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First-principles study of the rocksalt–cesium chloride relative phase stability in alkali halides

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We present a detailed investigation of observable properties associated with the relative stability of the rocksalt ($B1$) and cesium chloride ($B2$) phases in the AX ($A=\mathrm{Li}$, Na, K, Rb, Cs; $X=\mathrm{F}$, Cl, Br, I) crystal family. Thermodynamic $B1\rightarrow B2$ transition pressures and $\Delta Y=Y(B2)-Y(B1)$ differences in total energies, volumes, and bulk moduli at zero and transition pressures are computed following a localized Hartree-Fock method. The arrangement of the data in clear trends is shown to be mainly dominated by the cation atomic number. This behavior is well interpreted in terms of a variety of microscopic arguments that emerge from (i) the evaluation of the energy Hessian at the $B1$ and $B2$ points and (ii) the decomposition of the energy and pressure in anionic and cationic classical and quantum-mechanical contributions.

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I. INTRODUCTION

Alkali halides have traditionally demanded attention to validate new phenomenological models and first-principles methodologies directed to describe the observable phenomena in ionic crystals. A good deal of experimental information has also been collected for these systems. Specifically, the behavior under hydrostatic pressure of almost all of the 20 AX ($A=\mathrm{Li}$, Na, K, Rb, Cs; $X=\mathrm{F}$, Cl, Br, I) crystals has been critically examined with comparisons between theoretical and experimental results. Cohesive and thermal properties, equations of state (EOS), thermodynamic stability ranges of the most common rocksalt ($B1$) and cesium chloride ($B2$) phases, phase transition properties, and phase transition mechanisms have been investigated for particular crystals or groups of them within the AX family. See, for example, Refs. 1–21 and references therein.

Although variations of the above properties along the AX family are observed when changing either the cation or anion, it is found that the cation atomic number is the key parameter to systematize these data. For example, the experimental pressure range (in GPa) where the $B1$ is the thermodynamic equilibrium phase decreases from tens in the NaX series to zero in the CsX one (except CsF), passing through units in KX and tenths in RbX. The transition has not been reported for lithium halides. A change of the anion within each of these series has a weaker effect in the pressure ranges (see, for example, Ref. 7). Other transition-related properties have not been considered in detail previously, but are also expected to manifest a similar behavior.

In spite of the amount of experimental and theoretical work, attempts to elucidate the microscopic reasons behind this systematic behavior are scarce, if we ignore those studies based on the ionic model as illustrated by the pioneering work of Born and Huang.[1] Among the quantum-mechanical contributions, Majewski and Vogl[14] applied a semiempirical tight-binding method to explain successfully the chemical trends of a variety of observable properties in I-VII and II-VI crystals in terms of the balance between attractive (covalent) and repulsive (overlap) energetic contributions. Nevertheless, we notice that their reported $B1\rightarrow B2$ stabilization energies in the AX family do not show the expected strong cation dependence. A careful study of the physics underlying the relative thermodynamic stability of the $B1$ and $B2$ phases of CsCl has been reported by Pyper[22] in terms of the energetic components involved in the ionic interactions. That analysis relies on the many-body nature of the energy required to convert a free anion into the anion-in-the-lattice form, which is defined as the rearrangement energy. It is shown that this energy changes with interionic separations and may be considered independent of the crystal structure. The conclusions might likely be extended to other alkali-halide crystals but no calculations have been carried out to establish general behaviors.

It is our main goal in this work to perform a quantum-mechanical analysis of the microscopic factors that determine the relative thermodynamic stability of the $B1$ and $B2$ phases in the AX crystal family. We apply the *ab initio* perturbed ion (aiPI) method[23,24] to evaluate the $B1\rightarrow B2$ phase transition properties. A very useful feature of this method is that it produces self-consistent crystalline wave functions for the cation and anion components of the crystal, the total energy of which can be partitioned into anionic and cationic terms. Classical and quantum-mechanical contributions to these quantities can also be identified. Our study also includes the evaluation of the zero-pressure-energy Hessian eigenvalues of both phases. The energy curvature at the $B1$ and $B2$ points informs about the mechanical stability of the two structures and is seen to correlate also with the cation atomic number.

The aiPI method has been successfully applied previously to the calculation of the thermodynamic properties of a great variety of nonmetallic crystals. See, for example, Refs. 15–17, 25, and 26. In particular, static equilibrium cohesive properties of the 20 alkali-halide crystals at their corresponding experimental thermodynamic equilibrium phase at ambient conditions have been calculated.[17] The values obtained for the lattice parameters, lattice energies, and isothermal bulk moduli were found to have average relative errors of 3.0%, 4.3%, and 14.2%, respectively, with respect to mostly room-temperature experimental values. The theory-experiment agreement improved for the three properties when the computed values were compared with the available zero-temperature extrapolated data. Furthermore, the aiPI results on the phase transition properties of alkali chlorides are found to agree with available experimental data,[15,16] and the $B1 \rightarrow B2$ phase transition mechanism is also well described for the AX family with this methodology.[16,17]

The rest of the paper is organized as follows. The next section is devoted to presenting the computational model, the basics of the analysis of the mechanical stability of the $B1$ and $B2$ phases, and the energy and energy derivative decompositions. Section III presents the $B1 \rightarrow B2$ changes in the thermodynamic properties and the effect of the cation and the anion in the observed tendencies. In Sec. IV, we discuss the results derived from the diagonalization of the $B1$ and $B2$ energy Hessians. This section also includes an analysis of the relation between the internal stability of these phases and the possibility of obtaining the $B1 \rightarrow B2$ transition pressures from zero-pressure data of both phases. Section V contains the microscopic analysis based on the energetic decomposition of observables. Finally, the last section summarizes the main conclusions of our work.

