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Universal-binding-energy relations across the rock-salt–cesium chloride phase transition in alkali halides

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The fulfillment of universal-binding-energy relations across the rock-salt ($B1$)–cesium chloride ($B2$) phase transition in alkali halides is analyzed from a first principles point of view. We show that extensive *ab initio* quantum-mechanical calculations fully support the existence of universality in both intraphase intersystem and intrasystem interphase phenomena. For the latter problems, it is found that the fundamental requirement for a universal law to simultaneously describe both phases and the unstable intermediate steps along the transition path is the topological equivalence of the Gibbs energy profile at the $B1$ and $B2$ points. Several simple relations between thermodynamic quantities of both phases are put forward and discussed in reference to our theoretical data and their interest in experimental research. [S0163-1829(97)05929-8]

I. INTRODUCTION

The existence of corresponding state principles, generally referred to as universal equations, for the binding energy curves of a large class of bound systems arouses a great interest in many branches of physics, ranging from molecular spectroscopy to solid-state thermodynamics.[1] The universal-binding-energy relation (UBER) discovered by Rose *et al.* on bulk metals[2] has achieved great success as it has been generalized to hold on chemisorption,[3] adhesion,[4] cohesion in covalent diatomic molecules and solids,[5] and even on binding in nuclear matter.[6] These generalizations, however, have in common to deal only with intraphase phenomena. Here we show that the UBER concept can be extended to relate the properties of the two different phases involved in a phase transition, as long as the topology of the free energy surface is equivalent in both polymorphs.

The central concept in the corresponding state theories is that of reduced or scaled energies and distances. The UBER proposed by Rose *et al.*,[2] $E^*(a^*)$, is a global, biparametric, linear distance scaling that embodies information on the curvature at equilibrium of the binding energy function through the expression

$$E=E_0E^*(a^*),\quad a^*=(R-R_0)/l, \tag{1}$$

E_0 and R_0 being the energy and interatomic distance at equilibrium, and $l=\{E_0/[d^2E(R)/dR^2]_{R_0}\}^{1/2}$ a reducing parameter.

The ionic or partially ionic compounds do not fit correctly the above UBER. This has been shown to be a consequence of the long-range Coulombic contribution to the energy of those systems.[5,7] Ionic systems can be correctly represented by adding a simple charge transfer (CT) term to Eq. (1). This correction provides a partition of the bonding into covalent and ionic contributions, from the only use of thermodynamic data, which can be compared to the charge transfer values inferred from many other models.[8]

The search for universal relations encompassing an ever-growing class of compounds has led in recent times to the development of a hierarchy of extended UBER's with an always increasing number of free parameters.[1,9] Though very accurate, these models need too many parameters, most times very difficult to obtain either empirically or theoretically. It is our opinion that the major achievements of the universal binding theory emerge from the simplest models, which enlighten the relationship among many properties of different kinds of systems.[10] Their success also poses some very interesting questions to be investigated.

Among these queries is the fulfillment of UBER's across solid-state phase transitions. This issue is of primary interest in the study of condensed matter under high pressures, where the unavailability of thermodynamic data for high-pressure polymorphs unstable at 0 GPa has represented a serious handicap for years.[1] It should be noticed that the UBER equations do not extrapolate correctly to the limit of infinite pressure and that significant deviations may appear at $x=R/R_0=0.5$ and below.[11] However, to attain such strains on ionic solids, extremely high pressures are needed. In the case of the crystals studied here, for instance, this pressure limit goes from more than 100 GPa in CsI to more than 1 TPa in LiF.

In this paper, we present a first principles study of the universal binding theory across the $B1$-$B2$ phase transition on alkali halides. This particular problem has been selected because (a) a large body of experimental information has accumulated over the years on this polymorphic transition, (b) the ionic contribution to the energy leads to a non-straightforward application of the UBER, and (c) recent analyses of theoretically based transition mechanisms[12,13] have uncovered topological connections between the $B1$ and $B2$ phases that seem of general applicability and have important consequences on the scope and validity of the universality, as we are going to show.

