The Systematic Variation of Optical Properties of Alkali Halides: an Ab Initio Study

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In this paper we study a correlation between the optical properties, electronic structure and anion-cation electronegativity difference in three groups of alkali halides MX (M = Li, Na, K; X = F, Cl, Br, I). The electronic structure was calculated by first-principle, density-functional theory based full-potential linear augmented plane wave method. Then the complex dielectric function was computed, allowing determination of the optical absorption spectra in all compounds, up to incident radiation energy of 40 eV. The results were interpreted in terms of calculated band structures and correlated with the electronegativity difference in each compound, which was estimated on the basis of topological theory of Bader.

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1. Introduction

The alkali halides form a family of compounds which is considered to be the prototype of ionic compounds. They are insulators and crystallize in face centered cubic structure [1]. Some of them exhibit strong scintillation effects, being used as detectors (famous examples are LiF and NaI). The other may be colored by exposure to radiation or impurity doping. In any case, alkali halides are interesting optical materials and often serve to test new theories and calculation approaches [2].

Objective of the present work is to study a correlation between the optical properties, electronic structure, and the anion-cation electronegativity difference

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in several groups of alkali halides (defined by fixing a cation and varying the anion). Towards this aim we have calculated and analyzed the electronic structure of three groups of alkali halides MX (M = Li, Na, K; X = F, Cl, Br, I). Knowledge of the MX band structures permitted us to calculate imaginary part of the complex dielectric function and to determine the optical absorption spectra as functions of incident radiation energy up to 40 eV. We discuss the results in terms of calculated band structures and correlate them with cation-anion electronegativity difference in each compound. The latter is estimated on basis of topological theory of Bader [3].

2. Calculation details

The self-consistent band-structure calculations were performed by density-functional theory [4] based, full potential linear augmented plane wave (FP-LAPW) method [5] as embodied in WIEN2k computer code [6]. In this method, the electronic wave functions, charge density and crystal potential are expanded in spherical harmonics inside the non-overlapping spheres centered at each nuclear position (atomic spheres with radii R_{MT}), and in plane waves in the rest of the space (interstitial region). Inside atomic spheres the partial waves were expanded up to $l_{max} = 6$, while the number of plane waves in the interstitial was limited by the cut-off at $K_{max} = 8.0/R_{MT}$. The charge density was Fourier expanded up to $G_{max} = 14$. For Brillouin zone integration, a mesh of 8 k-points in the irreducible part of the zone (IBZ) was used. Calculations of the optical properties were performed utilizing 165 k-points in IBZ. Exchange and correlation effects were treated by generalized-gradient approximation (GGA96) [7].

Crystal structure of alkali halides is rock-salt, space group $Fm3m$, where the alkaline and halide atoms occupy 4a and 4b positions, according to Wyckoff's notation. Both positions are fixed by symmetry, thus the interatomic distances depend crucially on the lattice parameter values. To initiate the calculations we used the experimental values for these parameters from Ref. [1], and then performed series of calculations in order to relax these values and to find structures that correspond to energy minima. We found that the calculated lattice parameters differ from the experimental ones by few percents for all considered compounds.

3. Results
3.1. Bader analysis

Topological properties of electron density in all alkali halides have been evaluated on the basis of the Bader theory [3]. Points in the crystal space where the gradient of the electron density disappears are called critical points. These points can be classified according to a sum of signs of the corresponding Hessian matrix. The critical point with two negative and one positive Hessian eigenvalue is of special interest: it is called bond critical point (BCP). Its existence between any two atoms in solid indicates that these two atoms are chemically bonded.

On the basis of calculated electronic structure we determined the positions of critical points in MX compounds, and found the bond critical point between each alkaline and halide atom. The characteristics of these points are listed in Table.

TABLE

Properties of bond critical points in alkali halides. Interatomic distances and bond critical radii of alkaline $r_b(X)$ and halide $r_b(M)$ atoms (all in Å), eigenvalues $\lambda_{1,2}$ and λ_3 of the Hessian matrix in the plane perpendicular to bond directions and in the bond directions, respectively, Laplacian of the electron density and the electron density in critical point (in $e/Å^5$ and $e/Å^3$, respectively).