II. COMPUTATIONAL AND ALGEBRAIC ASPECTS OF THE MODEL

A. Computational details

The computational parameters chosen to perform the *ai* PI calculations in the AX family are essentially the same as the ones used in our previous studies of the EOS (Ref. 15) and phase transition mechanism (Ref. 16) of particular AX crystals, as well as in our analysis of the universal-binding-energy relations across the phase transition in the alkali-halide family.[17] The total energy of the crystal (E) has been computed for all 20 alkali halides in a wide range of volumes for both the $B1$ and $B2$ structures. Numerical as well as analytical equations of state (Birch[27] and Vinet *et al.*[28]) have been fitted to the corresponding E versus volume (V) data, yielding information on the pressure effects on E, V, B (bulk modulus), and B' (pressure derivative of B). Thermal effects are included through a quasiharmonic Debye model that only needs the computed $E(V)$ curve as input.[26]

From the *ai*PI $E(V)$ values of the $B1$ and $B2$ phases, we have evaluated the pressure at which the respective Gibbs potentials are equal, $G^{B1}=G^{B2}$, for each crystal. This defines the (thermodynamic) transition pressure. Accordingly, pressure ranges for which the $B1$ or the $B2$ are the thermodynamic equilibrium phases are obtained. At static conditions (0 K and no zero-point vibrational contributions) G reduces to the enthalpy $(E+PV)$, whereas at finite temperatures G includes the vibrational energy and entropy, which are estimated from our quasiharmonic Debye model. We will restrict our discussion to static conditions except in the analysis of transition pressures. All the thermodynamic properties at zero and transition pressures will be labeled, respectively, by the subscripts "0" (V_0, E_0, B_0, B'_0) and "tr" (V_{tr}, E_{tr}, B_{tr}, B'_{tr}).

B. Internal stability of $B1$ and $B2$ phases

The mechanical stability of the $B1$ and $B2$ phases at zero pressure has been analyzed in terms of the energy Hessian eigenvalues corresponding to small periodic perturbations from equilibrium within a primitive unit cell containing just one AX molecule. This unit cell corresponds to a nine-dimensional (9D) model $(a,b,c,\alpha,\beta,\gamma,x,y,z)$ of the $B1 \rightarrow B2$ phase transition mechanism.[16,20] The cation is at the origin of the cell, the anion at (x,y,z), and the space group is $P1$. Both the $B1$ and $B2$ phases lie at particular symmetry points on this 9D space: $B1$ is at $(a=b=c,\ \alpha=\beta=\gamma=60°,\ x=y=z=\frac{1}{2})$, and $B2$ is at $(a=b=c,\ \alpha=\beta=\gamma=90°,\ x=y=z=\frac{1}{2})$.

Symmetry imposes the block structure in the 9×9 Hessian matrix of the $B1$ phase shown in Ref. 25. The independent elements of this matrix are H_{aa}, H_{ab}, $H_{a\alpha}$, $H_{a\beta}$, $H_{\alpha\alpha}$, $H_{\alpha\beta}$, H_{xx}, and H_{xy}. The Hessian matrix of the $B2$ phase is obtained from the $B1$ matrix by making $H_{a\alpha}=H_{a\beta}=H_{\alpha\beta}=H_{xy}=0$. Analytical expressions for the eigenvalues and eigenvectors of both matrices can be easily derived. Notice that in the $B1$ phase, the sets (a,b,c) and (α,β,γ) are coupled to each other but not with (x,y,z), whereas in the $B2$ phase there is no coupling at all between these three sets.

C. Energy and energy derivatives decomposition

In the *ai*PI methodology, the total energy of the AX crystal can be partitioned into anionic and cationic components as follows:

$$E=E_{\mathrm{add}}^{A}+E_{\mathrm{add}}^{X}, \tag{1}$$

where E_{add}^{I}, the additive energy of the ion I in the AX crystal (I = A, X), is defined by: $E_{\mathrm{add}}^{I}=E_{\mathrm{net}}^{I}+\frac{1}{2}E_{\mathrm{int}}^{I}$. Here E_{net}^{I} is the sum of all intra-atomic energy terms for ion I, i.e., the expectation value of the free-ion Hamiltonian evaluated with the *ai*PI crystal-like ionic wave function, and E_{int}^{I} is the interaction energy of ion I with the rest of the crystal. The difference between the net energy and free-ion energy is called the deformation energy and it is due to the lattice effects on the ionic wave function. It should be emphasized that in the present version of the *ai*PI method only radial (isotropic) deformations of the ions are allowed. On the other hand, E_{int}^{I} can be further divided into the point charge or Madelung contribution (E_{pc}^{I}) plus the quantum-mechanical interaction energy (E_{q}^{I}): $E_{\mathrm{int}}^{I}=E_{\mathrm{pc}}^{I}+E_{\mathrm{q}}^{I}=-\alpha/R+E_{\mathrm{q}}^{I}$, where α is the Madelung constant for the crystal, and R is the nearest-neighbor distance. In both structures, $E_{\mathrm{pc}}^{A}=E_{\mathrm{pc}}^{X}$ since the anionic and the cationic positions are equivalent.

Alternatively,

$$E=E_{\mathrm{net}}+\frac{1}{2}E_{\mathrm{int}}=E_{\mathrm{net}}+\frac{1}{2}E_{\mathrm{pc}}+\frac{1}{2}E_{\mathrm{q}}, \tag{2}$$

where each term is the sum of the cationic and anionic components.

