.19	6.16	0.2591	–	6.40	0.2554
3	6.14		0.2672		6.25	0.2617
RbBr 1	6.27		0.2580		6.48	0.2549
2	6.18	6.41	0.2488	–	6.67	0.2454
3	6.33		0.2513		6.55	0.2497

Note: (1) Gordon, Kim [5]; (2) Cohen, Gordon [6]; (3) calculation with potentials [4].

Table 2. Pressure of polymorphic transformation of alkali halide crystals

Crystal	p_0, kbar					
	Gordon, Kim [5]	Cohen, Gordon [6]	Zhdanov, Polyakov [8]	Wedephol [9]	numerical calculation with potentials [4]	experiment [10]
LiF	550	480	200	–	302	100–310
LiCl	160	144	–	–	149	110–140
LiBr	110	105	110	–	100	70–105
NaF	142	129	–	245	154	17–200
NaCl	49	49	190	290	138	18–250
NaBr	35	39	–	–	45	30–53
KF	51	51	–	–	89	20–100
KCl	21	24	–	110	29	20–36
KBr	19	17	24	80	29	18–36
RbF	32	30	–	–	34	12–100
RbCl	16	16	22	–	17	5–31
RbBr	12.4	12.4	13	–	14	5–25

tion of the lattice, which resulted in a rise of the bond energy up to 10% and in an approximately corresponding reduction of the lattice constant. One can assume that the Gordon–Kim theory inadequately describes the interaction of ions over long distances (~8 a.u. and more), because a correct calculation of the dispersion interaction is necessary in this case. As mentioned above, seven coordination spheres were included in our calculations. The data of Table 1 indicate that the pair interaction potentials [4] include fairly correctly the dispersion term, because during their use no drastic increase in the bond energy of the lattice is observed (and accordingly, no reduction of the lattice constant), and a good agreement is observed with experiment when the higher coordination spheres are included.

We will now turn to the calculation of the characteristics of polymorphic transformation. The results of calculation of the phase transition pressure for a number of alkali halide crystals are given in Table 2.

In analyzing the data of Table 2, one can easily see that the results of our study are in rather good agreement with the experimental data and with the results of other authors (the transition pressure p_0 for NaCl crystal is an exception). However, in [6] and [8], the interaction between only the nearest neighbors was included, while in [5] and [9] the effect of second neighbors is included. It is clear that the inclusion of the second coordination sphere results in some increase in the pressure of polymorphic transformation. However, the inclusion of the higher coordination spheres (up to the seventh one inclusive) does not result in a significant increase in the transition pressure p_0. Note that, in the case of lithium halides, the pressure p_0, on the contrary, drops down compared to the results obtained in [5] and [6]. Furthermore, a very high discrepancy in the values of the pressure of polymorphic transformation according to Wedephol [9], and Gordon and Kim [5, 6] is incomprehensible. Note that all of these researchers used the Thomas–Fermi–Dirac functional in their calculations. In so doing, Wedephol [9] obtained a value of the bond energy that was, by and large, 10–12% lower than in the calculations by Gordon and Kim and Zhdanov and Polyakov (see Table 1) for almost the same lattice constant. Because the wave functions used in these calculations are taken from the same source [11], one can draw a conclusion on a certain error in the numerical methods used by the authors of those papers.

CHANGE OF CHARACTERISTICS OF CRYSTALS UPON POLYMORPHIC TRANSFORMATION

The changes of the characteristics of alkali halide crystals occurring upon phase transformation are of certain interest. Given in Table 3 are the values of the absolute and relative (in percent) changes of the lattice constant and cohesion energy during transition from the NaCl structure to the CsCl structure ($B1 \longrightarrow B2$). As follows from Table 3, the relative change of the lattice constant during polymorphic transformation exceeds the relative change of the cohesion energy on the average by 50–55%. It is also interesting to compare the relative changes of the volume of crystals during their phase transformation. The respective results are given in Table 4. We will dwell in more detail on the notation used. The relative change of the crystal volume $-(\Delta V/V_{01})$ may be defined as the ratio of the difference of volumes of the more stable phase at a given pressure to the volume of the given phase in the absence of external pressure. This value is usually written as $-(\Delta V_t/V_{01})$. Therefore,

$$-\frac{\Delta V_t}{V_{01}} = \frac{V_{t1} - V_{t2}}{V_{01}}, \tag{7}$$

where V_{ti} is the volume of the B_i phase at some pressure p, and V_{01} is the volume of the B_i phase in the absence of external pressure. Relation (7) makes it possible to analyze the relative changes of the volumes of both phases of the crystal subjected to polymorphic transformation. The respective quantities appearing in Table 4 are defined as follows:

