**Ab initio**, crystal field and experimental spectroscopic studies of pure and Ni\(^{2+}\)-doped KZnF\(_3\) crystals

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**HIGHLIGHTS**

- Detailed ab initio calculations of physical properties of pure and Ni\(^{2+}\)-doped KZnF\(_3\) were performed.
- Microscopic crystal field effects on the Ni\(^{2+}\) 3d states were studied.
- Crystal field calculations of the Ni\(^{2+}\) energy levels in KZnF\(_3\) were presented.

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**ABSTRACT**

Pure and Ni\(^{2+}\) doped KZnF\(_3\) single crystals were studied using the combination of the DFT-based ab initio methods, crystal field theory and experimental spectroscopic techniques. The electronic, optical and elastic properties have been calculated and compared with available experimental data and good agreement was achieved. Elastic anisotropy of pure KZnF\(_3\) was modeled; calculations of the sound velocity, Debye temperature, Grüneisen parameter and specific heat capacity were performed. Comparison of the calculated results for the pure and doped material, which is reported for the first time for the considered material, enabled to identify the changes in the optical and electronic properties, which are due to the introduced nickel impurity ions. In particular, it was shown that the lowest Ni 3d states appear in the host’s band gap at about 1.0 eV above the valence band. The changes of the electron density distribution after doping were also shown. Microscopic analysis of the crystal field effects based on the performed ab initio calculations of the Ni\(^{2+}\) density of states at different external pressures enabled to estimate the constants of the electron–vibrational interaction, Huang-Rhys factor, Stokes shift and local bulk modulus around impurity ions. The crystal field calculations of the Ni\(^{2+}\) energy levels were performed to analyze and assign the experimental absorption spectrum. Such a combination of the ab initio and semi-empirical calculating techniques leads to a complementary picture of the physical properties of KZnF\(_3\):Ni\(^{2+}\) and can be applied to other doped crystals.

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1. Introduction

The halogen-based cubic perovskite crystals ABX\(_3\) (where A and B are the mono- and divalent cations, respectively, and X is a monovalent halogen anion) are a subject of numerous theoretical and experimental studies due to combination of their relatively simple crystal structure, easiness of preparations and doping with different impurity ions and variety of other electrical, optical, magnetic etc properties. The typical representatives of this group of compounds are the potassium zinc fluoride KZnF\(_3\) and potassium magnesium fluorides KMgF\(_3\). So far, their properties have been studied mainly with respect to the spectroscopic characteristics of various impurity ions embedded into this host, with the transition metal and rare earth ions being the most frequently used impurities. Thus, the following impurities and phenomena in doped KZnF\(_3\) have been studied: interaction of the Cu\(^{2+}\)–Mn\(^{2+}\) pairs [1], spectra of V\(^{2+}\) [2], Co\(^{2+}\) and Cr\(^{3+}\) and laser action of these ions [3,4], the Jahn-Teller effect for Fe\(^{2+}\) ion [5] and Cr\(^{3+}\) ions [6], Co\(^{2+}\) excited state absorption [7] and Co\(^{2+}\) energy level calculations [8], absorption and emission spectra of Ni\(^{2+}\) [9], Mn\(^{2+}\) [10], Cu\(^{2+}\) [11], Nd\(^{3+}\) [12], Dy\(^{3+}\) [13], Yb\(^{3+}\) [14], Eu\(^{2+}\) and Ce\(^{3+}\) ions [15], the pressure induced energy levels crossing for Cr\(^{3+}\) [16], the Cr\(^{3+}\) spectra and energy levels [17], interaction of Cr\(^{3+}\) ions with vacancies [18], ab initio studies of V\(^{2+}\) [19] and Cr\(^{3+}\) energy levels using the potential embedded method [20]. The spectra of divalent europium ions in a similar KMgF\(_3\) structure were also reported [21]. All those...
impurities substitute for divalent Zn or Mg ions and occupy the 6-fold coordinated position. By choosing divalent dopants with ionic radius close to that one of the substituting ions it may be possible to minimize the lattice deformations, thus creating impurity centers with perfect (or nearly perfect) $O_h$ symmetry.

