Structure and optical properties of copper impurity in LiF and NaF crystals from *ab initio* calculations

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ABSTRACT

This letter reports the results of *ab initio* calculations of absorption spectra of Cu^+ ion embedded in LiF and NaF matrices. The calculations have been performed in embedded cluster approach at hybrid density functional theory (DFT) level. We propose the model of oscillator strength and absorption intensity calculations for forbidden $3d^{10} \rightarrow 3d^9 4s$ transitions based on the linear dependence between transitions dipole matrix elements and copper ion displacements. For LiF:Cu^+ crystal one should expect two bands in absorption spectra at 5.32 and 5.88 eV with different intensity ratios: the low energy band is more intense than the high energy band.

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1. Introduction

The optical properties and electronic structure of monovalent copper ions have been well investigated for a variety of crystalline matrices. In the most of alkaline halide crystals impurity copper ion is known to substitute lattice cation with the formation of the off-center configuration [1]. This leads to intensive $3d^{10} \rightarrow 3d^9 4s$ transition bands in the spectra of optical absorption (OA) as the displacement of copper ion from the cation site makes these forbidden transitions allowed. In such crystals as LiCl, NaF, NaCl and KF, where the ground state of Cu^+ ion is the on-center configuration, the $3d^{10} \rightarrow 3d^9 4s$ optical absorption bands are still observable because they are allowed vibronically. This can be seen, particularly, from the strong temperature dependence of the absorption spectra [2].

Among the well-investigated crystalline matrices there is, however, one important exception. The monovalent copper ion is very difficult to introduce into monocrystalline LiF matrix without changing its charge state, hence, almost no data are available on LiF:Cu^+. In Refs. [3–5] the experimental data on the LiF:Cu^+ crystals optical properties have been reported, but their interpretation is complicated by the lack of knowledge of how the LiF:Cu^+ optical absorption spectra should look like and by inevitable presence of oxygen and hydroxyl impurity centers. Therefore, *ab initio*

calculations of LiF:Cu^+ crystals OA are needed for unambiguous interpretation of the experimental data.

The first quantum-chemical calculation of spatial structure and optical properties of Cu^+ ion in NaF host has been performed by Winter et al. [6] in Hartree–Fock approach using the cluster containing 33 ions. These calculations were reexamined by Meng et al. [7] and corrected for correlation using many-body perturbation theory. The energies of $3d^{10} \rightarrow 3d^9 4s$ transitions for NaF:Cu^+ crystal were also estimated in Refs. [8,9] within the self-interaction corrected local-spin-density approximation and multiple-scattering Xα approach, respectively. The transition energies calculated in all mentioned works agree well with the experimental data, but the predicted value of nearest neighbors relaxation toward Cu^+ ion varied from negligible in Refs. [6,7] to 0.2 Å in Ref. [9]. The distances between the nearest neighbors and the impurity as well as vibration modes were defined more accurately by Luaña et al. [10–12] within *ab initio* perturbed ion (aiPI) method. The oscillator strength of Cu^+ of $3d^{10} \rightarrow 3d^9 4s$ transitions was recently estimated by Uhl et al. for NaF [13] and NaCl [14] hosts. The calculations of LiF:Cu^+ optical properties are to be found only in the Ref. [15] and were performed with plane-wave DFT method.

It is important for the interpretation of the experimental optical absorption spectra of LiF:Cu^+ crystals to know not only the integral intensity and approximate position of the absorption bands but the shape of these bands as well. We have developed a semi-numerical model for the evaluation of OA bands shape of vibronically allowed transition at different temperatures. This model is based on essentially the same assumptions as that of Refs. [13,14] and provides the same temperature dependence of OA bands integral intensity.

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However, it allows us also to calculate the OA cross-section as a function of absorption energy.

In this letter we report the results of an *ab initio* density functional theory (DFT) calculations of the 3d → 4s and 3d → 4p absorption of Cu⁺ ion embedded in LiF, and, for the purpose of comparison with existing data and establishing the validity of calculation technique, also in NaF crystals. The calculations were performed with an embedded cluster approach with the lattice relaxation and polarization taken into account. We report the calculated absorption spectra based on the simple model of the vibronically allowed transition intensity calculation.