Moreover, this energetic partition can be transferred by means of simple algebraic manipulations to other fundamental observables as the pressure and bulk modulus. For example, the static pressure of the crystal can be written as follows:

TABLE I. Static and 300 K transition pressures P_{tr} and P_{tr}^{300} and static $\Delta Y \equiv Y(B2)-Y(B1)$ values for some cohesive properties of the alkali-halides at $P=0$ and $P=P_{\mathrm{tr}}$ according to aiPI calculations. P and B in GPa, V in bohr^3/molecule, and E in kJ/mol.

crystal	P_{tr}	P_{tr}^{300}	ΔV_0	ΔV_{tr}	ΔE_0	ΔE_{tr}	ΔB_0	ΔB_{tr}
LiF	252.2	243.6	−4.39	−2.96	61.18	66.66	5.89	−83.14
LiCl	78.9	78.0	1.69	−10.75	74.07	75.69	−7.02	−10.52
LiBr	94.2	93.6	−2.12	−8.83	75.76	74.26	−4.66	−9.99
LiI	112.6	110.7	−5.53	−10.83	75.32	108.91	−3.38	−53.37
NaF	12.1	12.4	−24.89	−19.57	23.66	21.18	11.93	15.45
NaCl	21.2	20.6	−22.39	−23.97	45.27	45.40	−3.02	−9.58
NaBr	15.9	15.8	−34.82	−29.39	45.89	41.86	−2.86	−1.30
NaI	15.5	15.6	−39.19	−33.59	54.58	46.75	−4.07	3.04
KF	5.6	5.8	−31.59	−25.07	14.01	12.63	4.02	4.40
KCl	2.0	2.2	−68.34	−55.77	10.98	9.99	3.54	3.56
KBr	1.6	1.6	−77.55	−69.00	10.66	10.11	1.34	1.07
KI	2.7	2.5	−82.72	−76.78	19.06	18.42	−0.77	−1.48
RbF	−0.8	−0.2	−40.94	−44.62	−2.86	−2.99	9.41	9.25
RbCl	0.1	0.3	−95.89	−94.10	1.23	1.22	4.31	4.32
RbBr	−0.0	0.1	−104.66	−104.99	−0.24	−0.24	2.74	2.75
RbI	0.8	0.8	−115.83	−106.34	8.27	7.94	0.78	0.45
CsF	−4.9	<-2.6	−48.17	−98.58	−28.57	−43.36	27.32	21.03
CsCl	−1.8	<-1.3	−103.51	−182.96	−21.03	−29.16	2.58	4.63
CsBr	−1.8	−1.5	−119.33	−229.57	−24.38	−36.32	2.52	4.21
CsI	−0.9	−0.7	−147.00	−205.77	−13.21	−15.93	1.69	2.52

$$P=-\left(\frac{dE}{dV}\right)=-\left(\frac{dE_{\mathrm{add}}^{A}}{dV}\right)-\left(\frac{dE_{\mathrm{add}}^{X}}{dV}\right)=P_{\mathrm{add}}^{A}+P_{\mathrm{add}}^{X}, \qquad (3)$$

with $P_{\mathrm{add}}^{I}=P_{\mathrm{net}}^{I}+\frac{1}{2}P_{\mathrm{int}}^{I}=P_{\mathrm{net}}^{I}+\frac{1}{2}P_{\mathrm{pc}}^{I}+\frac{1}{2}P_{\mathrm{q}}^{I}$.

The necessary energy derivatives in both this and previous subsections have been numerically computed from the aiPI energy using a Richardson-iterated, finite-difference limit formula.[29]

III. PHASE TRANSITION THERMODYNAMIC PROPERTIES

Experimental results show that the 16 halides of Li, Na, K, and Rb plus CsF crystallize on the $B1$ structure under room conditions, whereas CsCl, CsBr, and CsI crystallize on the $B2$ phase. The crystals thermodynamically stable in the $B1$ phase tend to undergo a $B1\rightarrow B2$ phase transition when increasing the pressure. The equilibrium $B1\rightarrow B2$ transition pressure strongly depends on the cation but only slightly on the anion: it is about 23 and 27 GPa for NaF and NaCl, respectively,[11–13] and it ranges from 1.7 to 2.0 GPa for the potassium halides (except KF) and from 0.3 to 0.6 GPa for the rubidium halides (except RbF).[4,7] The transition pressure seems to be about 4 GPa for KF,[8] within 1–3.5 GPa for RbF,[3,4,7] and about 2 GPa for CsF.[7] The $B1\rightarrow B2$ transition has not been observed in lithium halides, NaBr, and NaI. The last two systems transform to an orthorhombic TlI-type structure at around 30 GPa.[30]

Our computed static and 300 K transition pressures P_{tr} and P_{tr}^{300} are collected in Table I along with ΔY values $[\Delta Y=Y(B2)-Y(B1)]$ for the energy, volume, and bulk modulus at $P=0$ and $P=P_{\mathrm{tr}}$. Overall, our results provide a reasonable picture of the zero-pressure phase stability. In agreement with experimental observations, the $B1$ phase is predicted to be the thermodynamically stable one for crystals containing small cations, whereas it is the $B2$ for the cesium halides. Only two crystals (RbF and CsF) are erroneously found to have the $B2$ as the lowest-energy structure at ambient conditions. Moreover, the calculated transition pressures show the two different trends along the AX family observed experimentally when changing either the cation or anion and, overall, are in reasonable agreement with the experimental values. In particular, our results agree better with the experiment than those recently reported by Mei *et al.* using a density-functional method based on localized densities.[21]

The grouping of the P_{tr} values by the cation also applies to the computed ΔE, ΔV, and to a less extent to ΔB, both at zero and the transition pressures. For example, considering the ΔV_{tr} values for the ACl sequence, we see that the decrease on going from Li to Rb is monotonous and greater than 80 bohr^3/molecule. This result qualitatively agrees with the experimental one, the ΔV_{tr} experimental values (in bohr^3/molecule) for these systems being about -9 (NaCl), -47 (KCl), and -70 (RbCl).[2,4,13] On the other hand, the experimental ΔV_{tr} values (in bohr^3/molecule) are about -28 (KF), -47 (KCl), -50 (KBr), and -51 (KI) for the KX series and about -21 (RbF), -70 (RbCl), -75 (RbBr), and -85 (RbI) for the RbX one.[3,4,8] Aside from the fluoride, a change of the anion within each of these series has a weak effect in ΔV_{tr}. We can

TABLE II. Lowest eigenvalue of $B1$ and $B2$ Hessians and estimates of the static transition pressures for the alkali halides. $P_{\rm tr}^{(n)}$ $(n=0,2,3)$ denotes the estimates obtained from the three formulas of lower order (see text), by using the aiPI data of the $B1$ and $B2$ phases at $P=0$. Eigenvalues in Hartree and pressures in GPa. $(B1B2)=$(mm) or (mM) refers to the 9D model: m = local minimum, and M = local maximum. * means that the system is more stable in the $B2$ phase than in the $B1$ phase.