The purpose of our work is twofold. On the one hand and following the suggestion of Schlosser, Ferrante, and Smith,[7] we will test the fitting of the simple CT UBER proposed by these authors to first principles calculations on both phases of the alkali halides. We will show that not only selected empirical data, but also results from extended calculations support the charge transfer model. Second, we will use this in-

TABLE I. Static theoretical AIPI equilibrium properties for the 20 alkali halides at the correlated level. Each system is described by 3 rows and 3 columns. Columns contain, respectively, the primitive cell parameter (Å), the cohesive energy (kJ/mol), and the isothermal bulk modulus (GPa). The first row refers to the $B1$ phase and the second to the $B2$ one. Third-row entries are experimental data, most of them obtained at room temperature (Ref. 15).

	F			Cl			Br			I		
Li	2.761	1094.7	83.49	3.662	840.8	31.77	3.882	824.2	28.58	4.359	728.0	16.58
	2.424	1033.5	92.09	3.269	766.7	23.85	3.450	748.4	23.38	3.865	652.6	16.51
	2.843	1011.8	66.51	3.635	854.0	29.68	3.890	821.5	23.52	4.259	763.6	17.17
Na	3.194	983.2	65.06	3.958	792.9	29.37	4.197	776.4	26.70	4.632	696.1	15.61
	2.684	959.5	75.46	3.435	747.6	25.72	3.612	730.5	23.84	4.009	641.5	12.68
	3.277	928.1	46.48	3.988	788.9	23.68	4.224	753.4	19.47	4.576	705.8	14.87
K	3.785	824.5	30.43	4.620	682.9	15.43	4.804	676.8	15.55	5.221	616.0	11.27
	3.229	810.5	34.38	3.906	671.9	19.22	4.061	664.7	16.91	4.454	597.0	10.63
	3.782	825.1	30.22	4.449	715.5	17.35	4.667	690.8	14.64	4.996	650.4	11.51
Rb	3.805	830.0	27.74	4.794	685.0	15.04	4.962	675.1	13.39	5.385	617.5	11.13
	3.250	838.1	34.88	3.994	693.7	21.79	4.122	683.3	18.39	4.516	613.6	12.96
	3.997	789.5	26.68	4.654	692.0	15.58	4.872	665.5	13.24	5.192	629.3	10.49
Cs	3.636	869.4	31.72	4.759	676.9	9.99	4.878	687.6	10.45	5.459	606.6	7.30
	2.995	898.0	59.17	3.934	698.0	12.58	4.069	699.7	13.01	4.535	620.2	9.02
	4.242	722.7	23.50	4.100	675.1	16.20	4.295	652.2	14.20	4.568	619.1	11.40

formation together with our previous results on the $B1$-$B2$ transition to gain physical insight into the implications of universality and the sources affecting its accuracy across the polymorphic change. The paper is organized as follows. In Sec. II, we will center on the discussion of intraphase intersystem universality. Section III will deal with interphase intrasystem universality. Finally, we will present the conclusions of our investigation and some suggestions for future work.

II. INTRAPHASE UNIVERSALITY

To start with, we have analyzed the ability of the simple CT UBER (Refs. 5 and 7) to independently fit the data of the $B1$ and $B2$ phases. The basic data for this test are the curves of total energy versus lattice parameter for the 20 usual alkali halides (those not including Fr or At) in the $B1$ and $B2$ phases. These curves have been obtained by performing *ab initio* perturbed ion (AIPI) quantum-mechanical calculations.[13,14] The predicted static equilibrium data from these curves (our reference scaling parameters from now on) are collected in Table I. These values have average relative errors of 3.0%, 4.3%, and 14.2% with respect to mostly room-temperature experimental values[15] in lattice parameters, binding energies, and isothermal bulk moduli, respectively. When comparing these computed values with the available 0 K extrapolated data, the theory-experiment agreement is simultaneously improved for the three magnitudes.[13]