2. Calculation details

2.1. Embedded cluster approach

The DFT calculations were performed using embedded QM (quantum mechanical) cluster method implemented in the GUESS computer code [16]. This method allows a combination of accurate quantum chemical calculations within a small defect-containing cluster and its nearest neighborhood with a classical description of the rest of crystal at the molecular mechanics level.

The QM cluster is surrounded by a large number (about 700 in this work) of atoms described classically with the shell model and pair potentials. About 70 cations between classical region and QM cluster were replaced with the interface atoms. The atoms of interface region connect the QM cluster with the rest of crystal and interact quantum mechanically with the QM cluster and classically with the classical region. All atoms of the classical, interface and QM regions are allowed to relax during the geometry optimization, thus simulating the deformation and polarization of the crystal lattice by the presence of the defect. For the classical region we have used the pair potentials parameters in the Buckingham form for LiF and NaF crystals from Ref. [17] and adjusted them so that they are compatible with the GUESS code. The interface atoms have specially selected ECPs and pair potentials to minimize the distortion of electronic and spatial structure at the QM cluster edge.

The classical region, in turn, is surrounded by several thousands of fixed point charges to mimic the correct Madelung potential of the crystal. The GUESS code is not capable of calculating the electronic structure of QM cluster, but calls another quantum-chemical program (in this case, the GAUSSIAN 03 [18]), and adds classical terms to find the total energy of the system. The applicability of the embedded cluster calculation method for defects in ionic crystals is described in more detail in Refs. [19,20].

Calculations have been performed for a cluster containing 12 lithium or sodium ions (Me) and 14 fluorine ions; the copper ion was placed in the central position instead of alkali ion – [Me₁₂F₁₄Cu⁺]⁻¹ (Figure 1). The 6–31G* basis sets on fluorine, lithium and sodium ions, and m6-31G [21] basis set on copper ion were used. All cations in 6 Å vicinity of QM cluster were replaced by the interface ions, which had LANL1 ECP (Hay–Wadt large core pseudopotential) and no basis functions.

The basis set dependence of the results was checked for NaF:Cu⁺, with Sapporo-TZP-2012 and Sapporo-DKH3-TZP-2012 [22] bases on the copper ion and 6–31⁺⁺G** basis on fluorine ions. Improving the basis set for the copper ion does not significantly change either the both excitation energies or the transition dipole moments (Table 1). However, adding diffuse orbitals to the neighboring fluorine ions leads to the optical absorption energies overestimated by more than 1 eV, while without them the overestimation is about 0.4 eV. This is because in ionic crystals diffuse orbitals on the anions make a negligible contribution to the occupied states, but may possibly contribute to spurious virtual molecular orbitals,
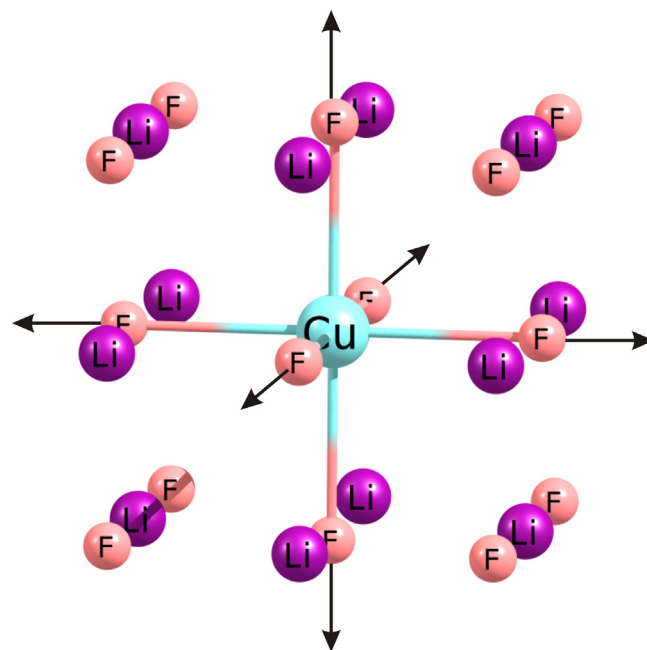

Figure 1. Cluster [Li₁₂F₁₄Cu⁺]. Arrows indicate the displacements of ions during geometry optimization run.

thus reducing the accuracy of the excited state representation and slowing down SCF convergence.