$$-\frac{\Delta V_{B1}}{V_{01}} = \frac{V_{01} - V_{B1}}{V_{01}}, \tag{8}$$

$$-\frac{\Delta V_{B2}}{V_{01}} = \frac{V_{01} - V_{B2}}{V_{01}}, \tag{9}$$

where V_{B1} and V_{B2} are the volumes of the $B1$ and $B2$ phases corresponding to the pressure p_0 (i.e., the pressure of phase transformation), and V_{01} is the volume of $B1$ phase in the absence of external pressure. The quantity $-(\Delta V_t/V_{01})$, whose values are given in the third column of Table 4, are determined according to (7) but at $p = p_0$.

On analyzing the data of Table 4, one may notice that the inclusion of the second and third coordination spheres in [6] leads to an increase in the constants $-(V_{B1}/V_{01})$ and $-(V_{B2}/V_{01})$ for lithium, sodium, and potassium halides in comparison with the values of the same constants in the approximation of only the first coordination sphere [5]. In this case, for lithium halides, this increase is about 60%, while for the potassium halides it is only 7–10%. On the contrary, in the KCl, RbCl, and RbBr crystals, the inclusion of the second and third neighbors leads to a reduction of the constants $-(V_{B1}/V_{01})$ and $-(V_{B2}/V_{01})$ by 8–12%. It is interesting to note that for the KCl and KBr crystals we observe an increase in the constant $-(V_{B2}/V_{01})$ and a decrease in the constant $-(V_{B1}/V_{01})$ by about 8%. The constant $-(\Delta V_t/V_{01})$ for all alkali halide crystals decreases if the effect of the second and third neighbors is taken into account. In this case, we observe the above-mentioned tendency: for lithium halides, the decrease in the constant $-(\Delta V_t/V_{01})$ is about 70%, and for rubidium halides it is 7–9%. The results obtained with inclusion of the higher coordination spheres (up to the seventh one inclusive) using the pair interaction potentials [4] have confirmed the foregoing remarks. Furthermore, the data of Table 4 indicate that the use of our approximation improves the agreement with the experimental data of the values of the constants characterizing the relative change of the volumes of the ionic crystals during polymorphic transformations.

Table 3. The change of the cohesion characteristics of ionic crystals during polymorphic transformation

Crystal		$\Delta R(B2–B1)$, au	$\Delta U(B1–B2)$, au	ε_R, %	ε_U, %
LiF	1	0.18	0.014	4.93	3.38
	2	0.18	0.0138	4.93	3.47
	3	0.14	0.0243	3.72	5.86
LiCl	1	0.2	0.0098	4.28	2.98
	2	0.23	0.0096	4.83	3.00
	3	0.15	0.0083	2.05	2.54
LiBr	1	0.21	0.0087	4.17	2.84
	2	0.24	0.0088	4.74	2.91
	3	0.20	0.010	3.93	3.24
NaF	1	0.19	0.0094	4.35	2.65
	2	0.18	0.0092	3.94	2.72
	3	0.06	0.0146	2.35	3.12
NaCl	1	0.21	0.0065	3.89	2.23
	2	0.21	0.0067	3.89	2.38
	3	0.12	0.0105	3.18	2.61
NaBr	1	0.18	0.0061	3.14	2.22
	2	0.23	0.0083	3.95	2.35
	3	0.23	0.0020	3.98	2.55
KF	1	0.16	0.0056	3.26	1.72
	2	0.17	0.0062	3.32	2.00
	3	0.07	0.0070	2.37	0.64
KCl	1	0.19	0.0041	3.30	1.47
	2	0.19	0.0048	3.18	1.80
	3	0.14	0.0029	2.38	1.07
KBr	1	0.17	0.0039	2.81	1.46
	2	0.20	0.0044	3.22	1.71
	3	0.24	0.0076	3.93	1.87
RbF	1	0.14	0.042	2.68	1.36
	2	0.17	0.048	3.17	1.61
	3	0.11	0.0013	2.08	1.44
RbCl	1	0.15	0.0031	2.49	1.15
	2	0.21	0.0037	3.39	1.43
	3	0.11	0.0055	1.79	2.06
RbBr	1	0.21	0.0031	3.35	1.20
	2	0.19	0.0034	2.93	1.37
	3	0.22	0.0019	3.48	0.78

Note: (1) Gordon, Kim [5]; (2) Cohen, Gordon [6]; (3) Our results.