The studies of the neat KZnF$_3$ compound are not as numerous. The heat capacity and lattice dynamics of neat KZnF$_3$ were reported [22]. Early non-empirical calculations of structural characteristics [23] should be also mentioned. Recently, an experimental study of the undoped material absorption was published [24]. Finally, the structural, electronic and optical properties of KZnF$_3$ were studied recently [25] using the full potential linear augmented plane wave approach as implemented in the widely used Wien2K code.

In the present work we report the results of the combination of the \textit{ab initio} and crystal field calculations for the pure and Ni$^{2+}$-doped KZnF$_3$ crystals (supported by the experimental spectroscopic measurements) with the main aim of studying a wide range of the structural, electronic, optical, elastic and thermodynamic properties of these systems. Comparison of the obtained results for the undoped and doped host allows to follow the changes in the electronic and optical properties induced by the introduced impurity. Besides, the energetic position of the Ni 3d states in the host subcon is needed to offer further insights. We note that this is the first estimation of this kind for the studied system. In addition to the \textit{ab initio} studies, the crystal field theory was employed to analyze the splitting of the Ni$^{2+}$ terms in crystal field. As a new result obtained from the performed \textit{ab initio} analysis, we report the pressure and distance dependences of the crystal field strength 10Dq and estimations of the Huang-Rhys factor and Stokes shift for KZnF$_3$:Ni$^{2+}$. Calculations of the crystal field parameters and diagonalization of the crystal field Hamiltonian resulted in getting the complete energy level scheme of the Ni$^{2+}$ in KZnF$_3$, which was compared to the experimental absorption spectrum. We believe that such an application of two different approaches—the density functional theory (DFT) based \textit{ab initio} methods and semi-empirical crystal field theory—gives an opportunity of drawing a complementary picture of the physical properties of the system under consideration, since the properties, calculations of which are beyond the border of applicability of one method, can be studied by the second one, and vice versa. From this point of view, KZnF$_3$ is an excellent system, since it is a cubic crystal, the charges of Zn and Ni ions are equal, and the nearest environment of an impurity ion forms an ideal octahedron.

In the next sections we describe the structure of KZnF$_3$ and details of calculations, the main results and their relation to the available experimental data and finally the paper is concluded with a short summary.

2. Methods of calculations and crystal structure

The potassium zinc fluoride KZnF$_3$ has a cubic crystal structure, with space group Pm\(3m\) (No. 221), lattice constant 4.0611 Å, and one formula per unit cell [26]. Fig. 1 shows one unit cell of KZnF$_3$: the Zn ions are located at the center of a unit cell and coordinated by six fluorine ions; the K ions are at the corners of a unit cell, and the F ions are placed at the centers of a unit cell faces. The experimentally measured Zn–F and K–F distances are (in Å) 2.03055 and 2.87163, respectively [26].

If KZnF$_3$ is doped with transition metal or rare earth ions, they substitute for the Zn ions, entering the ideal octahedral positions (if the substituting ion is also divalent as Zn$^{2+}$, no charge compensation is needed and the possible lattice deformations are due to the ionic radii mismatch only).

For the performed \textit{ab initio} calculations we have used the CASTEP module [27] of the Materials Studio 5.0 package; both the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof functional [28] or the Ceperley-Alder-Perdew-Zunger parameterization [29,30] in the local density approximation (LDA) were applied to treat the exchange-correlation effects. The ultrasoft pseudopotentials were employed for a description of interaction between the ionic cores and valence electrons. The electronic configurations used for the calculations were 3s$^2$3p$^6$4s$^1$ for K, 3d$^{10}$4s$^2$ for Zn, 2s$^2$2p$^5$ for F, and 3d$^3$ s$^2$ for Ni. The convergence parameters were set as follows: the energy tolerance 10$^{-5}$ eV/atom, the force tolerance 0.03 eV Å$^{-1}$; the stress tolerance 0.05 GPa, and the maximum displacement 10$^{-3}$ Å. The Monkhorst-Pack k-points grid sampling was set as 6×6×6 for pure KZnF$_3$. The plane–waves cut off energy (which determines the number of the plane waves in the basis set) was 330 eV. To model the Ni$^{2+}$ doping, we have considered the 3×3×1 supercell with one Zn ion replaced by one Ni ion. The k-points grid was chosen as 2×2×4 for the structural optimization and as 3×3×6 for the calculations of the electronic and optical properties.