For the DFT calculations we used the modified B3LYP functional containing 40% of Hartree–Fock and 60% of DFT exchange energies, which showed the most adequate electron state localization and was successfully employed for DFT calculations of defects in fluoride crystals [19,20]. Optical energies and dipole matrix elements of transitions were calculated with the time dependent DFT (TDDFT) method.

2.2. Absorption intensity model for forbidden 3d¹⁰ → 3d⁹4s transitions

At the equilibrium geometry (copper ion is centered in the cation site) the 3d¹⁰ → 3d⁹4s transitions are forbidden. However, when thermal vibrations of the Cu⁺ ion are considered, these transitions are allowed. Therefore non-zero dipole matrix elements are observed if the copper ion position is shifted from its central site (Figure 2). The transition dipole moments demonstrate an approximately linear dependence on the Cu⁺ ion displacement up to ∼0.2–0.3 Å (*i.e.* in the region where Cu⁺ ion vibrations take place). Hence, a simple model is proposed for the absorption intensity and its temperature dependence. The basic assumptions for this model are described below.

In the Born–Oppenheimer approximation the wave functions of the initial and final states can be written as

$$\psi_{i,f}(r, R) = \Phi_{i,f}(r, R)\chi_{i,f}(R),$$

where r stands for electronic and R for the nuclear coordinates. For the electronic part of transition dipole moment the following approximation can be made:

$$\mathbf{d}_{if}(R) = \left\langle \Phi_i \middle| \mathbf{d} \middle| \Phi_f \right\rangle \approx \boldsymbol{\alpha}\mathbf{x} \tag{1}$$

Here $\mathbf{x}$ is the copper ion displacement from its central position (Figure 2) and the proportionality coefficient $\boldsymbol{\alpha}$ is, in general, a tensor. Then we can find the transition dipole moment between the initial and final states with vibrational quantum numbers n_i and n_f

Table 1
Basis set dependence of transition energies and dipole moments at different Cu^+ ion positions in NaF crystal.

Basis	Displacement of Cu^+ ion from central site on ⟨1 0 0⟩ axis (Å)					
	0		0.1		0.2	
	Energy (eV)	D	Energy (eV)	D	Energy (eV)	D
m6-31G	4.49	0	4.51	0.0079	4.53	0.0152
	4.89	0	4.90	0.0086	4.91	0.0175
Sapporo TZP 2012 [15]	4.58	0	4.59	0.0074	4.60	0.0139
	4.96	0	4.96	0.0089	4.96	0.0178
Sapporo DKH3 TZP 2012 [15] + diffuse functions on F ions	4.84	0	4.84	0.0017	4.85	0.0024
	5.21	0	5.21	0.0085	5.21	0.0162

The table presents values of energy and transition dipole moment (D) only for excited states 2 and 3 corresponding to $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1T_g$ transitions, respectively.
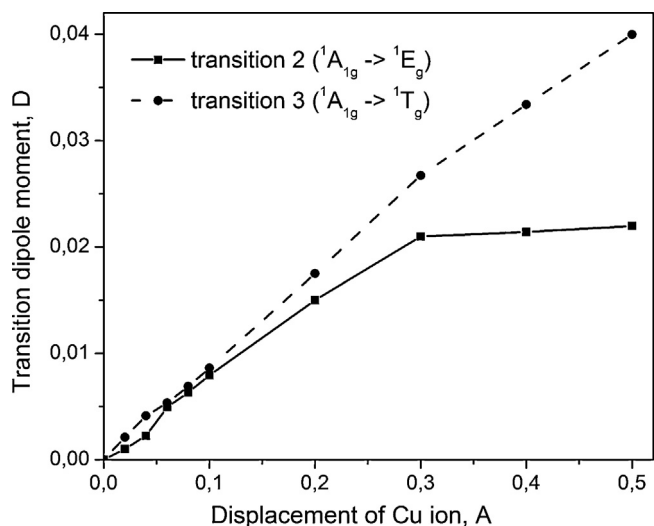