AX	$\epsilon_{\rm min}(B1)$	$\epsilon_{\rm min}(B2)$	$(B1,B2)$	$P_{\rm tr}^{(0)}$	$P_{\rm tr}^{(2)}$	$P_{\rm tr}^{(3)}$
LiF	0.1842	−0.0575	(mM)	156.57		85.30
LiCl	0.1990	−0.1408	(mM)	−490.71	27.94	−17.50
LiBr	0.2062	−0.1350	(mM)	400.32	29.00	−16.34
LiI	0.2322	−0.1493	(mM)	152.58	16.39	−8.72
NaF	0.1179	0.1456	(mm)	10.65	13.06	11.86
NaCl	0.1359	−0.0233	(mM)	22.65	19.68	16.96
NaBr	0.1405	−0.0033	(mM)	14.77	14.38	−28.11
NaI	0.1542	−0.0615	(mM)	15.60	9.33	−8.97
KF	0.0804	0.1047	(mm)	4.97	6.09	5.43
KCl	0.0690	0.1197	(mm)	1.80	2.09	1.98
KBr	0.0694	0.1412	(mm)	1.54	1.67	1.63
KI	0.0784	0.0755	(mm)	2.58	2.74	2.60
RbF	0.0565	0.2006	(mm*)	−0.78	−0.75	−0.75
RbCl	0.0616	0.2260	(mm)	0.14	0.14	0.14
RbBr	0.0591	0.2494	(mm*)	−0.03	−0.03	−0.03
RbI	0.0638	0.1670	(mm)	0.80	0.85	0.83
CsF	0.0351	0.4928	(mm*)	−6.65	−5.39	−5.14
CsCl	0.0367	0.3210	(mm*)	−2.28	−1.93	−1.84
CsBr	0.0351	0.4007	(mm*)	−2.29	−1.97	−1.86
CsI	0.0467	0.2925	(mm*)	−1.01	−0.90	−0.88

see that this is also the case with the theoretical values in Table I. Experimental $\Delta E_{\rm tr}$ data for K and Rb halides move from around 8 to around 3 kJ/mol.[3] Our results also show this cation dependence, the agreement being better in the KX crystals.

Finally, the computed ΔB increases from negative values in the LiX and NaX crystals (except in LiF and NaF) to positive ones in KX, RbX, and CsX (except KI). The change in the sign of ΔB has been also obtained by Hofmeister from experimental vibrational frequencies using a semiempirical model,[18] although her positive values started with the Rb halides. As a general result, we can conclude that the cation atomic number is the key parameter needed to systematize the $B1 \rightarrow B2$ transition properties. A microscopic explanation of this fact will be given in the next sections.

IV. MECHANICAL STABILITY: DIAGONALIZATION OF THE $B1$ AND $B2$ ENERGY HESSIANS

Here we discuss the results obtained from the diagonalization of the previously presented energy Hessians computed at static conditions and zero pressure. Table II shows the lowest eigenvalue $\epsilon_{\rm min}$ of both the $B1$ and $B2$ Hessians in the 20 alkali halides. The lowest eigenvalue is positive for all $B1$ structures. Thus, at zero pressure this phase is a true minimum on the 9D surface and, consequently, all the crystals studied are mechanically stable in the $B1$ phase (internal stability) within this model. We also notice that changes in $\epsilon_{\rm min}(B1)$ along the AX family are again dominated by the cation atomic number: $\epsilon_{\rm min}$ decreases steeply in passing from Li to Cs crystals and, with some exceptions, increases slightly with the anion size.

On the other hand, $\epsilon_{\rm min}$ $(B2)$ increases as the cation size increases, the effect of changing the anion being weaker with a somewhat erratic behavior in the fluorides. $\epsilon_{\rm min}(B2)$ is negative for the lithium halides and also negative, though smaller in absolute value, for the sodium halides (except NaF). However, it takes positive values for NaF and the potassium, rubidium, and cesium halides. LiCl and LiI also have a second negative eigenvalue. Thus, at zero pressure the $B2$ phase is a true minimum for the systems containing big cations (K, Rb, and Cs) (these systems are mechanically stable in this phase) and a saddle point for those containing small cations (which are mechanically unstable in the $B2$ phase). Consequently, (i) it should be possible to quench metastable $B2$ potassium and rubidium halides at zero pressure from the corresponding stable high-pressure $B2$ crystals and (ii) this should not be the case for the lithium and sodium halides. As far as we know there is no experimental evidence confirming statement (i) or contradicting statement (ii).

In the $B1$ phase, the eigenvector corresponding to $\epsilon_{\rm min}$ may be followed to construct a $B1 \rightarrow B2$ transition path. This eigenvector is $(c_1,c_1,c_1,c_2,c_2,c_2,0,0,0)$ in the $(a,b,c,\alpha,\beta,\gamma,x,y,z)$ basis for all the crystals, c_1 and c_2 being constants for a given system. Then, this eigenvector has the direction $a=b=c$, $\alpha=\beta=\gamma$, $x=y=z=\frac{1}{2}$. The highest symmetry compatible with this movement is $R\overline{3}m$, and the path lies on a two-dimensional ($2D$) surface corresponding to a modified Buerger mechanism.[16,20]