To test the simple CT model with our theoretical data, we write the binding energy of the system under study as a sum of a covalent and a Madelung correcting term:

$$E(R)=CE^*(a^*)-\frac{MC_t^2}{R}, \tag{2}$$

where E^* is the function describing the covalent contribution with well depth C. To simplify the problem we have chosen the parameter-free Rydberg function $E^*(x)=-(1+x)\exp(-x)$. M and C_t are the Madelung constant and the CT parameter associated with the Coulombic contribution to the binding energy. It must be understood that a^* [Eq. (1)] is scaled with respect to the covalent term only. The E_0 and R_0 values used for scaling energies and distances, respectively, are directly extracted from the AIPI calculation (see Table I).

Thus, Eq. (2) has been fitted to the AIPI binding curves with C_t and l [Eq. (1)] being the only free parameters. In Table II, best fitting parameters for the $B1$ phases are collected. Results for the $B2$ phases are very similar, giving rise to slightly more covalent crystals, and will not be discussed here. The overall mean square deviation (about 10 J mol^{-1}) is excellent, and shows that the CT model is a physically sound way of recovering the UBER found in nonionic cohesive systems. In good agreement with other procedures, covalent contributions to the binding energy are always very small, though they play a non-negligible role on the heavier, more polarizable crystals. We have observed that C and C_t are very sensitive to the range of R values used in the fitting. If the points used gather around the equilibrium position, the CT answer describes a highly ionic system with very small covalent contribution and charge transfer. However, if we decided to introduce points belonging to higher-pressure configurations (smaller lattice parameters), the CT answer moves to a more covalent description. This behavior, not reported up to now, is in agreement with our chemical intuition and points to the widely accepted ionic-to-covalent-to-metallic transformation induced by pressure.

III. INTERPHASE UNIVERSALITY

We move now to extend our universality arguments to the simultaneous description of both phases. It has been shown

TABLE II. Best rms parameters of the fitting of the CT model of Schlosser *et al.* (Ref. 7) to the $B1$ AIPI binding energy curves. The covalent contribution to the energy is only included for completeness, being dependent on the actual C_t and l fitted variables. a_0 stands for the equilibrium geometry of the covalent contribution.

	$\log_{10}(C/E_0)$	C_t	l/a_0
LiF	-2.86282	0.99799	0.16148
LiCl	-1.90600	0.99386	0.18080
LiBr	-1.26086	0.97511	0.18596
LiI	2.10881	1.02523	0.10923
NaF	-1.98171	0.99661	0.15512
NaCl	-1.85662	0.99036	0.15017
NaBr	-1.40911	0.98785	0.15621
NaI	-1.14480	0.96332	0.17378
KF	-1.40547	0.97384	0.18068
KCl	-1.20980	0.96195	0.18154
KBr	-1.62992	0.99680	0.14845
KI	-1.28027	0.97154	0.15732
RbF	-1.37862	0.98468	0.20184
RbCl	-0.79728	0.88185	0.19799
RbBr	-1.00658	0.96538	0.18287
RbI	-1.04004	0.96464	0.17323
CsF	-1.30640	0.98165	0.21297
CsCl	-0.77272	0.92149	0.28224
CsBr	-1.13468	0.98419	0.20683
CsI	2.23431	1.04451	0.10493

in a recent study[12] that under quite general assumptions the $B1$-$B2$ transition path is biparametric in nature. Using the rhombohedral primitive cell ($a=b=c, \alpha=\beta=\gamma=60°$) for the $B1$ phase and the cubic primitive cell ($a=b=c, \alpha=\beta=\gamma=90°$) for the $B2$, the phase change involves the displacement of the system through the two-dimensional a-α Gibbs surface (with $a=b=c$ and $\alpha=\beta=\gamma$ at every point). The minimum Gibbs energy paths found are very asymmetric and depend on pressure, with large Gibbs energy barriers between the end-point configurations. One of the main contributions of Ref. 12 was the discovery of the important role that symmetry plays in establishing the topology of the a-α surface, and the subsequent importance of the surface topology in determining the physical properties associated with the transitions.[12]

