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LETTERS

Secondary Interactions and Bond Critical Points in Ionic Crystals

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The sufficiency of the condition of the existence of a (3,−1) (bond) critical point of charge density between *atoms in a crystal* for a bonding interaction between these particular atoms has been studied for the example of the ionic LiF and NaF crystals. Results of calculations of ionic lattice energies using the experimental (X-ray diffraction) pseudoatom static charge densities, and the crystal chemistry consideration of these rock-salt crystals, favors the insufficiency of this condition in the case of secondary interatomic interactions. In general, this situation in which a bond critical point arises between two ions displaying a secondary interaction, while a chemical bond itself is absent, seems to be quite possible for crystals formed from ions with noticeably different sizes.

Introduction

Bader's quantum-topological theory of atoms in molecules[1] suggests a powerful approach for chemical bond analysis in a system. The definition and classification of the chemical bond in topological analysis are based on the existence of a saddle point, a (3,−1) critical point (CP), of the total electron density, ρ, between neighboring atoms and on the properties of charge density at this point.[1] This point, at which $\nabla\rho$ vanishes, is characterized by the one positive curvature, λ_3, along the internuclear line and two negative curvatures, λ_1 and λ_2, in the perpendicular directions. Initially the topological approach was mainly applied to analysis of the theoretical molecular charge densities. The field of its application to the experimental (X-ray diffraction) crystal charge densities is rapidly developing now.[2] Recent theoretical[3,4] and experimental[4] (see also Figure 8 in ref 2) studies of the LiF crystal and experimental study[4] of the NaF crystal revealed the existence of a (3,−1) CP of the static charge densities between two neighboring fluoride ions in the (100) planes of these rock-salt crystals. This point appeared well-defined in the case of the LiF crystal ($\lambda_1 \approx \lambda_2 = -0.2$ e A^{-5}; $\lambda_3 = 1.4$ e A^{-5}), though poorly defined for the NaF crystal ($\lambda_1 = -0.07$ e A^{-5}, $\lambda_2 = -0.02$ e A^{-5}; $\lambda_3 = 0.48$ e A^{-5}). According to Bader's topological theory of atoms in molecules,[1] occurrence of the (3,−1) critical point between any atoms in a system under equilibrium is necessary and sufficient for the chemical bonding between these atoms, and this point in this case is referred to as a bond critical point (BCP). That is why a conclusion was made[3] about a specific type of secondary bonding interaction between neighboring F ions in the LiF crystal, though no interpretation of the nature of this bonding interaction was presented. However, it seems that the latter should be a subject of special interest. An interpretation of the nature of the secondary interaction and of the corresponding CPs in these ionic crystals based on the lattice energy studies using the experimental (X-ray diffraction) pseudoatom static charge densities and on the crystal chemistry consideration is presented in this work.

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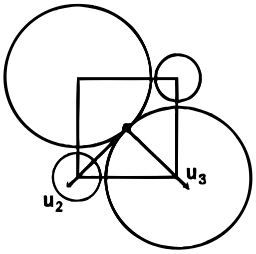

Figure 1. Scheme of the close packing of "large" anions and "small" cations in the (100) plane of the rock-salt structure. The (3,−1) critical point at the center of plane is indicated by a dot. $\mathbf{u}_2$ and $\mathbf{u}_3$ are the principle vectors of the Hessian of the charge density at the (3,−1) critical point.

Results and Discussion

In the previous studies the experimental charge densities of the LiF[4] and NaF[5] crystals were approximated by the flexible κ-model,[6] describing the pseudoatom static charge densities in the form:

$$\rho_i = \rho_{core} + P_{val}\kappa^3\rho_{val} \tag{1}$$

Here ρ_{core} and ρ_{val} are spherically-averaged Hartree−Fock core and valence charge densities of the free ions, except for the ρ_{val} of cations where free atom Hartree−Fock densities were used; κ is dimensionless expansion/contraction parameter, which can be refined in the fitting procedure along with the population P_{val}. The κ-refinement revealed valence populations of fluoride ions in the LiF and NaF crystals to be respectively 7.93(4)[4] and 7.95(1)[5] e. The independent κ-refinement of the LiF diffraction data within the Hansen and Coppens multipole model,[7] using only free atom Hartree−Fock core and valence densities and introducing second valence monopoles on the F pseudoatoms, resulted in the quite similar valence population of the fluorine atom of 7.97(10) e. These results can be interpreted as ionic charges in the both crystals being fairly close to the formal values ±1 e. Moreover, the experimentally determined F ionic charges are in good agreement with those calculated for the LiF molecule (q = 0.938 e) using Bader's theoretically well founded partitioning approach.[1] This allows us to base our further considerations on the point that predominantly ionic interaction takes place in these crystals making an $F^- - F^-$ bonding pair interaction improbable.

