

UDC 535.37

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**COPPER IMPURITY IN LiF AND NaF CRYSTALS FROM *ab initio* CALCULATION: STRUCTURE AND OPTICAL PROPERTIES<sup>1</sup>**

In this paper we present the results of *ab initio* DFT calculations of  $3d^{10} \rightarrow 3d^9 4s$  and  $3d^{10} \rightarrow 3d^9 4p$  transitions of  $Cu^+$  ion embedded in LiF and NaF matrix. The calculations have been made with lattice polarization and by taking deformation into account.

**Keywords:** copper impurity, alkali halides, embedded cluster calculation.

**1. Introduction**

Alkali halide crystals doped with copper ions have been studied for more than 30 years. In connection with these extensive studies a large experimental data on the optical properties of  $Cu^+$  ions in various matrix were observed. The study of monovalent copper ions in crystals LiF attract the most interest connecting with the creation of thermoluminescent detectors based on LiF: Mg,Cu,P. It is assumed that the storage of energy in the detectors associated with radiation conversion of magnesium centers, as in the case of crystals LiF:Mg,Ti (DTG-4) [1]. The role of the copper ions in the thermoluminescence is still not clear. In papers [2, 3] the results of the LiF: $Cu^+$  crystals optical properties were presented, but *ab initio* theoretical study of the electronic and spatial structure of the copper ion in lithium fluoride crystal was not carried out.

Structure and optical properties of  $Cu^+$  ions are well known for a number of alkali halide crystals (NaF: $Cu^+$  [4], NaCl: $Cu^+$  [5], LiCl: $Cu^+$  [6], etc.). Copper ion replaces lattice cation, and off-center configuration was observed in most matrix when the  $Cu^+$  ion displaced from the position of the substituted cation along the [111] axis. However, for such crystals as LiCl, NaF, NaCl and KF off-center configuration was not observed. Optical absorption of  $Cu^+$  ion in the ultraviolet region (4–4,5 eV in most alkali halide crystals) is due to partly forbidden transitions between the ground  $3d^{10}$  and  $3d^9 4s$  excited states. Octahedral crystal field split 3d state into triply degenerate components  $t_{2g}$  and doubly degenerate components  $e_g$ , so two main bands are observed in the absorption spectra of NaF: $Cu^+$  crystal. The strong temperature dependence of all these bands is apparent, indicating the vibronic nature of the transition moment [12].

In this paper we present the results of *ab initio* DFT calculations of lattice relaxation and the energies of the  $3d \rightarrow 4s$  and  $3d \rightarrow 4p$  absorptions of  $Cu^+$  ion embedded in LiF and NaF crystals.

**2. Calculation details**

The density functional theory (DFT) calculations were performed using embedded QM (quantum mechanical) cluster method implemented in GUESS computer code [7]. This method allows accurate quantum chemical calculations within a small cluster containing the defect and its immediate surroundings.

This QM cluster is surrounded by a large number of atoms that classically described by the model of pair potentials. The classical and QM cluster atoms are allowed to shift in the lattice relaxation process, which is due to deformation and polarization of the lattice by the presence defect. For the classical region we have the pair potentials parameters in buckingham form for LiF and NaF crystals from [8] and slightly adjust them so that the elastic and dielectric constants are agree well with the experimental data (Table 1, 2).

Table 1

**Parameters of pair potentials for LiF**

	$A, eV$	$\rho, \text{Å}$	$C, eV \cdot \text{Å}^6$
Classical region			
Li – Li	266	0,1364	4,1
Li – F	588	0,2614	0
F – F	611	0,2753	4,1
Interface region			
$Li_{face} - Li_{QM}$	266	0,1364	4,1
$Li_{face} - F_{QM}$	200	0,2614	0
Shell parameters	$Y,  e $	$k, eV \cdot \text{Å}^{-2}$	
F	-1,93	55,69	

<sup>1</sup> This work was partially supported by Federal Target Program “Scientific and scientific-pedagogical personnel of innovative Russia” in 2009–2013.

Table 2

## Parameters of pair potentials for NaF

	$A$ , eV	$\rho$ , Å	$C$ , eV·Å <sup>6</sup>
Classical region			
Na – Na	2602	0,1031	4,61
Na – F	1145	0,2741	2,91
F – F	301	0,1213	1,31
Interface region			
Na <sub>face</sub> – Na <sub>QM</sub>	400	0,1031	4,61
Na <sub>face</sub> – F <sub>QM</sub>	150	0,2741	2,91
Shell parameters			
F	$Y,  e $	$k, \text{eV} \cdot \text{Å}^{-2}$	
	-1,34	38,83	

$A$ ,  $\rho$ ,  $C$  – parameters of Buckingham potential  $U(r) = A \exp(-r/\rho) - C/r^6$ ;  $Y$  – shell charge;  $k$  – spring constant.