Figure 2. The transition dipole matrix elements dependence on the Cu^+ ion displacement.

$$\langle \Psi_i | d | \Psi_f \rangle \approx \alpha \langle n_i | x | n'_f \rangle$$

$$= \sqrt{\frac{\hbar}{2m\omega_0}} \alpha \left(\sqrt{n_i+1} \langle n_i + 1 | n'_f \rangle + \sqrt{n_i} \langle n_i - 1 | n'_f \rangle \right)$$

The nontrivial part of this formulation arises from the fact that vibrations in the initial and final electronic states have different frequencies and consequently the Frank–Condon approximation is inapplicable. In these cases the harmonic Hamiltonians are:

$$H_0 = \frac{p^2}{2m} + \frac{m\omega_0^2 x^2}{2} = \hbar\omega_0 \left(a^+ a + \frac{1}{2} \right),$$

$$H_1 = \frac{p^2}{2m} + \frac{m\omega_1^2 x^2}{2} = \hbar\omega_1 \left(b^+ b + \frac{1}{2} \right)$$

where ω_0 and ω_1 are the vibration frequencies in the initial and final electronic states and the annihilation and creation operators b, b^+ are linearly connected to a, a^+:

$$b = \frac{1}{2\lambda} [(\lambda^2 + 1)a + (\lambda^2 - 1)a^+]$$

The λ and μ are the parameters defined by the ratio of vibration frequencies:

$$\lambda^2 = \frac{\omega_1}{\omega_0}, \quad \mu = \frac{\omega_1 - \omega_0}{2(\omega_1 + \omega_0)} \quad (2)$$

Then we can find the connection between the ground states of two oscillators: $|0'\rangle = \sqrt{\frac{2\lambda}{\lambda^2+1}} \exp(-\mu a^{+2})|0\rangle$ and all overlap matrix elements between the vibrational states can be numerically calculated via the relations:

$$\langle 0'|2k\rangle = (-2\mu)^k \sqrt{\frac{2\lambda}{\lambda^2+1} \frac{(2k-1)!!}{(2k)!!}}, \quad \langle 0'|2k+1\rangle = 0 \quad (3)$$
$$2\lambda\langle n'|m\rangle = (\lambda^2-1)\sqrt{m+1}\langle n-1'|m+1\rangle + (\lambda^2+1)\sqrt{m}\langle n-1'|m-1\rangle$$

The absorption intensity at the frequency ω (more precisely, the absorption cross-section for single Cu^+ ion) can be calculated using the formula:

$$\sigma(\omega) = \frac{2\pi^2\hbar\omega\varepsilon}{m\omega_0 c} (1 - e^{-(\hbar\omega_0/T)}) \sum_{n,m} e^{-(n\hbar\omega_0/T)} |\langle\Psi_i|d|\Psi_f\rangle|^2$$
$$\times \delta(\omega - \omega_{el} - m\omega_1 + n\omega_0) \quad (4)$$

where the summation goes over all vibrational sublevels of electronic ground and excited states, ε is the high frequency dielectric constant of the crystal and m is the copper ion mass. The parameters ω_0, ω_{el}, λ and μ can be extracted from the calculated terms of ground and excited states. The α parameters can be fitted from the transition dipole moments calculated for a number of different copper ion displacements. For this purpose we selected several points along the ⟨1 0 0⟩ direction to which the copper ion was displaced from a cation position and calculated the ground state geometry and excited states at each of these points. Then, the dependence between the transition dipole matrix elements and copper ion displacements were constructed (see Figure 2) and the α parameters for all five transitions were fitted using Eq. (1).

This method is closely related to the one used by Uhl et al. [13,14]. However, our approach allows for the prediction of the shape of absorption bands, in addition to their integral intensities.

3. Results and discussion

3.1. Ground state calculations

Firstly, we calculated the lattice distortion induced by the presence of a Cu^+ ion within LiF and NaF crystalline matrices. We observed only on-center configurations of the copper ion in our calculations for both crystals; the copper ion returned back to the on-center position during the geometry optimization, if it was shifted in initial geometry along any of directions ⟨1 0 0⟩, ⟨1 1 0⟩ or ⟨1 1 1⟩. Table 2 summarizes the results of the TD DFT and geometry optimization calculations, where the first (R_1), second (R_2) and third (R_3) shell relaxations of Cu^+ neighbors are presented. Our calculation predicts that the nearest neighbors relaxed inwards by 0.075 Å. The shift is due to the smaller ionic radius of copper ion in relation to sodium. Note that the literature gives different

Table 2

Results of ground state calculation and transition energies for NaF:Cu$^+$ and LiF:Cu$^+$ crystals.