Bond	Distance	$r_b(X)$	$r_b(M)$	$\lambda_{1,2}$	λ_3	$\nabla^2\rho_C$	ρ_C
Li–F	2.045	0.791	1.254	−0.617	4.442	3.208	0.127
Li–Cl	2.589	0.878	1.711	−0.256	1.860	1.348	0.073
Li–Br	2.775	0.906	1.869	−0.191	1.401	1.018	0.062
Li–I	3.024	0.936	2.088	−0.141	1.036	0.755	0.054
Na–F	2.350	1.087	1.263	−0.369	3.268	2.530	0.114
Na–Cl	2.846	1.169	1.676	−0.199	1.634	1.237	0.074
Na–Br	3.014	1.198	1.816	−0.160	1.296	0.976	0.065
Na–I	3.258	1.234	2.024	−0.123	0.969	0.723	0.055
K–F	2.716	1.318	1.397	−0.388	2.661	1.884	0.109
K–Cl	3.186	1.487	1.700	−0.207	1.345	0.930	0.076
K–Br	3.365	1.531	1.834	−0.161	1.114	0.791	0.063
K–I	3.597	1.572	2.025	−0.129	0.829	0.572	0.057

Analysis of the data in Table confirms that ionic character of the M–X bond decreases as anion varies from F to I in all three groups (the positive eigenvalue, Laplacian and BCP electron density decrease, while the interatomic distance increases [8]).

3.2. Electronic structure

Calculated electronic structures are presented in Fig. 1, where the electronic densities of states (DOS) are shown in the energy interval around the Fermi level.

The DOS of Na group of alkali halides is very similar to DOS of the Li group, and therefore not presented here. In the Li group the relevant states are just the halide s-states, situated deeper in energy, and the halide p-states, which dominate the band attached to the Fermi level. The valence region of the K group is different since the K p-states position themselves near to the halide s-states. Conduction band is similar in all groups, consisting of the mixture of the alkali and halide s-, p- and d-states.
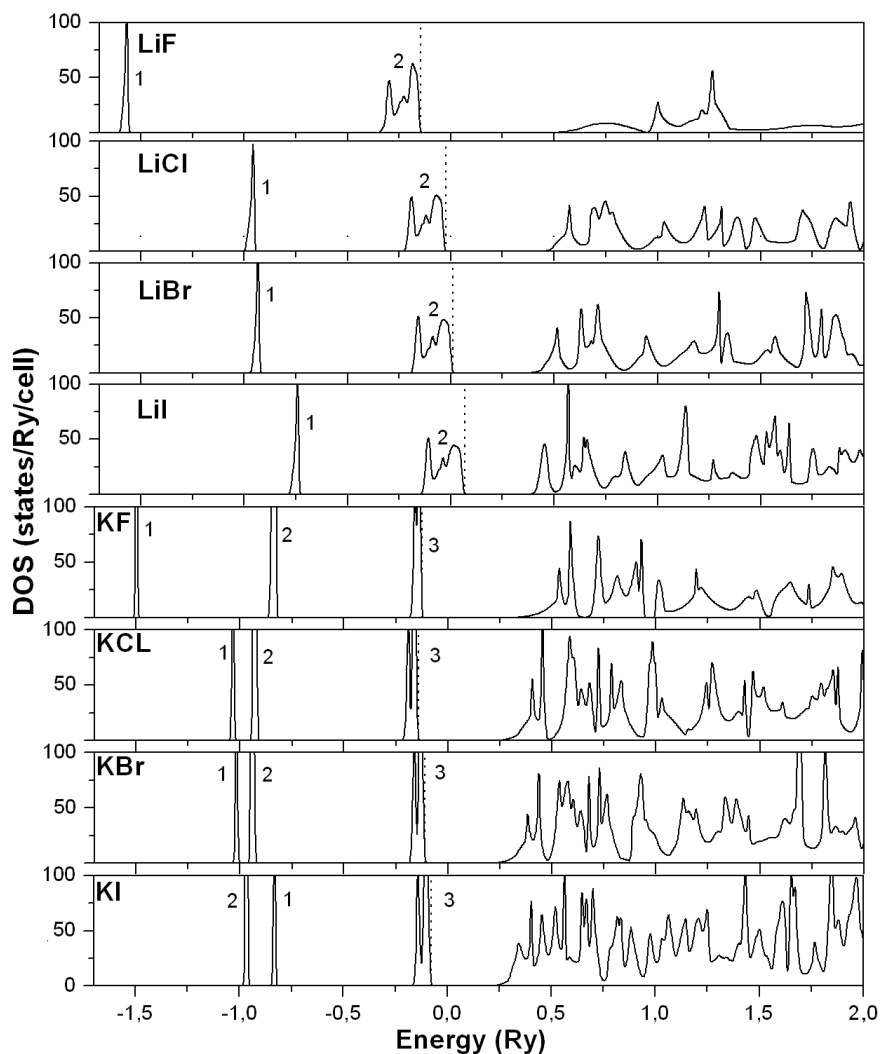
Fig. 1.   Electronic DOS in the Li and K groups of alkali halides. Dashed line denotes Fermi level.