The quantum and classical area were surrounded by several thousands of point fixed charges for correct Madelung potential in the system. GUESS program does not calculate the electronic structure of QM cluster, but calls another quantum-chemical program (in this case, the Gaussian 03 [9]), and adds classic terms to find the total energy of the system. The embedded cluster calculation method applicability for defects in ionic crystals are described in [10, 11] in more details.

We used 6–31G\* basis set on fluorine, lithium and sodium ions. We replaced all cations in the radius of 6 Å around QM cluster with interface ions, which had LANL1 ECP (Hay-Wadt large core pseudopotential) and no basis functions.

For DFT calculations we used the modified B3LYP functional (40 % of Hartree-Fock and 60 % of DFT exchanges), which showed most adequate electron state localization and was successfully used for DFT calculations of defects in fluoride crystals [10, 11].

### 3. Results and discussion

Calculations have been performed in a cluster containing 12 lithium or sodium ions and 14 fluorine ions, the copper ion was placed in the central position –  $[\text{Me}_{12}\text{F}_{14}\text{Cu}^+]^{-1}$  (Fig. 1). The main problem for quantum chemical calculations was the problem of the copper ion basis choice. Today there are many all-electron basis sets; however, it was necessary to choose the one that would be good to describe the electronic structure of the ground state. Therefore a series of calculations have been done for NaF:Cu<sup>+</sup> crystal. These methodological calculations are due to well investigation of NaF:Cu<sup>+</sup> absorption spectrum [12, 13]. The calculations were done for the all-electron basis set 6–31G, its modification m6-31G, all-electron basis set DZVP2, as well as the SDD basis set with ECP.

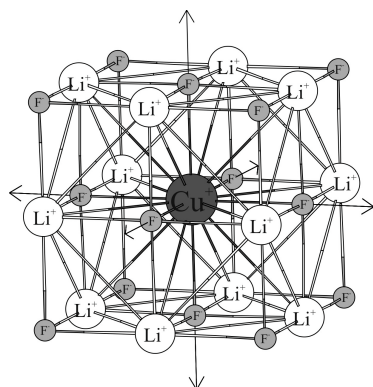


Fig. 1. Cluster  $[\text{Li}_{12}\text{F}_{14}\text{Cu}^+]$ . Arrows indicate the displacements of ions during geometry optimization run.

the relaxation process from the shifting position along different directions (100, 110 and 111). Table 3 shows very small displacements of sodium and fluorine ions for all used basis sets. This fact is due to similar ionic radii of Na<sup>+</sup> and Cu<sup>+</sup> ions (0,92 and 0,98 Å, respectively). Relaxation energy (the difference between the total energy of the relaxed and nonrelaxed defect) also proved to be quite small. Note that the results of our calculations are not agree with the results of [14, 15] where the displacement of the nearest ions was about 0,1 Å.

As was mentioned above, the crystal field splits the 3d<sup>10</sup> (<sup>1</sup>A<sub>1g</sub>) ground state in double degenerate e<sub>g</sub> and triply degenerate t<sub>2g</sub> levels. 3d<sup>9</sup>4s excited state of the ion Cu<sup>+</sup> consists of two singlet and two triplet terms, relevant e<sub>g</sub> and t<sub>2g</sub> states: <sup>1</sup>E<sub>g</sub>, <sup>3</sup>E<sub>g</sub>, <sup>1</sup>T<sub>2g</sub>, <sup>3</sup>T<sub>2g</sub>. Thus the singlet-singlet and singlet-triplet transitions observed in the absorption spectrum, the experimental energies are given in [13]. The calculated energies of 3d<sup>10</sup> → 3d<sup>9</sup>4s and 3d<sup>10</sup> → 3d<sup>9</sup>4p transitions are overestimated by 0,3 eV relative to the experimental data. The Table 3 shows that the more accurate values of 3d<sup>10</sup> → 3d<sup>9</sup>4s transitions are observed in the calculations

with SDD basis set. The energy of the crystal field splitting (10 Dq) and the energies of  $3d^{10} \rightarrow 3d^9 4p$  transitions are in better agreement with the using of m6-31G basis set.

The results of calculations for the crystal LiF:Cu<sup>+</sup> are presented in Table 4. Calculations was performed for different bases as well as in the case of the NaF:Cu<sup>+</sup> crystal. Energy relaxation and displacement of fluoride ions during the lattice relaxation were quite significant because of the greater ionic radius of Cu<sup>+</sup> (0,98 Å) compared with the Li<sup>+</sup> ion (0,68 Å). Directions of the displacements are shown in Fig. 1. The table shows also that the transitions energy and crystal field splitting for LiF:Cu<sup>+</sup> crystal are much larger than that calculated for NaF:Cu<sup>+</sup>, which is also associated with a large lattice distortion.