We have encountered three dissimilar topologies in the Gibbs energy profiles at zero pressure that evolve gradually with the system examined as pressure is applied. Selected crystals that clearly illustrate this variety are found in Fig. 1. We need to emphasize that the $B2$ critical point shifts from a relative maximum in LiCl to a minimum in KCl. The CsCl profile is presented to show that the deepening of these minima may eventually lead to the stabilization of the $B2$ phase.

The connection between these arguments and universality may be inferred easily now. It is only in the systems displaying Gibbs surfaces with identical topologies at the $B1$ and $B2$ points (the ''mm'' systems in Table III) where one may assure the existence of suitably large neighborhoods of those points that can be isomorphically mapped one onto the other after adequate linear scalings. As thermodynamic magnitudes are linked to the local properties of the Gibbs surface, linear universality should not be searched for but in crystals exhibiting identical topologies (IT systems in the following).

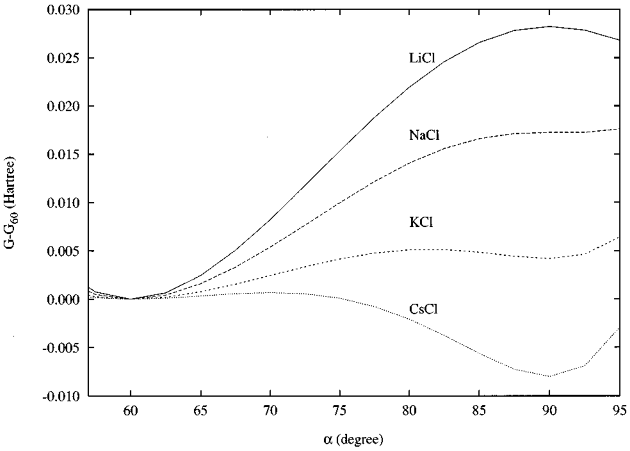

FIG. 1. Computed zero-pressure Gibbs energy profiles along the a-α transition path for some representative systems. The energies have been scaled so as to coincide at the $B1$ configuration. The three different topologies of the $B2$ critical point (maximum, saddle, and minimum) are apparent.

To investigate the universality across the transition, we have decided to use the simplest scaling model in which the energies and geometries of each phase are divided by their respective equilibrium values: E/E_0 and a/a_0. In this way, we are sure to find simple relations among magnitudes in the two phases not masked by the scaling parameters. It is easy to show that the relations we are going to present are also fulfilled in the linearly scaled model [Eq. (1)]. Figure 2 shows the reduced binding energy curves for a prototype IT system, NaF, at different values of α. Not only the $B1$ and $B2$ phases, but even the unstable intermediate steps follow closely, though not perfectly, the UBER. Similar results have been found for other systems, the agreement among different α curves being better for IT systems than for non-IT crystals. In the light of this theoretical analysis, we think that the interest in experimentally testing the UBER in crystal deformations, as Banerjea and Smith[10] first suggested, should be renewed.

Let us now examine the consequences of this behavior. In our transition model, the binding energy of the crystal is a

TABLE III. Theoretical topological properties of the 20 alkali halides at the static $B1$,$B2$ equilibrium configurations. Each system is labeled with a two-character code plus, possibly, a star. The first and second characters refer to the $B1$ and $B2$ points, respectively. ''m'' stands for local minimum, ''M'' for local maximum, and ''s'' for a quasisaddle situation (the precise determination of a zero second-order derivative is a difficult question). The star implies a system that is more stable in the $B2$ than in the $B1$ phase.