3.3. Optical absorption

Complete description of how any material responds to the electromagnetic disturbance is contained in its complex dielectric function. Imaginary part of this function is directly proportional to the optical absorption spectrum. It can be computed from knowledge of the electronic band structure of a solid [9]. On the basis of calculated band structure we computed the imaginary part of dielectric function for all alkali halides up to incident radiation energy of $\hbar\omega = 40$ eV. Results are presented in Fig. 2.
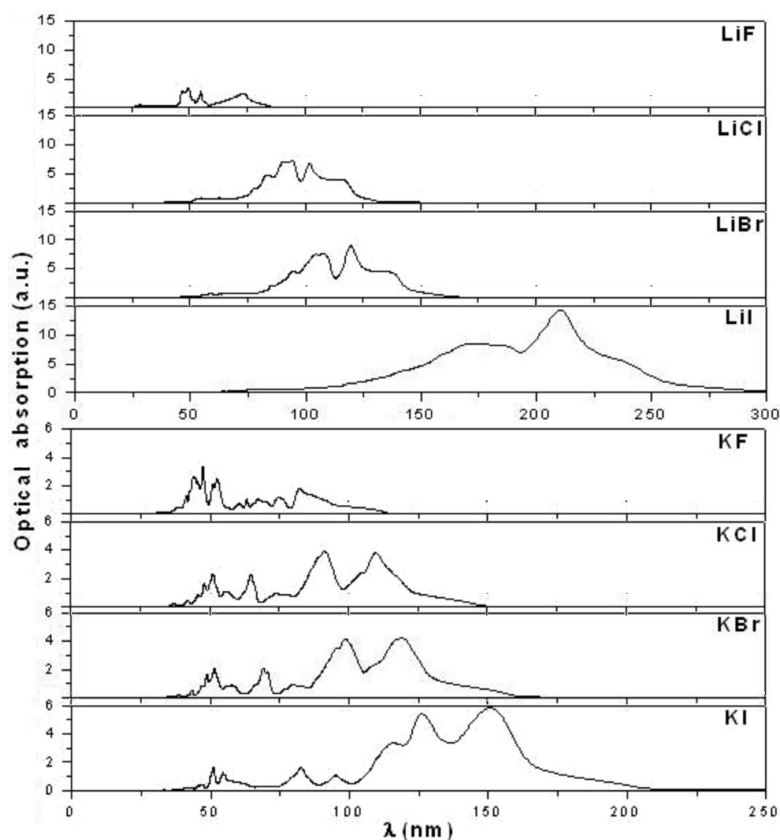
Fig. 2. Imaginary part of dielectric function for Li and K group of alkali halides, as calculated by the FP-LAPW method.

4. Conclusions

The Bader analysis showed that ionic character of the M-X bond decreases as anion varies from F to I in all three groups of MX alkali halides. At the same time the band gap decreases, while the band structures around the gap stay very similar. In groups with M = Li, Na the top of the valence region consists of two distinct bands: halide *s*-states and the mixture of the alkaline *s*- and the halide *p*-states. The ultraviolet (UV) optical absorption occurs in very compact energy regions, 7–8 eV wide. Positions of optical peaks decrease in energy scale as anion changes from F to I. The group with M = K exhibits different band structure in the vicinity of the gap: the K *p*-states position themselves between the halide *s*- and *p*-states. This fact makes the UV absorption region less compact, causing appearance of various additional optical peaks at higher energies for each compound in the group.

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