On the other hand, ϵ_{min} is threefold degenerate in the $B2$ phase of all the systems, this eigenvalue being closely related to the c_{44} elastic constant of the phase. This eigenvector is $(0,0,0,c_1,c_2,c_3,0,0,0)$ in the $(a,b,c,\alpha,\beta,\gamma,x,y,z)$ basis, c_1, c_2, and c_3 being arbitrary constants. Then, the eigenvectors associated with ϵ_{min} only involve angular (α,β,γ) changes and, due to their threefold degeneration, ϵ_{min} may be used to construct a $B2\rightarrow B1$ path starting in a direction with arbitrary angular changes. This kind of transition path is not symmetry fixed. We think that this arbitrariness might be related to the experimentally observed breaking of the crystals upon successive compression-decompression cycles,[9,31] but we will leave a full discussion of these facts for a forthcoming paper devoted to the different mechanisms of the $B1\rightarrow B2$ phase transition in alkali halides. Finally, the second negative eigenvalue found in the $B2$ phase of LiCl and LiI is $(0,0,0,0,0,0,c_1,c_2,c_3)$; that is, it is related to an additional instability of these systems with respect to changes in the ionic internal positions.

Let us turn to the relation between the internal stability of the phases and the possibility of obtaining good estimates of the $B1\rightarrow B2$ transition pressures from the zero-pressure data of both phases. This is a very relevant aspect, since the hysteresis exhibited by these transitions may result in large uncertainties in the experimental determination of equilibrium values for the transition pressures.[4–6,12,13] Besides the theoretical values, zero-pressure data for high-pressure phases could be faithfully obtained by fitting an adequate EOS (Ref. 19) to P-V experimental data.

As we commented above, the static thermodynamic transition pressure P_{tr} is defined through $\Delta G(P_{\mathrm{tr}})=\Delta E(P_{\mathrm{tr}})+P_{\mathrm{tr}}\Delta V(P_{\mathrm{tr}})=0$. Then,

$$P_{\mathrm{tr}}=-\frac{\Delta E(P_{\mathrm{tr}})}{\Delta V(P_{\mathrm{tr}})}=-\frac{\Delta E_{\mathrm{tr}}}{\Delta V_{\mathrm{tr}}}. \tag{4}$$

If we use the above equation along with the data collected in Table I, the steep decrease of P_{tr} with the cation size can be related to the steep decrease of ΔE_{tr} and the steep increase of $|\Delta V_{\mathrm{tr}}|$ as the cation size increases. On the other hand, the small dependence of the transition pressure on the anion size is connected to a cancellation effect, since both ΔE_{tr} and $|\Delta V_{\mathrm{tr}}|$ slightly increase with the anion size.

These data may be related to zero-pressure transition properties. If we expand $\Delta E(P)$ as a power series in P around $P=0$,

$$\Delta E(P)=a_0+a_1P+a_2P^2+a_3P^3+a_4P^4+\cdots, \tag{5}$$

and integrate the $T=0$ K equation $d\Delta V(P)=(-1/P)d\Delta E(P)$ to relate ΔV at P to its zero-pressure value, the equation for P_{tr} can be rewritten in this way

$$P_{\mathrm{tr}}=-\frac{\Delta E_{\mathrm{tr}}}{\Delta V_{\mathrm{tr}}}=-\frac{\Delta E_0+a_2P_{\mathrm{tr}}^2+a_3P_{\mathrm{tr}}^3+a_4P_{\mathrm{tr}}^4+\cdots}{\Delta V_0-2a_2P_{\mathrm{tr}}-\frac{3}{2}a_3P_{\mathrm{tr}}^2-\frac{4}{3}a_4P_{\mathrm{tr}}^3-\cdots}, \tag{6}$$

where

$$a_2=\frac{1}{2}\ \Delta\left(\frac{V_0}{B_0}\right),\quad a_3=-\frac{1}{3}\ \Delta\left(\frac{V_0(B_0'+1)}{B_0^2}\right),\quad \ldots .$$

The truncation of the expansion for ΔE, and consequently for ΔV, leads to a hierarchy of relations for the estimation of P_{tr} in terms of the $B1$ and $B2$ data at $P=0$. Let us consider the three lower-order models: (i) Zero order. By neglecting all the expansion coefficients except a_0, we obtain the equation $P_{\mathrm{tr}}^{(0)}\approx-\Delta E_0/\Delta V_0$.[14] (ii) Second order. Considering also $a_2\neq 0$, we obtain a formula that gives $P_{\mathrm{tr}}^{(2)}$ in terms of ΔE_0, ΔV_0 and $\Delta(V_0/B_0)$. (iii) Third order. By making $a_0\neq 0$, $a_2\neq 0$, and $a_3\neq 0$, we obtain a formula that also involves the B_0' values in both phases.

Table II shows the transition pressure estimates for the alkali halides obtained by using the aiPI data of the $B1$ and $B2$ phases at $P=0$, as described above, to be compared to the static transition pressures obtained from the "full" aiPI calculations (P_{tr} in Table I). As a general result, we observe that, with the exception of the LiX crystals, the zero-order estimation $P_{\mathrm{tr}}^{(0)}$ reproduces qualitative and almost quantitatively the trends of P_{tr} both as the cation size increases (for a given anion) and as the anion size increases (for a given cation). The effect of increasing the order of the model can be described as follows. For those systems displaying only positive-energy Hessian eigenvalues in both the $B1$ and $B2$ phases at zero pressure [(mm) or (mm*) in Table II], the accuracy of the P_{tr} estimation increases with *n*, the order of the model. This is the case for all the crystals but the LiX and NaX series, except NaF. Contrarily, in those systems having positive eigenvalues in the $B1$ phase but one (or two) negative eigenvalues in the $B2$ phase [(mM) in Table II], the accuracy does not increase with *n*.