Although the GGA- and LDA-calculated band gaps are usually underestimated due to well-known limitations of the DFT-based methods, the pressure behavior of the calculated band gaps (pressure coefficients), structural and elastic properties of the studied crystals are calculated very well, yielding good agreement with the experimental data, as will be shown below.

3. Results of \textit{ab initio} calculations: pure KZnF$_3$

3.1. Structural, electronic and optical properties

After optimization of the KZnF$_3$ crystal structure at ambient pressure the following lattice constants (in Å) were obtained in the present work: 4.14898 (GGA); 3.9810 (LDA). The difference between these values and experimental data (4.0611 Å [26]) is +2.19% and −1.97%, respectively. The other calculated values reported earlier (all in Å) 3.973 (LDA), 4.129 (GGA) [25] and 3.897 [31] are all close to our results, which confirms validity and reliability of the performed calculations. As a common feature with the previous results, our calculations show the LDA/GGA lattice constants to be a little under-/overestimated, respectively, with respect to the experimental data.
It is also worth noting that—although the crystal structure of KZnF$_3$ is cubic—a recent study of a group of perovskites like KNiF$_3$, KZnF$_3$, and KMnF$_3$ [32] predicted that KMnF$_3$ is unstable against fluorine octahedra tilting, whereas KZnF$_3$ is just at the verge of such an instability, still being able to preserve its cubic structure.

The calculations of the electronic, optical, and elastic properties were performed using the optimized crystal structures. Fig. 2 shows the calculated band structure at the highly symmetric points of the Brillouin zone and along directions between them. It appears that the calculated band gap is 3.644 eV (GGA) and 3.731 eV (LDA), which agrees well with other calculations [25] (3.681 and 3.81 eV, correspondingly). The maximum of the valence band is realized at the R point, whereas the conduction band minimum occurs at the G point. Therefore, the indirect character of the KZnF$_3$ band gap is confirmed. All states of the conduction band exhibit strong dispersion, which would manifest itself in high electrons mobility, especially in the vicinity of the G point—the center of the Brillouin zone. The profile of some energetic states of the valence band, on the contrary, is flat, especially along the R - M direction and in the vicinity of the G point; therefore, the holes mobility in these regions would be low.

Fig. 3, which shows the calculated density of states (DOS) diagrams for pure KZnF$_3$, helps to assign the electronic bands as follows: a wide conduction band (from 3.7 to about 17 eV) consists mainly of the K 4s and Zn 4s states, which are hybridized with the F 2p states. The valence band, stretching from about −6 to 0 eV, is made of the F 2p states and Zn 3d states. It is seen that the F 2p states are localized at the top of the valence band, whereas the Zn 3d states are located closer to its bottom. The K 3s and 3p states are sharply peaked at about −27 eV and −10 eV, respectively. Finally, the F 2s states give rise to the narrow electronic band around −20 eV. There is also a slight difference between the GGA and LDA calculated DOS: the F LDA distribution of the electronic states is shifted a little bit to the lower energies. Besides, the Zn 3d states in the LDA approximation are distributed more "smoothly", producing two almost equivalent maxima in the valence band.

Strongly localized distributions of the potassium electron states and considerable delocalization of the fluorine 2p and zinc 3d states (Fig. 3) can be directly related to the calculated atomic populations and electron density difference in the space between the ions of crystal lattice.

Table 1 collects the calculated atomic populations for KZnF$_3$. It should be pointed out that in principle calculations of the atomic populations are possible, if the linear combination of atomic

![Fig. 2. Calculated band structure of pure KZnF$_3$. The GGA- and LDA-calculated electronic bands are shown by the solid lines and filled circles, respectively. The Fermi level is set as zero. The coordinates of the special points of the Brillouin zone are (in terms of the reciprocal lattice’s unit vectors): X(1/2, 0, 0); R(1/2, 1/2, 1/2); M(1/2, 1/2, 0); G(0,0,0).](image_url)

![Fig. 3. Calculated partial and total density of states (DOS) diagrams for pure KZnF$_3$. From top to bottom: K, Zn, F DOS and total DOS. The GGA and LDA results are shown; the LDA DOS values were multiplied by −1 for clarity.](image_url)