Crystal	NaF:Cu$^+$		LiF:Cu$^+$
	Exp. [26]	Calc.	Calc.
R$_1$ (Cu$^+$–F$^-$ distance, first shell) (Å)	–	2.24	2.13
R$_2$ (Cu$^+$–Me$^+$ distance, second shell) (Å)	–	3.13	2.79
R$_3$ (Cu$^+$–F$^-$ distance, third shell) (Å)		3.85	3.39
Energy of 3d^{10}→3d^{9}4s $\quad$ $^1A_{1g} \to {}^1E_g$	4.07	4.49	5.32
transitions (eV) $\quad\quad\quad\quad$ $^1A_{1g} \to {}^1T_g$	4.47	4.89	5.88
Crystal field splitting (10 Dq) (eV)	0.40	0.35	0.56
Energy of 3d^{10}→3d^{9}4p transitions (eV)	7.37	7.63	6.88

Table 3

Calculated parameters for 3d^{10} → 3d^{9}4s transitions of Cu$^+$ ion in NaF host.

Transition[a]	ω_{el} (eV)	λ	α, D (Å)
1	4.49	1.064	0.000
2	4.49	1.126	0.085
3	4.89	1.050	0.088
4	4.89	1.050	0.088
5	4.89	1.063	0.000

[a] The 1 and 2 correspond to $^1A_{1g} \to {}^1E_g$ transitions and numbers 3, 4 and 5 to $^1A_{1g} \to {}^1T_g$ transitions.

Table 4

Calculated parameters for 3d^{10} → 3d^{9}4s transitions of Cu$^+$ ion in LiF host.

Transition[a]	ω_{el} (eV)	λ	α, D (Å)
1	5.33	1.077	0.000
2	5.33	1.097	0.048
3	5.89	1.019	0.009
4	5.89	1.019	0.009
5	5.89	1.053	0.000

[a] The 1 and 2 correspond to $^1A_{1g} \to {}^1E_g$ transitions and numbers 3, 4 and 5 to $^1A_{1g} \to {}^1T_g$ transitions.

values of the ionic radii in the octahedral crystal symmetry: for Li$^+$ ion – from 0.68 to 0.9 Å; for Na$^+$ ion – from 0.98 to 1.16 Å; and for Cu$^+$ ion – from 0.91 to 0.96 Å [24–26]. Thus, we can conclude that the copper ion radius lie between the values for lithium and sodium. The results of the relaxation calculations are in good agreement with the previously reported distances for the first shell around Cu$^+$ (R$_1$) (*e.g.* about 2.20 Å of the values obtained in Ref. [15]).

In the on-center configuration of the Cu$^+$ ion, the octahedral crystal field splits the 3d states into triply degenerate components T_{2g} and doubly degenerated components E_g. The Cu$^+$ ion 3d^{9}4s excited state consists of two singlet and two triplet terms, the E_g and T_{2g} states, respectively: ^1E_g, ^3E_g, $^1T_{2g}$, $^3T_{2g}$. Thus the singlet–singlet and singlet–triplet transitions can be observed in the absorption spectrum [23]. Here we present only the results of singlet–singlet calculations. The calculated energies of the 3d$^{10} \to$ 3d^{9}4s and 3d$^{10} \to$ 3d^{9}4p transitions differ from the experimental data by a 0.4 eV for Cu$^+$ ion embedded in NaF crystal. The overestimation of transition energies for Cu$^+$ ion was observed also for the embedded cluster calculations in different basis sets [13].