The above results can be interpreted as follows. First, we should bear in mind that the energy expansion is around $P=0$ and, therefore, the performance of Eq. (6) is better for those crystals with low P_{tr} values. Second, both the $B1$ and $B2$ points are minima in the 9D model Gibbs energy surface at $P=P_{\mathrm{tr}}$. If this is also the case at $P=0$ (mm or mm* systems), then we have energy surfaces topologically equivalent for both phases at both pressures and, thus, we may expect that an expansion of $\Delta E(P)$ as a power series in P around $P=0$ will work to obtain reasonable values of ΔE and their pressure derivative at $P=P_{\mathrm{tr}}$. On the contrary, when one or two second derivatives of the $B2$ energy at $P=0$ are negative (mM systems), we have topologically different Gibbs energy surfaces at $P=0$ and $P=P_{\mathrm{tr}}$ and, consequently, it is to be expected that the expansion will not work properly.

V. MICROSCOPIC DECOMPOSITION OF PHASE TRANSITION MAGNITUDES

We look for a general explanation of the relative stability of the $B1$ and $B2$ structures as due to one specific type of ion and/or to a particular energetic component of the total energy. The anionic and cationic contributions to ΔE_0 are col-

TABLE III. Energy decomposition at zero pressure (kJ/mol). $\Delta Y \equiv Y(B2) - Y(B1)$. Note that $\Delta E_0 = \Delta E^A_{\mathrm{add}} + \Delta E^X_{\mathrm{add}}$. I means A or X.

AX	$\Delta E^A_{\mathrm{net}}$	$\Delta E^X_{\mathrm{net}}$	$\frac{1}{2}\Delta E^I_{\mathrm{pc}}$	$\frac{1}{2}\Delta E^A_{\mathrm{q}}$	$\frac{1}{2}\Delta E^X_{\mathrm{q}}$	$\Delta E^A_{\mathrm{add}}$	$\Delta E^X_{\mathrm{add}}$
LiF	−1.96	5.23	38.38	−21.73	2.89	14.69	46.49
LiCl	−0.54	−9.08	36.49	−15.06	25.77	20.89	53.18
LiBr	−0.36	−2.16	32.39	−14.96	28.46	17.07	58.69
LiI	−0.16	1.89	28.06	−11.53	28.99	16.37	58.95
NaF	0.10	15.84	10.88	−11.00	−3.04	−0.01	23.67
NaCl	0.40	2.82	22.13	−15.84	13.63	6.69	38.58
NaBr	0.32	7.43	17.59	−14.50	17.44	3.42	42.47
NaI	0.12	7.53	18.02	−12.48	23.37	5.66	48.92
KF	−0.09	0.82	15.69	−6.55	−11.56	9.05	4.96
KCl	0.22	6.42	9.64	−10.19	−4.75	−0.33	11.30
KBr	0.18	6.38	9.11	−10.94	−3.16	−1.66	12.33
KI	0.16	5.42	11.41	−11.81	2.46	−0.24	19.29
RbF	−1.17	1.87	11.55	−9.31	−17.34	1.07	−3.93
RbCl	0.05	11.43	4.09	−10.40	−8.02	−6.27	7.50
RbBr	0.23	9.29	4.59	−10.93	−8.01	−6.10	5.87
RbI	0.52	8.09	7.15	−11.16	−3.50	−3.49	11.75
CsF	66.23	11.41	0.00	−61.79	−44.43	4.45	−33.02
CsCl	6.05	19.71	1.34	−29.69	−19.77	−22.31	1.27
CsBr	4.36	15.80	0.30	−28.14	−17.00	−23.48	−0.90
CsI	1.56	13.45	2.71	−22.83	−10.80	−18.57	5.36

lected in Table III along with the particular energetic components of these ionic energies.

Both the cationic and anionic additive energies stabilize the $B1$ phase in LiX and NaX (except NaF), the contribution of the anions to this stabilization being more important than that of the cations. On the contrary, anions and cations contribute with different sign to the final stability in most of the KX, RbX, and CsX systems, the anions favoring the $B1$ phase and the cations the $B2$ one. Note that the relative size of Cs$^+$ and F$^-$ (Cs$^+$ is bigger than F$^-$) inverts the role of the two ions in CsF, and probably the same happens in RbF. The balance results in a more stable $B1$ phase in KX, RbCl and RbI, and a more stable $B2$ phase in RbF, RbBr, and CsX. Then, whereas the anionic contribution to ΔE_0 is positive in most of the systems, the cationic term changes from positive to negative values when the size of the cation increases, thus being responsible for the stabilization of the $B2$ structures (except RbF and CsF).

We now analyze the particular energetic components of the anionic, cationic, and total energies. It is seen in Table III that the contribution of $\Delta E^A_{\mathrm{net}}$ to the $B1$-$B2$ relative stability is negligible (smaller than 1 kJ/mol), the exceptions being the crystals of the CsX family and specially CsF, where $\Delta E^A_{\mathrm{net}}$ takes the greatest value among all the alkali halides. Moreover, $\Delta E^X_{\mathrm{net}}$ takes positive values (except for LiCl and LiBr) and, generally, increases slightly with the cation size, thus stabilizing the $B1$ phase with respect to the $B2$ one even in those crystals where the computations predict a $B2$ lower-energy phase.

On the other hand, both $\Delta E^I_{\mathrm{int}} = \Delta E^I_{\mathrm{pc}} + \Delta E^I_{\mathrm{q}}$ $(I = A, X)$ decrease with the cation size (more steeply the anionic term), ΔE_{int} becoming negative in RbX and CsX. These negative values come from the quantum terms, since the Madelung contributions are always positive (see Table III). Note that ΔE^I_{pc} $(I = A, X)$ is zero for $r = R(B2)/R(B1) = 1.0086$, where R is the nearest-neighbor distance in each phase, and increases with r. This explains that $\Delta E^A_{\mathrm{pc}} = \Delta E^X_{\mathrm{pc}}$ takes large and positive values for LiX ($r \sim 1.08$) and positive and small values for CsX ($r \sim 1.01$). Besides, ΔE^A_{q} takes negative values in all systems, larger in absolute value for the cesium halides, and ΔE^X_{q} decreases as the cation size increases, passing from positive values in LiX and NaX (except NaF) to large negative values in CsX (though smaller in magnitude than those of $\Delta E^{\mathrm{Cs}}_{\mathrm{q}}$).