![Fig. 4. Electron density difference distributions in KZnF$_3$. Top: in the plane containing the Zn and F ions; bottom: in the plane containing the K and F ions. See text for more details.](image_url)
orbitals (LCAO) is used for the basis set, whereas CASTEP is the plane-wave based method. The plane wave states are projected onto a localized basis [33], and after that the atomic populations are evaluated. As seen from this table, the effective Mulliken charges [34] of Zn and F are considerably different from those expected from the formal valence based on the chemical formula. Such a circumstance indicates that the covalent interaction between the Zn and F ions is quite significant, when compared to that one between the K and F ions. On the other hand, the calculated charge of potassium is closer to its formal charge +1, which allows to conclude that the K ions are bound to the crystal lattice mostly by the ionic bonds. This conclusion is supported by the results shown in Table 2. Several interesting features of the KZnF3 diatomic molecules are the electron density difference. The top-most picture shows the plane containing the Zn and F ions. Interaction between the Zn and F ions is clearly seen. The bottom figure shows the plane of the K and F ions, with practically absent covalent interaction between the K and F ions (note that the lower limit in the lower figure has been changed a little, in comparison with the upper figure). This has been done on purpose, to make the K ions noticeable, since with identical scales in both figures the K ions were completely indistinguishable. So, the Zn–F bonds are mostly covalent, and the K–F bonds are mainly ionic.

After calculations of the electronic structure, the optical properties can be calculated in CASTEP in a straightforward way. In particular, the imaginary part \( \text{Im}(\epsilon(\omega)) \) of a dielectric function \( \epsilon(\omega) \) (which is proportional to the absorption spectrum of a solid) is calculated by direct numerical evaluations of the matrix elements of the electric dipole operator between the occupied states in the valence band and empty states in the conduction band as follows:

\[
\text{Im}(\epsilon(\omega)) = \frac{2e^2\pi}{\varepsilon_0 c^2} \sum_{k \in \text{c}} |\langle \Psi^e_k | \hat{\mathbf{r}} | \Psi^v_k \rangle|^2 \delta(E^e_k - E^e - E).
\]

where \( \epsilon \) is the polarization vector of the incident electric field, \( \mathbf{r} \) and \( e \) are the electron’s radius-vector and electric charge, respectively, \( \Psi^e_k \), \( \Psi^v_k \) are the wave functions of the conduction and valence bands, respectively, \( E = \hbar \omega_0 \) is the incident photon’s energy, and \( \varepsilon_0 \) is the dielectric permittivity of vacuum. The summation in Eq. (1) is carried out over all states from the occupied and empty bands, with their wave functions obtained in a numerical form after optimization of the crystal structure. It should be kept in mind that Eq. (1) involves certain approximations. For example, the local field effects (influence of the polarizability of a crystal onto the electric field inside the sample) are not accounted for. In addition, the excitonic effects are also not treated by any means. Moreover, an intrinsic error in the matrix elements for optical transitions exists due to the fact that the pseudo-wave functions are used in the calculations, which deviate from the true wave functions in the core region (Ref [27], and references therein).

The real part \( \text{Re}(\epsilon(\omega)) \) of the dielectric function \( \epsilon \), which determines the dispersion properties and refractive index values, is estimated then by using the Kramers–Kronig relation:

\[
\text{Re}(\epsilon(\omega)) = \frac{1 + \epsilon_0}{\pi} \int_0^\infty \frac{\text{Im}(\epsilon(\omega')) \omega'd\omega'}{\omega^2 - \omega'^2}
\]

The calculated dielectric function \( \epsilon \) is shown in Fig. 5. The absorption edge (the rise of the Im(\( \epsilon \))) starts at 4.5 eV, which corresponds to the direct transition between the valence and conduction bands at the \( G \) point. A wide absorption band, which extends up to 20 eV, is due to different combinations of the valence and conduction bands’ states; its width is directly related to the width of the conduction band (Fig. 3). The square root of Re(\( \epsilon \)) is equal to the refractive index \( n \). The literature data for KZnF3 give value of \( n = 1.467 \) at 589 nm (~2.1 eV) [35]. The data from Fig. 5 give the estimation of \( n = 1.41 \) at 2.1 eV, which is in good agreement with the experiment.