The modulus of elasticity B was calculated by the formula

$$B = V\left(\frac{d^2U(R)}{dV^2}\right)_{R = R_0}, \tag{10}$$

Table 4. The relative change of the volume of alkali halide crystals during their polymorphic transformation

Crystal		Theoretical calculation				Experimental data			
		$\frac{\Delta V_{B1}}{V_{01}}$	$\frac{\Delta V_{B2}}{V_{01}}$	$\frac{\Delta V_t}{V_{01}}$	$B\times10^{11}$, dyn/cm^2	$\frac{\Delta V_{B1}}{V_{01}}$	$\frac{\Delta V_{B2}}{V_{01}}$	$\frac{\Delta V_t}{V_{01}}$	$B\times10^{11}$, dyn/cm^2
LiF	1	0.275	0.335	0.06	9.30	–	–	–	8.67
	2	0.533	0.553	0.02	7.61				
	3	–	–	–	8.90				
	4	0.612	0.597	0.017	8.14				
LiCl	1	0.223	0.298	0.076	3.60	–	–	–	3.54
	2	0.475	0.492	0.017	3.32				
	3	–	–	–	4.00				
	4	0.522	0.499	0.016	3.28				
LiBr	1	0.212	0.290	0.078	2.70	–	–	–	–
	2	0.478	0.492	0.014	2.65				
	3	–	–	–	3.10				
	4	0.490	0.534	0.015	2.51				
NaF	1	0.172	0.266	0.094	5.30	–	–	–	5.14
	2	0.280	0.332	0.053	4.46				
	3	–	–	–	5.30				
	4	0.319	0.394	0.047	5.02				
NaCl	1	0.145	0.249	0.104	2.42	0.357	0.394	0.037	2.85
	2	0.214	0.281	0.067	2.18				
	3	–	–	–	5.20				
	4	0.269	0.302	0.045	2.11				
NaBr	1	0.140	0.246	0.106	2.19	–	–	–	2.29
	2	0.189	0.257	0.068	2.18				
	3	–	–	–	–				
	4	0.194	0.249	0.060	2.23				
KF	1	0.110	0.228	0.118	3.80	–	–	–	3.19
	2	0.153	0.239	0.086	3.54				
	3	–	–	–	3.90				
	4	0.172	0.244	0.091	3.38				
KCl	1	0.096	0.220	0.124	2.25	0.085	0.197	0.112	2.02
	2	0.116	0.216	0.100	1.86				
	3	–	–	–	2.19				
	4	0.094	0.202	0.094	1.94				
KBr	1	0.090	0.217	0.127	1.70	0.088	0.193	0.105	1.80
	2	0.093	0.198	0.105	1.60				
	3	–	–	–	1.81				
	4	0.092	0.196	0.098	1.58				
RbF	1	0.084	0.214	0.130	3.30	–	–	–	–
	2	0.125	0.220	0.085	2.96				
	3	–	–	–	3.13				
	4	0.144	0.236	0.081	2.80				
RbCl	1	0.075	0.209	0.134	1.90	0.030	0.170	0.105	1.85
	2	0.073	0.193	0.120	1.71				
	3	–	–	–	1.77				
	4	0.062	0.184	0.124	1.80				
RbBr	1	0.070	0.208	0.188	1.90	0.033	0.166	0.133	1.59
	2	0.052	0.178	0.126	1.49				
	3	–	–	–	1.62				
	4	0.044	0.169	0.126	1.45				

Note: (1) Gordon, Kim [5]; (2) Cohen, Gordon [6]; (3) Zhdanov, Polyakov [8]; (4) Our results.

where V is the elementary cell volume (for an fcc lattice of the NaCl type, $V = 2R^3$). The difference in the values of modulus of elasticity calculated in view of only the first coordination sphere and taking into account the higher spheres (up to the seventh one inclusive) amounts, for different crystals, from 40 to 110%. Note that the inclusion of even the third neighbors results in a difference in the crystal compressibility of about 80% on the average. For example, for a LiF crystal in the approximation of the first coordination sphere, $-(\Delta V_t/V_{01}) = 0.06$; when seven spheres are included, this constant is 3.53 times lower. It is for lithium halides that the effect of the higher coordination spheres is most significant, while for sodium and potassium halides this effect decreases and, for rubidium halides, the inclusion of the higher spheres leads to a difference in the results of 10–15% compared to the approximation of the first coordination sphere.

In conclusion, note that the results of this study strongly suggest the inclusion of the higher coordination spheres when studying the structural phase transitions in alkali halide crystals.

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