From these results we can understand why the anions favor the $B1$ phase but the cations stabilize the $B2$ one in RbX and CsX. Whereas the positive values of the anionic net (or deformation) energies counteract their negative interaction components, the negligible cationic net terms give rise to negative cationic energies dominated by the interaction component, thus stabilizing the $B2$ phase with respect to the $B1$ one. On the other hand, analysis of the particular energy components of ΔE_0 shows that the quantum-mechanical interaction term (mainly the anionic one) is the dominant factor in the increasing stability of the $B2$ phase with respect to the $B1$ phase as the cation size increases.

Pyper has pointed out that the dispersion energy plays a crucial role in making the $B2$ phase more stable than the $B1$ phase in CsCl.[22] From our calculations, the quantum interaction term is the responsible for this stabilization. Both the cation and anion interaction quantum terms are negative, and both are dominated by the quantum-mechanical exchange term. The *ai*PI method uses a nondiagonal spectral resolu-

TABLE IV. Ionic contributions to pressure at $P=0$ and $P=P_{\mathrm{tr}}$ equilibrium configurations (in GPa). $P_{\mathrm{add}}^{X}=-P_{\mathrm{add}}^{A}$ at $P=0$ and $P_{\mathrm{add}}^{A}+P_{\mathrm{add}}^{X}=P_{\mathrm{tr}}$ at $P=P_{\mathrm{tr}}$.

	$P=0$		$P=P_{\mathrm{tr}}$	
AX	$P_{\mathrm{add}}^{X}(B1)$	$P_{\mathrm{add}}^{X}(B2)$	$P_{\mathrm{add}}^{X}(B1)$	$P_{\mathrm{net}}^{X}(B1)$
LiF	8.6	13.2	207.9	180.4
LiCl	5.2	6.0	69.0	64.8
LiBr	3.4	4.5	77.8	67.9
LiI	2.3	3.0	83.3	79.6
NaF	4.7	6.9	13.7	16.4
NaCl	3.0	4.4	20.5	21.9
NaBr	1.9	3.1	14.1	13.3
NaI	1.3	2.2	12.0	9.2
KF	1.9	1.6	5.6	7.0
KCl	0.9	1.6	2.7	4.1
KBr	0.7	1.3	2.0	3.2
KI	0.5	1.0	2.4	2.8
RbF	2.4	1.6	1.9	4.0
RbCl	1.1	2.1	1.2	2.4
RbBr	0.9	1.5	0.8	2.1
RbI	0.6	1.0	1.2	2.0
CsF	4.0	1.2	0.1	3.8
CsCl	1.9	2.8	−0.4	0.7
CsBr	1.4	2.1	−0.5	0.8
CsI	0.8	1.4	0.0	1.1

tion approximation to the nonlocal exchange potential,[23] and it has been argued[32] that this approximation to the exact exchange may mimic part of the dynamical correlation energy among the ions, which is associated with the dispersion energy. This argument could then relate our result to that obtained by Pyper.

The energetic analysis contributes to understanding the behavior exhibited by the alkaline halides at zero pressure and also, though only indirectly through estimations of the transition properties [Eq. (6)], the pressure ranges of stability of the $B1$ and $B2$ phases. A direct study is also possible by means of the decomposition of P. In Table IV, we collect the ionic contributions to the pressure at $P=0$ and at $P=P_{\mathrm{tr}}$. These contributions are in general nonzero due to both the ionic environment and the external hydrostatic pressure. Notice that a positive (negative) contribution to the pressure implies that the corresponding energy term is repulsive (attractive). At $P=0$, the anionic pressure (P_{add}^{X}) is positive and, therefore, the cationic pressure (P_{add}^{A}) is equal in absolute value but negative, for all the systems and in both phases. This is related to the fact that the sign of P_{add}^{A} is dominated by the point-charge interaction attractive energy term, whereas the net (or deformation) repulsive component dominates the sign of P_{add}^{X}. Here $P_{\mathrm{add}}^{X}=-P_{\mathrm{add}}^{A}$ decreases in passing from LiX to KX and increases slightly from KX to CsX.

Let us now turn to discuss the partition of the static transition pressure. The anion (mainly its net pressure term P_{net}^{X}) is mainly responsible for the positive value of P_{tr} in LiX, NaX, and KX, and the cation (more precisely, its interaction term) is mainly responsible for the negative value of P_{tr} in CsX. The strong dependence of P_{tr} on the cation can be roughly explained in terms of the decrease of the anionic net contribution as the cation size increases. This is an energetic consequence of the different magnitude of the isotropic deformations suffered by a given anion in AX crystals containing different cations. The anionic net energy term is less repulsive as the size of the cation (or the volume of the crystal) increases, giving rise to a less positive contribution of this term to the total pressure. On the contrary, a given cation remains nearly undeformed whatever the anion in the crystal is, and, consequently, the cationic net energy and pressure terms are mostly insensitive to the size of the anion. The conclusions in both this and the preceding paragraph are approximately phase independent though P_{add}^{X} is somewhat larger in the $B2$ phase than in the $B1$ phase in most of the systems (see Table IV), due to the higher density of the $B2$ structure.

VI. CONCLUSIONS

We have used a localized Hartree-Fock model to perform a microscopic study directed to the understanding of the systematic behavior exhibited by the $B1$-$B2$ phase stability in the alkali-halide crystal family. We have focused on the thermodynamic $B1\rightarrow B2$ transition pressures and the $\Delta Y=Y(B2)-Y(B1)$ differences in total energies, volumes, and bulk moduli at zero and transition pressures.