From the structural point of view, appearance of the (3,−1) CP at the $^1/_4$,$^1/_4$,0 positions in the LiF and NaF rock-salt crystals could be accounted for by the peculiarities of the close packing of ions in the crystal lattices: "small" cations are placed in octahedral holes between "large" anions that "touch" each other (Figure 1).[2,4,8] In this case, the maximum of charge density at the point $^1/_4$,$^1/_4$,0 is observed both in the direction perpendicular to the (100) plane and along the cation−cation line, yielding correspondingly two negative curvatures λ_1 and λ_2. These two negative curvatures and one positive curvature, λ_3, along the anion−anion line define a saddle point, a (3,−1) CP, at the $^1/_4$,$^1/_4$,0 position. It is quite evident that the the (3,−1) CP between neighboring fluoride ions is more stable (more negative value[4] of λ_2) in the LiF crystal, where Li ion (r_{Li+} = 0.90 Å [9]) is considerably smaller than F ion (r_{F-} = 1.19 Å [9]), than in the NaF crystal. In the latter crystal the size of the Na ion (r_{Na+} = 1.16 Å [9]) is quite close to that of fluoride ion yielding almost flat charge density distribution along Na−Na line[4] (λ_2 = −0.02 e/Å^5).

Thus, we do have an interaction line—a line through the charge density distribution linking nuclei along which ρ is maximum with respect to any other line—between neighboring fluoride ions in both LiF and NaF crystals. We also have an equilibrium state in these crystals. In molecules at equilibrium geometry such an accumulation of charge in the area between a pair of atoms is necessary and sufficient for achieving a balance of forces at the nuclei and the minimum energy, and thus for the bonding interaction between these atoms.[1] In this case the corresponding interaction line is called a bond path. However, in a crystal the situation seems to be more complicated, and the equilibrium is not described by interaction (or charge accumulation) between only a certain pair of atoms, but the whole infinite crystal should be taken into consideration. The minimum of crystal energy is achieved through the competing contributions of both different stabilizing attractive and destabilizing repulsive interactions between different atoms in the crystal. Moreover, due to the point symmetry of the atomic positions, the balance of forces on nuclei (though not necessarily thermodynamic stability) in these ionic crystals could be achieved with any charge density distribution, even with the simple point-charge model. In this sense the existence of only nonbonding repulsive interactions between neighboring fluoride ions in these crystals under equilibrium seems not *a priori* meaningless. An adequacy of this crystal model could be tested by a calculation of the ionic lattice energy using real charge density distribution.

The crystal lattice energy, U, of an ionic crystal can be treated by the sum of the following dominant contributions:[10]

(1) Coulombic (electrostatic) long-range attractive and repulsive energies (Madelung energy), V_{tot}—net attractive effect;

(2) Additional non-Coulombic short-range repulsive energy that results from the overlapping of the closed shells of the neighboring atoms (Pauli exclusion)—repulsive effect.

It was shown previously[5] that the equilibrium crystal lattice energy in the NaF crystal can be well described within the pseudoatom static charge density model by taking into account for the F−F interaction only a nonbonding repulsive (both Coulombic and non-Coulombic) contribution. Similar calculations were performed for the κ-model of the LiF crystal[4] (see Appendix). The resulting value of U = −998.87 kJ/mol is in satisfactory agreement with the both experimental[11] (U = −1036 kJ/mol) and Hartree−Fock[12] (U = −1026.34 kJ/mol) results. The agreement can be noticeably improved by changing the valence density population parameters by one esd, yielding more complete charge transfer between ions. This results in the calculated value of the lattice energy U = −1029.19 kJ/mol. The gain in the total lattice energy of the LiF crystal due to the short cation−anion bond length exceeds the energy loss due to the corresponding cation−cation and anion−anion distance shortening. This yields the stable LiF crystal structure, where the primary Li−F interaction is stabilized by the almost complete valence charge transfer from Li to F (V_{LiF} = −605.49 kJ/mol), while the secondary Li−Li and F−F interactions themselves are destabilizing (V_{LiLi} = 423.76 kJ/mol; V_{FF} = 411.84 kJ/mol).