The displacements of nearest ions during the lattice relaxation are much larger for the LiF:Cu$^+$ crystal than for NaF:Cu$^+$ because of the greater ionic radius of Cu$^+$ ion compared with that of Li$^+$ ion [24–26]. The displacement of the first shell around the Cu$^+$ ion is 0.11 Å and the directions of the nearest ions relaxation are shown in Figure 1. Note that the results of our calculations for LiF:Cu$^+$ relaxation show a disagreement with the results of Ref. [12], where the distance between Cu$^+$ and the nearest fluorines are predicted as 2.02 Å compared to 2.24 Å.

Table 1 also shows that the transition energies and crystal field splitting for LiF:Cu$^+$ crystal are much larger than those calculated for NaF:Cu$^+$; this is also associated with a large lattice distortion. The value of 3d$^{10} \to$ 3d^{9}4s and 3d$^{10} \to$ 3d^{9}4p calculated energies for Cu$^+$ embedded in LiF are, probably, overestimated by approximately the same value (~0.4 eV) as in an NaF matrix, and one can expect the appearance of two bands in the absorption spectrum of LiF:Cu$^+$ crystal at ~4.9 and ~5.5 eV.

3.2. Absorption spectra calculations

As stated above, the 3d$^{10} \to$ 3d^{9}4s transitions of on-center Cu$^+$ ion are vibronically allowed, and their intensity increases with temperature [2]. A one-dimensional potential energy surface (PES) scan has been performed in the ground and excited states for the copper ion displaced along ⟨1 0 0⟩ crystal axis from its on-center site. From the values of the ground and excited states obtained by this PES scan, we fitted the vibration frequency of the electronic ground state $\omega_0 = 0.0131$ eV = 105.7 cm^{-1} for NaF and $\omega_0 = 0.0155$ eV = 124.8 cm^{-1} for LiF. In addition, we have evaluated the parameters of the 3d$^{10} \to$ 3d^{9}4s transitions using Eqs. (1) and (2) (Tables 3 and 4, where numbers 1 and 2 correspond to transitions from ground to E_g state and numbers 3, 4 and 5 correspond

to T_{2g} state). Numerical calculations of the absorption intensity where performed by substituting these parameters into Eq. (4). It is difficult to calculate the vibration modes accurately using the embedded QM cluster approach. With the GUESS method, geometry optimization can be performed for all atoms in the QM and classical regions, however, calculation of the second derivatives of the total energy is not implemented in this software. Since such a calculation is unlikely to be accurate at interface connecting the QM cluster and the classical region, we have calculated the transition dipole moments for a number of configurations with only the Cu$^+$ ion displaced, and have considered these displacements as the dominant contribution to T_{1u} mode. Ref. [13] reports an equivalent calculation using the vibrational coordinate obtained from a calculation in which the border with the QM cluster was frozen. This also brings some distortion into vibrational modes, reducing the accuracy of the calculation. Moreover, the effect of such distortion is difficult to estimate quantitatively. The large difference in the mass of the Cu$^+$ ion and the lattice ions guarantees that the motion of the Cu$^+$ ion makes the dominant contribution to the T_{1u} mode. On this basis, we assume that our approach and that of Ref. [13] have approximately the same validity.

Figure 3 demonstrates the oscillator strength as a function of temperature. The behavior of the result obtained for NaF:Cu$^+$ is in a good agreement with experiment [27]. Similar results for the temperature dependence were calculated by Uhl et al. [13]. It is evident that the oscillator strength calculated for transitions from ground to E_g excited states for NaF:Cu$^+$ is higher than that for transition to T_{2g} states, as is also observed for the experimental absorption spectra [2].