Table 3

**Results of ground state calculation and transition energies for NaF:Cu<sup>+</sup> crystal**

Basis	exp. [13]	6-31G	m6-31G	DZVP2	SDD	
Relaxation energy, eV	–	0,023	0,005	0,009	0,005	
Max. displacement of F ions, Å	–	0,017	0,004	0,019	0,004	
Max. displacement of Na ions, Å	–	0,025	0,012	0,004	0,011	
Energy of $3d^{10} \rightarrow 3d^9 4s$ transitions, eV	$^1A_{1g} \rightarrow ^3E_g$	3,80	2,35	4,04	3,99	3,87
	$^1A_{1g} \rightarrow ^1E_g$	4,07	2,71	4,43	4,41	4,31
	$^1A_{1g} \rightarrow ^3T_{2g}$	4,16	2,58	4,38	4,32	4,17
	$^1A_{1g} \rightarrow ^1T_{2g}$	4,47	2,94	4,78	4,74	4,62
Crystal field splitting (10 Dq), eV	0,40	0,23	0,35	0,33	0,31	
Energy of $3d^{10} \rightarrow 3d^9 4p$ transitions, eV	7,37	5,83	7,63	7,77	7,71	

Table 4

**Results of ground state calculation and transition energies for LiF:Cu<sup>+</sup> crystal**

Basis	6-31G	m6-31G	DZVP2	SDD	
Relaxation energy, eV	0,74	0,58	0,75	0,63	
Max. displacement of F ions, Å	0,158	0,142	0,164	0,147	
Max. displacement of Na ions, Å	0,029	0,037	0,045	0,037	
Energy of $3d^{10} \rightarrow 3d^9 4s$ transitions, eV	$^1A_{1g} \rightarrow ^3E_g$	3,34	4,96	4,71	4,68
	$^1A_{1g} \rightarrow ^1E_g$	3,68	5,32	5,10	5,11
	$^1A_{1g} \rightarrow ^3T_{2g}$	3,75	5,51	5,21	5,16
	$^1A_{1g} \rightarrow ^1T_{2g}$	4,09	5,88	5,62	5,61
Crystal field splitting (10 Dq), eV	0,41	0,56	0,52	0,50	
Energy of $3d^{10} \rightarrow 3d^9 4p$ transitions, eV	5,25	6,88	6,85	6,11	

Thus, for LiF:Cu<sup>+</sup> crystal one should expect two intense bands near 5,11 and 5,61 eV associated with the singlet-singlet  $3d^{10} \rightarrow 3d^9 4s$  transitions. However, these values can be corrected on ~ 0,3 eV (this over-estimation was observed for NaF:Cu<sup>+</sup> crystal), therefore one assume to appearance of two bands in the absorption spectrum in the region of ~ 4,8 and ~ 5,3 eV.

## REFERENCES

1. Radzhabov E. A. and Nepomnyashchikh A. I., Phys. Stat. Sol. A, **68**, 77 (1981).
2. Nepomnyashchikh A. I., Shalaev A. A., Subanakov A. K., et al., IOP Conference Series: Materials Science and Engineering, 15, 012043 (2010).
3. Nepomnyashchikh A. I., Shalaev A. A., Subanakov A. K., et al., Opt. Spectros., 111, 411 (2011).
4. McClure D. S. and Weaver S. C., J. Phys. Chem. Solids, 52, 81 (1991).
5. Pedrini C. and Jacquier B., J. Phys C: Solid State Phys., 13, 9925 (1980).
6. Simonetti J. and McClure D. S., Phys. Rev. B., 169, 471 (1977).
7. Sushko P. V., Shluger A. L., and Catlow C. R. A., Surf. Sci., 450, 153 (2000).

8. Stoneham A.M., Hand book of interatomic potentials – AERE Harwell (1981).
9. Frisch M.J., Trucks G.W., Schlegel H.B. et al., Gaussian 03 (Revision E.1). – Gaussian Inc., Pittsburgh PA (2007).
10. Mysovsky A.S., Sushko P.V., Radzhabov E.A., et al., Phys. Rev. B, 84, 064133 (2011).
11. Myasnikova A.S., Radzhabov E.A., and Mysovsky A.S., IEEE Trans. Nucl. Sci., 57, 1193 (2010).
12. Goldberg A.B. and McClure D.S., Chem. Phys. Lett., 87, 508 (1982).
13. Berg J.M. and McClure D.S., J. Chem. Phys., 90, 3915 (1989).
14. Luana V. and Florez M., J. Chem. Phys., 97, 6544 (1992).
15. Luana V. and Florez M., Pueyo L., J. Chem. Phys., 99, 7970 (1993).

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Article submitted October 18, 2012.

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