3.2. Pressure effects and elastic properties of KZnF3

Pressure is known to be a powerful tool to change the optical properties of a solid. One of the most straightforward ways to study theoretically the pressure effects is to perform the structural optimization, electronic and optical properties calculations at different hydrostatic pressures. Calculations of the optimized crystal structure, electronic and optical properties of pure KZnF3 were performed at several different (increasing) values of the hydrostatic pressure with the above-described calculating settings and convergence parameters. The results obtained for lattice constant, characteristic Zn–F distance and indirect band gap values are all collected in Table 2. Several interesting features of the KZnF3

\[
\begin{array}{cccccc}
\text{Pressure} P, \text{GPa} & \text{GGA} & \text{LDA} & \text{Zn–F, distances (all in Å)} & \text{and indirect band gap } \varepsilon_g \text{ (in eV)} & \text{for different values of hydrostatic pressure in KZnF3. The linear fit equations are also given at the bottom of each column.} \\
\hline
& a & E_g & \text{Zn–F, } d & a & E_g & \text{Zn–F, } d & a & E_g & \text{Zn–F, } d \\
0 & 4.1499 & 3.644 & 2.0749 & 3.9810 & 3.731 & 1.9905 \\
4 & 4.0762 & 3.778 & 2.0381 & 3.9302 & 3.839 & 1.9651 \\
8 & 4.0170 & 3.897 & 2.0085 & 3.8850 & 3.943 & 1.9425 \\
12 & 3.9682 & 3.990 & 1.9841 & 3.8479 & 4.027 & 1.9230 \\
16 & 3.9270 & 4.076 & 1.9635 & 3.8153 & 4.112 & 1.8977 \\
20 & 3.8890 & 4.159 & 1.9445 & 3.7860 & 4.191 & 1.8930 \\
\hline
a = 4.1332 – 0.0128P & E_g = 3.745 + 0.022P & d = 2.06660 – 0.0064P & a = 3.97120 – 0.0097P & E_g = 3.669 + 0.025P & d = 1.98500 – 0.0040P \\
\end{array}
\]
pressure behavior can be deduced from these data, and visual representation of these results helps in uncovering certain systematic variation of the calculated studied material’s structural and electronic characteristics.

Fig. 6 shows the graphical representation of the data from Table 2. The overall trend (shown by different symbols for different characteristic distances) suggests a linear dependence on pressure for all considered parameters, which is indeed confirmed by the linear fits (Table 2). As follows from the absolute values of the pressure coefficients for the lattice constant \( a \) are approximately twice as large as the pressure coefficients for the Zn–F distance (0.0128 Å GPa\(^{-1} \) versus 0.0064 Å GPa\(^{-1} \), GGA results and 0.0097 Å GPa\(^{-1} \) versus 0.0040 Å GPa\(^{-1} \), LDA results). This circumstance indicates that the decrease of the results and 0.0097 Å GPa\(^{-1} \) rather than on account of compressibility decrease of the Zn chemical bonds.

![Graphical representation of the data from Table 2.](image)

The calculated dependences of the band gap and Zn–F distance on pressure can be used also for evaluating the dependence of the charge transfer transitions on the interionic distances. If the charge transfer transition in pure KZnF\(_3\) is understood as excitation of one of the F 2p electrons to the conduction band, then the ratio of the band gap pressure coefficient to the Zn–F bond pressure coefficient is equal to the interionic distance dependence of the charge transfer energy. The blue shift of the charge transfer energy with decreasing Zn–F distance would occur at the rate of \(-3.4\) eV/Å (\(-277\) cm\(^{-1}/pm\)) for the GGA calculations and \(-6.25\) eV/Å (\(-504\) cm\(^{-1}/pm\)) for the LDA calculations. These estimations are well within the range of the typical values of the distance derivatives of the ligand-metal charge transfer transitions (from \(-300\) to \(-900\) cm\(^{-1}/pm\)) reported in Ref. [36].

The monotonic increase of the band gap with pressure (pressure coefficients of 0.022 and 0.025 eV GPa\(^{-1} \) for the GGA and LDA calculations, respectively) means a pressure-induced blue shift of the absorption edge. Such a behavior of the host can turn out to be important for detecting some highly located levels of impurity ions, which can be hidden in the conduction band at the ambient pressure and which then can be detected at the elevated pressure, when the conduction band moves up and, in a certain way, "releases" those levels.