The $B2$ phase is predicted to be more stable at zero pressure than the $B1$ phase for the cesium halides and RbF. Furthermore, the calculated transition pressures decrease steeply as the cation size increases, but are rather insensitive to changes in the anion. The classification of the transition pressures by the cation is also found in the ΔY values. Our theoretical results agree reasonably with the available experimental data. This picture suggests that the nonisotropic deformations suffered by the ions in these highly symmetric systems play a minor role in the analysis of the $B1$-$B2$ relative stability.[21,33]

Analysis of the mechanical (internal) stability of the $B1$ and $B2$ phases shows that the energy curvature of both structures also correlates with the cation atomic number. According to our results, it should be possible to obtain metastable $B2$ potassium and rubidium halides at zero pressure, but not lithium or sodium halides, by quenching the corresponding stable high-pressure $B2$ crystals. We have also found that it is possible to obtain good estimates of $B1\rightarrow B2$ transition pressures from zero-pressure data, but only for compounds in which both phases are mechanically stable at zero pressure.

The different significance of the anionic and cationic deformations in these crystals plays an essential role in the analysis of the underlying reasons that account for the relative stability of $B1$ and $B2$ phases. The anionic contribution to ΔE_0 favors the $B1$ phase in most of the systems, but the cationic energy term changes from positive to negative values when the size of the cation increases due to the negligible net energy terms. As a consequence, the cations are the responsible for the stabilization of the $B2$ structures (except RbF and CsF). Our analysis also provides a nice explanation for the strong decrease of P_{tr} as the cation size increases. Roughly, this change is due to the different magnitude of the anionic deformations induced by different cations resulting in very different anionic contributions to the transition pressure. Finally, whereas the anionic term dominates P_{tr} in LiX, NaX, and KX, the cation is the main responsible for the negative values of this magnitude in CsX.

This kind of microscopic analysis can also be applied to the mechanisms involved in the phase transitions in binary compounds as well as in more complex systems. In this way, we could contribute to the understanding of the microscopic origin of the energy barriers that the systems must overcome in passing from one phase to another and, therefore, the hysteresis phenomena.

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[1] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Oxford University Press, New York, 1954).

[2] W.A. Basset, T. Takahashi, H.K. Mao, and J.S. Weaber, J. Appl. Phys. **39**, 319 (1968).

[3] A.J. Darnell and W.A. McCollum, J. Phys. Chem. Solids **31**, 805 (1970).

[4] S.N. Vaidya and G.C. Kennedy, J. Phys. Chem. Solids **32**, 951 (1971).

[5] T.I. Petrunina, V.I. Soshnikov, and É.I. Éstrin, Sov. Phys. Crystallogr. **17**, 367 (1972).

[6] A. Lacam and J. Peyronneau, J. Phys. (Paris) **34**, 1047 (1973).

[7] C.W.F.T. Pistorius, Prog. Solid State Chem. **11**, 1 (1976).

[8] T. Yagi, J. Phys. Chem. Solids **39**, 563 (1978).

[9] O. Blaschko, G. Ernst, G. Quittner, G. Pépy, and M. Roth, Phys. Rev. B **20**, 1157 (1979).

[10] L.L. Boyer, Phys. Rev. B **23**, 3673 (1981).

[11] Y. Sato-Sorensen, J. Geophys. Res. **88**, 3543 (1983).

[12] T. Yagi, T. Suzuki, and S. Akimoto, J. Phys. Chem. Solids **44**, 135 (1983).

[13] X.Y. Li and R. Jeanloz, Phys. Rev. B **36**, 474 (1987).

[14] J.A. Majewski and P. Vogl, Phys. Rev. B **35**, 9666 (1987).

[15] J.M. Recio, A. Martín Pendás, E. Francisco, M. Flórez, and V. Luaña, Phys. Rev. B **48**, 5891 (1993).

[16] A. Martín Pendás, V. Luaña, J.M. Recio, M. Flórez, E. Francisco, M.A. Blanco, and L.N. Kantorovich, Phys. Rev. B **49**, 3066 (1994).

[17] A. Martín Pendás, J.M. Recio, E. Francisco, and V. Luaña, Phys. Rev. B **56**, 3010 (1997).

[18] A.M. Hofmeister, Phys. Rev. B **56**, 5835 (1997).

[19] U. Köhler, P.G. Johannsen, and W.B. Hozapfel, J. Phys.: Condens. Matter **9**, 5581 (1997).

[20] C.E. Sims, G.D. Barrera, N.L. Allan, and W.C. Mackrodt, Phys. Rev. B **57**, 11 164 (1998).

[21] W.N. Mei, L.L. Boyer, M.J. Mehl, M.M. Ossowski, and H.T. Stokes, Phys. Rev. B **61**, 11 425 (2000).

[22] N.C. Pyper, Chem. Phys. Lett. **220**, 70 (1994).

[23] V. Luaña and L. Pueyo, Phys. Rev. B **41**, 3800 (1990).

[24] M.A. Blanco, V. Luaña, and A. Martín Pendás, Comput. Phys. Commun. **103**, 287 (1997).

[25] J.M. Recio, M.A. Blanco, V. Luaña, R. Pandey, L. Gerward, and J. Staun Olsen, Phys. Rev. B **58**, 8949 (1998).

[26] E. Francisco, M.A. Blanco, and G. Sanjurjo, Phys. Rev. B **63**, 094107 (2001).

[27] F. Birch, Phys. Rev. **71**, 809 (1947).

[28] P. Vinet, J. Ferrante, J.H. Rose, and J.R. Smith, J. Geophys. Res. **92**, 9319 (1987).

[29] V. Luaña, M. Flórez, and L. Pueyo, J. Chem. Phys. **99**, 7970 (1993).

[30] J.M. Léger, J. Haines, C. Danneels, and L.S. de Oliveira, J. Phys.: Condens. Matter **10**, 4201 (1998).

[31] M. Watanabe, M. Tokonami, and N. Morimoto, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **33**, 294 (1977).

[32] A. Martín Pendás, Ph.D. thesis, University of Oviedo, 1992.

[33] P. Cortona, Phys. Rev. B **46**, 2008 (1992).