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Bonding mechanism of some simple ionic systems: Bader topological analysis of some alkali halides and hydrides revisited

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ABSTRACT

The ability of Bader's charge density topology analysis to explain various material properties has been examined for simple ionic systems of alkali halides and alkali hydrides. It was established that despite the fact that most of them share the same rock salt crystal structure phase, some of them belong to different topological classes. This fact was used to explain various experimentally observed properties of these materials, and to discuss their deviations from expected trends. Some phase transitions observed in these systems, and their possible relation to changes in the charge density topology have been also investigated from the same point of view. Reasons for anion-anion bond formation in some of them and its features are discussed, as well.

1. Introduction

The Quantum Theory of Atoms in Molecules (QTAIM) proposed by Richard Bader [1] is a theoretical approach based on the topological analysis of the charge density ($\rho(\mathbf{r})$), by which the space of a molecule or a crystal structure can be divided in a unique way into basins corresponding to atoms of investigated system. Scalar field of $\rho(\mathbf{r})$ and corresponding gradient vector field $\nabla\rho(\mathbf{r})$ contain by definition [2] a complete information about the ground state of a molecular or a crystal system, its bond properties, cohesion, and stability. The topology of $\rho(\mathbf{r})$ can be expressed locally with a unique set of critical points (*cp*) that satisfy condition $\nabla\rho(\mathbf{r})\cdot\mathbf{n} = 0$. Type of a critical point and its character is determined by the square Hessian matrix consisting of second-order partial derivatives of $\rho(\mathbf{r})$. Diagonalization of the Hessian matrix at the position of a *cp* gives three eigenvalues and the corresponding eigenvectors. The sum of these diagonal elements is Laplacian of the charge density at the position of a *cp*. Critical point is defined by the pair of numbers (ω,σ), whereby rank ω is the number of non-zero eigenvalues and signature σ is the sum of their algebraic signs.

There are four stable *cp*s of rank 3, that make a complete set. A (3,-3) is a local maximum of $\rho(\mathbf{r})$, defines the nuclear position and hence is named nuclear *cp* - *ncp*. A (3,-1) saddle point of $\rho(\mathbf{r})$, or *bonding cp* (*bcp*), is a local minimum along the direction perpendicular to the plane containing the line linking interacting atoms, so called "bond path" and a local maximum in that plane. A *ring cp* (*rcp*) or (3,+1) saddle-point is a local minimum of $\rho(\mathbf{r})$ in a plane in which "bond paths" of interacting

atoms form a closed contour, and a local maximum along the perpendicular direction. When at least two such "bond paths" contours enclose a part of space, in its interior appears a local minimum of $\rho(\mathbf{r})$, namely (3,+3) or a *cage* critical point (*ccp*).

In the paper by Pendás et al. [3], thorough investigation of alkali halides of the rock salt (B1) and caesium chloride (B2) structures were presented, from the quantum theory of 'atoms-in-molecules' point of view. They found that these simple ionic systems with the same crystal structure exhibit distinct topological properties, based on different ionic radii ratios.

In this paper, we have investigated B1 phase of alkali hydrides within broader picture together with alkali halides (AlkHa: Alk = Li, Na, K, Rb, Cs and Ha = F, Cl, Br, I) of the same phase. We have used QTAIM analysis and complementary Non-Covalent Interaction (NCI) approach (section 3.2), both being assigned as Quantum Chemical Topology (QCT) methods. In order to compare results with those available in the literature, we have used state-of-art electronic structure calculation. The obtained differences are discussed on the base of the subtleties of calculation approaches and the physics behind them.

2. Details of calculation

The calculations presented in this work have been performed using full potential linearized augmented plane waves method with the addition of localized orbitals (FP-LAPW + lo), as implemented in WIEN2k code. The method is described elsewhere [4]. The measure of quality,

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(over) completeness and size of basis set, $R_{MT}K_{max}$ value, was subject of convergence study and set at value equal to 8.0. The number of k points used for Brillouin zone sampling has also been the subject of convergence studies, and value of 120 k points in irreducible part of Brillouin zone (4000 in entire Brillouin zone) was chosen. Radii of MT spheres for alkali metals were chosen in the range of 0.899–1.164 Å, for halogen elements from 1.005 to 1.058 Å, while for hydrogen atom fixed value of 0.846 Å was used in all systems. The magnitude of the largest vector G_{max} in charge density expansion in the interstitial part of crystal space is selected to be 14. Lattice harmonics expansion within the MT sphere (by symmetrically allowed combinations of values of quantum numbers L and M) is set to be 10. High values of the last two parameters provided a detailed description of the charge density, which is necessary for a reliable topological analysis. Exchange correlation effects have been employed using generalized gradient approximation (GGA) and parameterization of Perdew, Burke and Ernzerhoff [5]. Full volume to energy optimization has been performed for all investigated compounds in order to obtain optimal forces and to validate calculations against experimental cell parameters. The obtained SCF converged charge density was then used as input for CRITIC2 [6,7] code. Additional tuning of $R_{MT}K_{max}$ parameter (up to 9.5) was performed in some cases to further reduce discontinuities in the density or its slope at MT sphere boundaries, without reaching overcompleteness of basis set, to avoid possible problems in topological analysis algorithms [8].