It should be noted that, in agreement with the general considerations, the decrease of the lattice parameter a in the LiF crystal relative to that in the NaF crystal results in the increase of both short-range non-Coulombic repulsive energy and long-range attractive Coulombic energy, V_{tot}. The latter effect is dominant yielding a noticeable increase in magnitude of the LiF negative lattice energy, U, in comparison with that of the NaF crystal.[5]

Thus, as could be expected the experimental pseudoatom crystal models of the LiF and NaF crystals, which take into account only repulsive interactions between fluoride ions, result in stable crystal lattices with equilibrium lattice energies quite

TABLE 1: Dependence of the Properties of the Critical Point of the Static Charge Density at the $^1/_4,^1/_4,0$ Position of the Li^+F^- Ionic Procrystal on the Variation of the Unit Cell Parameter[a]

unit cell parameter, Å	ρ_c, e/Å^3	$\nabla^2\rho_c$, e/Å^5	λ_1, e/Å^5	λ_2, e/Å^5	λ_3, e/Å^5
3.000	0.413	6.530	-1.47	-1.06	9.05
4.024	0.078	1.008	-0.20	-0.20	1.40
5.000	0.020	0.211	-0.04	-0.04	0.29
6.000	0.005	0.050	-0.01	-0.01	0.07
7.000	0.002	0.014	0.00	0.00	0.02

[a] The unit cell parameter in the real crystal[4] is 4.024 Å.

close to the experimental values. Moreover, the value of the disagreement between calculated and experimental lattice energies of the LiF crystal, even if fully accounted for by an unknown specific bonding interaction between neighboring fluoride ions, cannot counterbalance the strong pairwise F−F electrostatic repulsive interaction and, thus, cannot lead to the formation of a chemical bond between these ions (contrary to an earlier prediction[3] based upon the presence of the BCP between these ions).

The above considerations and results obtained favor the conclusion that appearance of the (3,−1) CP between neighboring fluoride ions in the LiF and NaF crystals should not be considered as a sign of the bonding interaction between these ions but rather as a result of the peculiarity of the closed pack structure geometry, when even repulsion (contraction[13]) of the ionic charge densities cannot result in the transformation of the (3,−1) CP into that of the (3,+1) type (minimum of charge density in the (100) plane). Such a situation does not seem possible in a molecule, where interatomic repulsion would lead to an atomic configuration with the maximum possible separation between corresponding atoms and, as a result, to absence of the BCP between them. The structurally driven stability of the (3,−1) CP in the position $^1/_4,^1/_4,0$ in the LiF crystal can be demonstrated by the example of the ionic procrystal (a hypothetical crystal constructed from the free spherical ions placed at the same sites as atoms in the real crystal) with the varying lattice parameter a (Table 1). This CP displays a positive value of $\nabla^2\rho$ and is observed until transformation of the saddle point into a flat area between the atoms ($\lambda_1 = \lambda_2 \approx 0$). The observed difference between λ_1 and λ_2 curvatures in case of $a = 3$ Å (Table 1) reflects the beginning of a noticeable influence of the Li pseudoatom charge densities on the topological properties at this point.

Conclusion

The present study brings up the question, is the existence of the BCP between *atoms in crystal* really a *sufficient condition for the bonding interaction between these particular atoms?* A similar question was brought up previously[4,8] on the basis of the existence of the (3,−1) CPs in the procrystals, which according to definition do not display any interatomic interactions at all. However, the ionic procrystal charge densities, though being very close to those in the real ionic crystals, are not true equilibrium densities, and thus, strictly speaking these (3,−1) CPs are not true BCPs, as initially defined.[1] From this point of view the basis for both bringing up and answering this question is more rigorous in the present work, where the real crystal charge densities are considered. Results of the calculations of ionic lattice energies, using the experimental pseudoatom static charge densities, presented in this and previous[5] work, and the crystal chemistry consideration of these rock-salt crystals, favors a negative answer to this question in the case of a secondary interatomic interactions. Recently published theoretical observations of the BCPs between neighboring I^- ions in the rock-salt LiI crystal,[14] and between neighboring cations in position A ($CsSrF_3$ and $CsBaF_3$) and neighboring anions (e.g., $KMgF_3$, $LiZnCl_3$, $CsBeI_3$, $LiBeI_3$) in the ionic cubic alkali perovskites ABX_3,[15] seem to provide additional examples of repulsive secondary interaction in crystals, displaying BCPs. In general, this situation when a BCP is present between two ions displaying secondary interactions, while a chemical bond itself is absent, seems to be quite possible for crystals formed from the ions with noticeably different sizes. However for the final answer on the question under consideration further detailed quantum-mechanical studies of the periodic systems seem to be needed.