Figure 4 presents the results of absorption spectra calculations for a copper ion in LiF and NaF matrix. The calculations were performed for three different temperatures. The spectra of NaF:Cu$^+$ crystal agree well with the experimental data of Ref. [2] and show the increase of absorption band intensity with temperature. However, this model does not correctly describe the low-energy shift of the absorption bands, but does qualitatively reproduce the temperature dependence. The absorption spectra of LiF:Cu$^+$ designate two bands of 3d$^{10} \to$ 3d^{9}4s transitions corresponding to crystal field splitting of 3d level. The structure of the spectra differs from that calculated for NaF:Cu$^+$ system: the low energy band is several times more intense than the high energy one.
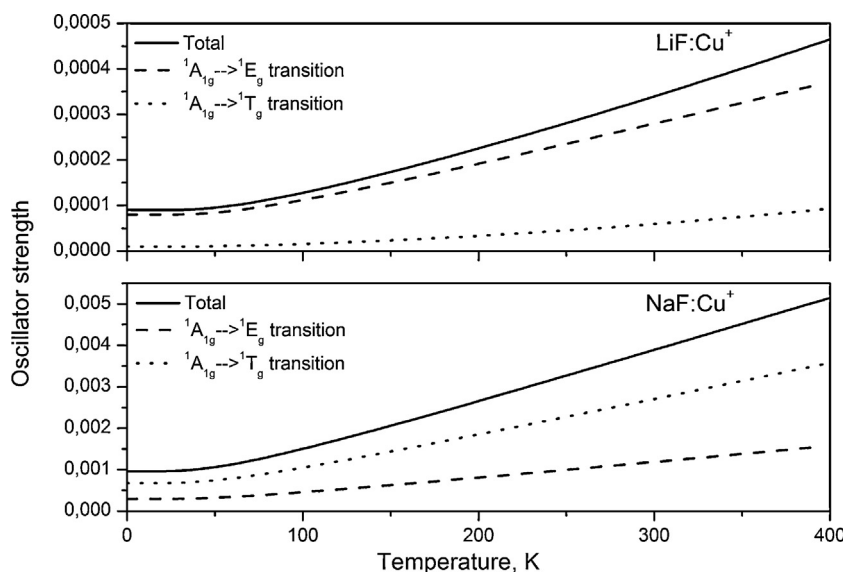
Figure 3. Temperature dependence of oscillator strength for $^1A_{1g} \to {}^1E_g$ and $^1A_{1g} \to {}^1T_g$ transitions obtained for Cu^+ ion in LiF (*up*) and NaF (*down*) host.
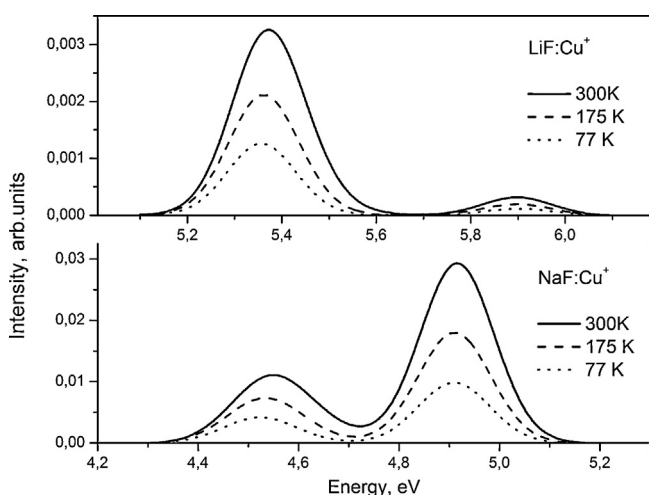

Figure 4. Calculated absorption spectra of LiF:Cu^+ and NaF:Cu^+ crystals.

4. Conclusions

The calculations of $3d^{10} \to 3d^9 4s$ and $3d^{10} \to 3d^9 4p$ optical transitions of the monovalent copper ion in LiF and NaF crystals have been performed with the embedded cluster approach using DFT. In order to correctly calculate optical spectra we propose the model of oscillator strength and absorption intensity calculations for forbidden $3d^{10} \to 3d^9 4s$ transitions based on the linear dependence between transitions dipole matrix elements and copper ion displacements. The dependence of the absorption spectra with temperature was calculated for the first time for an NaF:Cu^+ crystal, and show qualitative agreement with experiment. The calculated transition energies were overestimated by ∼0.4 eV for NaF:Cu^+ system compared to the experimental data.

The $3d^{10} \to 3d^9 4s$ transitions energies were also calculated for the copper ion embedded in LiF crystal, along with the absorption spectra. These contain two bands at 5.32 and 5.88 eV with different intensity ratios: the low energy band is several times more intense than the high-energy band. Hence, taking into account the overestimation value of about 0.4 eV, the absorption bands of LiF:Cu^+ might be expected to appear at 4.9 and 5.5 eV with the low energy band

being more intense. Their thermal behavior should also be similar to that of NaF:Cu^+.

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