	F	Cl	Br	I
Li	mM	mM	mM	mM
Na	mm	ms	ms	mM
K	mm	mm	mm	ms
Rb	mm*	mm*	mm*	mm
Cs	mm*	mm*	mm*	mm*

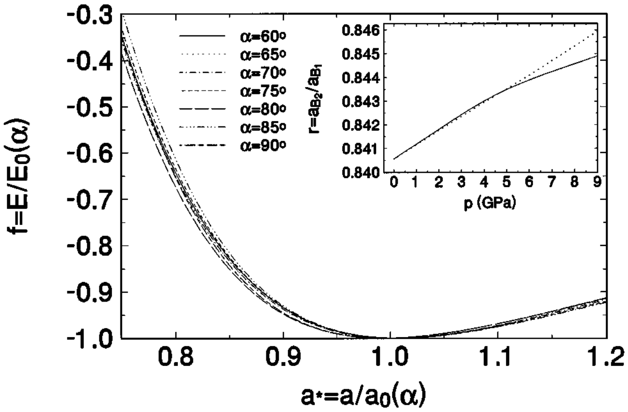

FIG. 2. Reduced binding energy curves at different values of α for the transition surface in NaF. $\alpha=60°$ and $\alpha=90°$ are the $B1$ and $B2$ end structures, respectively. Inset: computed (solid line) and predicted (dotted line) $r(p)$ function [Eq. (13)] for the same system.

function of a and α. It is to be noted that for each (a,α) point in the transition path a pair of E_0 and a_0 equilibrium values have been obtained. Figure 2 demonstrates that the two-dimensional E surface closely follows a universal function that can be factorized as

$$E(a,\alpha)=E_0(\alpha)f(a^*), \tag{3}$$

where $a^*=a/a_0(\alpha)$, $E_0(\alpha)$ is the binding energy found for the pseudophase with $\alpha=\alpha$, and f is the UBER. Notice that the appropriate Rydberg function in terms of the present definition of a^* is $f(x)=-x\exp(1-x)$. We can extract some consequences for the 0 K thermodynamics of the transition from Eq. (3). A first simple relation among pseudophases is found for the bulk moduli. Using $B=v(d^2E/dv^2)$, v being the molar volume, and defining the binding energy density of a system as $\rho(\alpha)=E_0(\alpha)/v_0(\alpha)$, we get the expression

$$B(\alpha)=-\frac{1}{9}\rho(\alpha)f''(1),\quad \frac{B(\alpha)}{B(\alpha')}=\frac{\rho(\alpha)}{\rho(\alpha')}. \tag{4}$$

Similar expressions are well known from qualitative reasonings since long ago, and have been discussed from different points of view many times.[16] We have checked Eq. (4) by comparing the actual theoretical bulk moduli of the $B2$ phase (see Table I) and those predicted from the values of the $B1$ structures. The latter results are shown in Table IV. It becomes clear that the relations we have derived are useful as a thumb rule for predicting trends in the behavior of bulk moduli changes across the transition. It is also apparent that the agreement with our actual theoretical $B2$ data is mainly controlled by the topological properties of the energetic surface previously discussed and that, if the analysis is restricted to IT systems, the agreement is very good, given the simplicity of the model. For the IT systems, the predicted B values usually coincide within 1 GPa with the computed ones (i.e., 75.66 vs 75.46 GPa in NaF or 12.96 vs 13.01 in CsBr). For the non-IT systems, the discrepancies are larger, around 5 GPa on the average, and the predicted B's show even contradictory trends in some crystals. In this sense, the predicted $B2$ bulk moduli are smaller (LiF) or larger (NaI) than the $B1$ values, while the contrary is true for the AIPI computed values.

TABLE IV. Bulk moduli of the $B2$ phases predicted from the AIPI values for the $B1$ structures through Eq. (4). All data in GPa.