3. Results and discussion

3.1. Topological classes

Many authors have used Bader's theory to analyse various characteristics of different solid state systems [9–18]. Among them is the mentioned theoretical study of alkali halides (AlkHa: Alk = Li, Na, K, Rb, Cs and Ha = F, Cl, Br, I) performed by Pendás et al. [3] using ab initio method of perturbed ion (aiPI) based on a localized Harti-Fock scheme [19]. Authors have classified different topological properties into classes according to the numbers of non-equivalent critical points $(n\ b\ r\ c)$ found in the crystal primitive cell and consequently brought out an interesting result that there are three different topological classes among alkali halides of the B1 crystalline phase. In the present work investigation of alkali halides charge topology is extended and complemented with an analysis of alkali hydrides in the same phase. The results show that all investigated alkali halides and hydrides, according to the aforementioned classification belong to either (2111), or (2211) topological class. These two classes differ in the way that beside bcp existing between cation and anion in the (2111), there is an additional bcp between neighboring anions in the (2211) class (see Table 1). A more precise treatment of exchange-correlation effects was used in this work in relation to the aforementioned method that discovered (2222) class, characterized by additional rcp and ccp low symmetry points. Generally, correlation effects increase the charge in bcp at the expense of the charge in low density regions [20], while use of the LDA (GGA) functionals increases it's delocalization and thus makes ρ (r) in the interstitial space smoother. This could be the explanation for the absence of local and global charge density minima and therefore (2222)
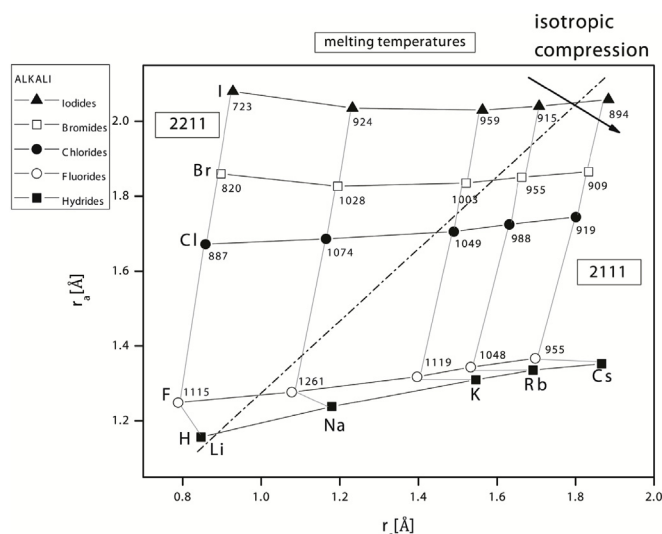

Fig. 1. Distribution of alkali halides and hydrides according to the values of their ionic radii(r_a-anions, r_c-cations). The dashed-dotted line represents the border between the two topological classes. The arrow points in the direction along which the topological transition induced by isotropic compression could be expected. The numbers shown are melting temperatures in K.

topological class in our calculations.

All alkali halides that crystallize in the B1 structure, as well as those few Cs compounds (CsCl, CsBr and CsI) that prefer the B2 phase, are wide band gap compounds. Electronegativities of their constitutive atoms vary in a broad range from 1.0 for Li to 4.0 for F [21], so these systems are known to be typical ionic compounds. Calculating ionicity according to Pauling's definition [22] alkali hydrides are similar to alkali iodides.

In alkali hydrides, halogen anion is replaced by another typical electron acceptor hydrogen, so the ionic nature of the compounds is in that sense preserved. Negatively charged hydrogen ion was considered to have a very large ionic radius of about 2.08 Å [21], but the experimental estimates give its value to be of about 1.30 Å in Alk-H compounds [23], providing very similar interatomic distances in alkali hydrides as those in alkali fluorides.

Ordering of the investigated compounds according to the values of their anion and cation radii, which are estimated from the calculated positions of cation-anion bcp are presented in Fig. 1. Apparently, anion-to-cation radius ratio (r_a/r_c, Table 2) is one of the parameters that control the appearance of the particular topological class. The borderline which divides two topological classes is presented in Fig. 1 by the dashed-dotted line implying the critical r_a/r_c value to be in the range from 1.09 to 1.18.

The smooth trends observed in Fig. 1 for alkali halides are expected considering their simple electronic structure and quite uniform change of their ionic radii. In the same figure experimental melting

Table 1

Positions and types of critical points of (2111) and (2211) topological classes.

Wyckoff position	coordinates	(2111) critical points	(2211) critical points
48 h	(0,y,y)	–	rcp
24e	(x,0,0)	bcp (cation-anion)	bcp (cation-anion)
24d	$(0, \frac{1}{4}, \frac{1}{4})$	rcp	bcp (anion-anion)
8c	$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	ccp	ccp
4b	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	ncp (anion)	ncp(anion)
4a	(0,0,0)	ncp (cation)	ncp (cation)

Table 2

Anion to cation radius ratio r_a/r_c of alkali hydrides and halides.(Light grey compounds belong to (2211), dark grey to (2111) class.

	r_a/r_c	Cations				
		Li	Na	K	Rb	Cs
Anions	**H**	1.37	1.05	0.85	0.79	0.72
	F	1.58	1.18	0.94	0.88	0.80
	Cl	1.95	1.45	1.14	1.06	0.97
	Br	2.07	1.53	1.21	1.11	1.02
	I	2.24	1.65	1.30	1.19	1.09