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Appendix

The calculation of the electrostatic contribution, V_{tot}, to the lattice energy was performed in the following way. The energies of the electrostatic interaction, V, of both the Li and F pseudoatoms with their neighbors within the unit cell parameter, a, separation were found by summarizing corresponding pair contributions V_{AB}[5]

$$V_{AB} = V_{zz} - Z_A\Phi^B(A) - Z_B\Phi^A(B) + V_{ee} \qquad (A1)$$

where $V_{zz} = Z_A Z_B / \mid \mathbf{R}_A - \mathbf{R}_B \mid$ is the Coulombic repulsion energy between nuclear charges Z_i of the pseudoatoms A and B, $\Phi^i(j) = \int \rho^i(\mathbf{r}) / \mid \mathbf{R}_j - \mathbf{r} \mid d\mathbf{r}$ is the potential at the nuclear position (point $\mathbf{R}_j$) of the pseudoatom j due to the charge distribution $\rho^i(\mathbf{r})$ of the pseudoatom i, and V_{ee} is the Coulombic repulsion energy between the pseudoatom electronic charge densities centered at the two nuclei. The electrostatic potentials $\Phi^i(j)$ were evaluated using the MOLPROP program.[16] The V_{ee} energies were presented in form[17,5]

$$V_{ee} = 2/\pi \int_0^\infty f_A(s)\, f_B(s)\, j_0(sR)\, ds \qquad (A2)$$

where $f_i(s)$ is the scattering factor of the spherical density $\rho^i(r)$, $s = 4\pi \sin\theta/\lambda$ is the magnitude of the scattering vector, R is the internuclear distance, and $j_0(sR)$ is the spherical Bessel function of zero order. The integration of (A2) was performed numerically by the Gaussian quadrature method, using Clementi−Roetti wave functions[18] for structure factor calculations.

Beyond the unit cell parameter separation the difference between pseudoatom electrostatic interaction and the point-charge model is negligible (≤0.03 kJ/mol). Hence, the Coulombic interaction of the both Li and F pseudoatoms with the rest of the crystal (beyond the a separation) was taken into account as: $\Delta V = -\mu q^2/r_0 - V_0$. Here the first term is the Madelung energy of the rock-salt lattice of the point charges $\pm q$, $\mu = 1.747\,565$ is the corresponding Madelung constant, $r_0 = a/2$, and V_0 is the energy of the electrostatic interaction of the point charge q with the neighboring point charges within the unit cell parameter separation in the rock-salt lattice. The total electrostatic interaction in the crystal was calculated from

$$V_{tot} = N_A\,[{}^1/_2(V_{Li} + V_F) + \Delta V] \qquad (A3)$$

where N_A is Avogadro's number. V_{tot} can be expressed[5] in terms of the effective Madelung constant, $V_{\mathrm{tot}} = -N_{\mathrm{A}}\,\mu^{\mathrm{eff}}\,q^2/r_0$, and a lattice energy U can be evaluated within the standard scheme[10] assuming the Born[19] short-range repulsive energy model:

$$U = -N_{\mathrm{A}}\mu^{\mathrm{eff}}q^2/r_0(1 - 1/n) \qquad \text{(A4)}$$

Here $n = (18Br_0^4/\mu^{\mathrm{eff}}q^2) + 1$, where $B = 76.9$ GPa is the experimental[20] bulk modulus of the LiF crystal. Finally the value of U obtained according to (A4) was corrected due to the incomplete charge transfer by adding the term[5] $-(1 - |q|)(I_{\mathrm{Li}} + A_{\mathrm{F}})$. Here I_{Li} and A_{F} are the ionization potential and electron affinity for Li and F, respectively.[11]

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