	F	Cl	Br	I
Li	82.36	28.80	26.14	15.08
Na	75.66	29.96	27.87	15.69
K	34.07	17.76	17.88	12.44
Rb	31.78	18.36	16.72	13.26
Cs	41.45	12.90	12.96	9.21

The thermodynamic function controlling the phase transformation for constant temperature and pressure is the Gibbs energy. The simply scaled version at 0 K conditions gives, for each α,

$$G^*(a;\alpha)=\frac{1}{E_0(\alpha)}[E(a;\alpha)+pv(a;\alpha)]=f+p^*v^*,$$

$$p^*=p/\rho(\alpha),v^*=v(a;\alpha)/v_0(\alpha), \tag{5}$$

the pressure and the volume being scaled by the equilibrium energy density and volume, respectively. As any system in thermodynamic equilibrium must be in a configuration that minimize the Gibbs function with respect to the free variables, Eqs. (3) and (5) lead to

$$p^*=-\frac{1}{3a^{*2}}f'(a^*), \tag{6}$$

$$G^*=f(a^*)-\frac{1}{3}a^*f'(a^*)=G^*(p^*). \tag{7}$$

Our reduced Gibbs function is then universal along the whole phase transition process. We gain further insight if we expand G^* as a power series in p^* around $p^*=0$:

$$G^*\simeq-1+p^*-\frac{9}{2f''(1)}p^{*^2}+\cdots. \tag{8}$$

The truncation of this expansion leads naturally to a hierarchy of universal relations that must hold across the transition, should the universality assumed in Eq. (3) be perfect. It is also clear that the range of applicability of these relations is mainly controlled by p^*. We have in this way not only the relations themselves, but also the keys to understand the factors that affect their accuracy.

The transition pressure can be expressed in terms of universal curves and equilibrium data as follows:

$$\frac{E_0(60)}{E_0(90)}G^*\left(\frac{\rho(90)}{\rho(60)}p^*(90)\right)=G^*(p^*(90)). \tag{9}$$

Truncating now G^* to first order in p^* and returning to nonreduced magnitudes, we obtain the well-known relation[17]

$$p_{\rm tr}^{(1)}=-\frac{\Delta E_0}{\Delta v_0}, \tag{10}$$

where Δ represents differences between final ($\alpha=90°$) and initial ($\alpha=60°$) values. Deviations from this rule can be overcome with our treatment through a second-order formula

$$p_{\rm tr}^{(2)}=-\frac{\Delta v_0+\sqrt{\Delta v_0{}^2+2(\rho/B_0)\Delta(v_0^2/E_0)\Delta E_0}}{(\rho/B_0)\Delta(v_0^2/E_0)}. \tag{11}$$

The performance of Eq. (11) over Eq. (10) shares many features with the discussion following Eq. (4). As an example, in NaF, $p_{\rm tr}^{(1)}=10.6$ GPa, $p_{\rm tr}^{(2)}=12.79$ GPa, and $p_{\rm tr}^{(\rm AIPI)}=12.13$ GPa, while in LiCl the first order answer is nonsense, $p_{\rm tr}^{(1)}=-588.74$ GPa, and the second-order value $p_{\rm tr}^{(2)}=47.03$ GPa is to be compared with the AIPI result 78.82 GPa.

Many other approximate and useful relations may be found whose behavior across the transition runs parallel to the one we have just described. We shall only consider the conduct of the lattice parameter (or volume). Assuming reduced pressures not too large, we may expand Eq. (6) around $a^*=1$ to first order and find an approximate relation between applied pressures and equilibrium lattice parameters:

$$a^*\simeq 1-\frac{3}{f''(1)}p^*. \tag{12}$$

Using now the universality criterium and defining the pressure-dependent ratio $r(p)=a(90,p)/a(60,p)$, we find

$$\begin{aligned} r(p)&\simeq r(0)\left[1+\frac{3p}{f''(1)}\left(\frac{1}{\rho(90)}-\frac{1}{\rho(60)}\right)p\right]\\ &\simeq r(0)\left[1-\frac{1}{3}\left(\frac{1}{B(90)}-\frac{1}{B(60)}\right)p\right]. \end{aligned} \tag{13}$$

This relation is fulfilled very well by most IT systems (see the inset in Fig. 2 for an example), showing that the slope of the r ratio depends fundamentally on which phase has the greater energy density (or bulk modulus). It is also to be noticed that the IT systems display smaller energy densities in the $B1$ structure than in the $B2$ one and that the converse is true for the non-IT crystals, LiF being the only exception to this rule.

The present discussion has been mainly directed to demonstrate the existence—at least approximate—of universal relations between the $B1$ and $B2$ properties. Our theoretical data, moreover, also support the universality along the whole transition path, as was briefly commented above. This leads to the existence of universal relations in the much more complex realm of transition kinetics. In this field, however, it is difficult to propose experimental confirmation of theoretical results, given the large number of variables and phenomena involved, and conclusions extracted from theory must be managed with care.

In Fig. 3 we show the reduced transition energetic profiles for a prototypical set of alkali halides at their transition pressure. We observe again a good universal behavior, with the systems grouping naturally into two well-differentiated categories that correspond faithfully to our topological classification. As a consequence of the behavior depicted in Fig. 3, the geometry (α) of the transition state as well as the activation barrier, and thus the transition rate can be described with independence of the system, once they are appropriately reduced. A deeper study of these important questions should rely in many lacking experimental information.

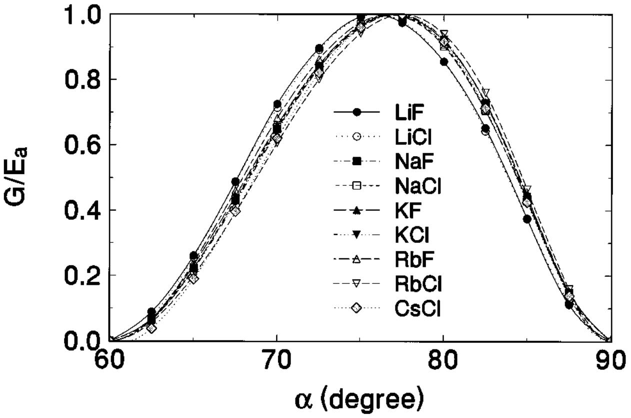

FIG. 3. Reduced transition energetic profiles along the reaction path for a representative set of alkali halides at their thermodynamic transition pressures. Static Gibbs functions are referred to their $B1$ value in each case and have been scaled by the corresponding activation barrier E_a.

IV. CONCLUSIONS AND PROSPECTS

We have shown in this paper that *ab initio* calculations carried out in the alkali halide family support the existence of UBER's in mainly ionic compounds not only when intraphase intersystem universality is examined, but also when interphase intrasystem problems are considered. Our results demonstrate how reliable static solid-state simulations can be used to gain some insight on difficult experimental questions.

In this sense, we think it necessary to perform new experiments to study UBER's in deformation processes and phase transitions in solids. We have found some principles that may assist future work in those issues. The most important of them is, in our opinion, the topological connection. We have shown that the topological properties of the phase transition energetic surface at the points of interest are crucial in determining the fulfillment of universal relations across the change. It is also important to notice that the energy density of a crystal phase is directly related to the surface topology.

On the other hand, we have proposed a set of simple relations between geometric and thermodynamic properties of both phases whose justification lies in the factorization of the reduced transition energetic surface into single variable terms. Though our calculations are generally in very good agreement with these relations, they still need further experimental confirmation. In the case of a positive answer to this question, we feel that the expressions will be very useful in high-pressure research, where usually there is only limited information on the thermodynamic properties of metastable phases.

Last and as the scope of this investigation is concerned, we think that the present results are deep in nature and could be generalizable to other families of compounds and to other types of phase changes. We believe it worthwhile to further study this point.

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