The calculated at different pressures values of the unit cell volume \( V \) can be easily fitted to the Murnaghan equation of state [37]:

\[
\frac{V}{V_0} = \left( 1 + P \frac{B'}{B} \right)^\frac{1}{\gamma},
\]

Fig. 7. Calculated values of the relative volume change of a unit cell (filled symbols) and fits to the Murnaghan equation of state (solid lines) for KZnF\(_3\). Open circles are the experimental values [38].

Table 3

<table>
<thead>
<tr>
<th>( C_{11} )</th>
<th>( C_{12} )</th>
<th>( C_{44} )</th>
<th>( B )</th>
<th>( dB/dP )</th>
<th>( E )</th>
<th>( \nu )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present work</td>
<td>GGA</td>
<td>99.21</td>
<td>38.04</td>
<td>29.05</td>
<td>58.43</td>
<td>6.22</td>
</tr>
<tr>
<td></td>
<td>LDA</td>
<td>160.42</td>
<td>52.75</td>
<td>32.94</td>
<td>88.64</td>
<td>4.43</td>
</tr>
<tr>
<td>Calc. [25]</td>
<td>GGA</td>
<td>111.75</td>
<td>49.76</td>
<td>31.37</td>
<td>70.43</td>
<td>3.66</td>
</tr>
<tr>
<td></td>
<td>LDA</td>
<td>170.72</td>
<td>63.54</td>
<td>45.05</td>
<td>99.27</td>
<td>5.032</td>
</tr>
<tr>
<td>Exp. [29]</td>
<td></td>
<td>77.60</td>
<td>80.27</td>
<td>97.60</td>
<td>97.60</td>
<td>80.27</td>
</tr>
<tr>
<td>Exp. [40]</td>
<td></td>
<td>134.4</td>
<td>52.7</td>
<td>38.3</td>
<td>80.27</td>
<td>97.60</td>
</tr>
<tr>
<td>Exp. [41]</td>
<td></td>
<td>145.4</td>
<td>52.7</td>
<td>39.0</td>
<td>83.6</td>
<td>97.60</td>
</tr>
</tbody>
</table>

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where \( V_0 \) is the volume at the ambient pressure, \( B \) and \( B' = dB/dP \) are the bulk modulus and its pressure derivative, respectively. The results of these calculations are shown in Fig. 7; the calculated values of \( V/V_0 \) excellently follow the fitting lines in both GGA and LDA calculations. The extracted from such a fit values of \( B \) and \( B' \) are given in Table 3; they agree reasonably with other data. In addition, the experimental data corresponding to the given in Table 3; they agree reasonably with other data. In addition, the experimental data corresponding to the given in Table 3; they agree reasonably with other data. In addition, the experimental data corresponding to the given in Table 3; they agree reasonably with other data. In addition, the experimental data corresponding to the given in Table 3; they agree reasonably with other data.

However, although the knowledge of the \( B \) and \( B' \) values is sufficient for an analysis of the hydrostatic pressure effects, the complete description of the elastic properties of a solid implies knowledge of the components of the elastic constants tensor \( C_{ij} \). These calculations are also available in CASTEP. For a cubic crystal, there are three independent \( C_{ij} \) constants: \( C_{11}, C_{12}, C_{44} \), and their linear combination gives the value of the bulk modulus \( B \) as \( B = (C_{11} + 2C_{12})/3 \). The obtained \( C_{ij} \) values are presented in Table 3. As seen from this Table, the LDA results are in somewhat better agreement with the experimental data. Consistency of the performed calculations of the bulk moduli is emphasized by the close values of \( B \) obtained from the “volume—pressure” dependence and from the elastic constants calculations.

We have also calculated the elastic constants \( C_{ij} \) at different pressures, these results are shown in Fig. 8. As seen from the figure, all calculated elastic parameters grow up linearly with pressure, with the following linear approximations (GGA/LDA results): \( C_{11} = 105.48 + 6.82P \) (154.80 + 7.76P); \( C_{12} = 39.12 + 3.34P \) (52.19 + 3.00P); \( C_{44} = 28.64 + 0.16P \) (32.02 + 0.48P); \( B = 61.24 + 3.83P \) (86.39 + 4.59P). In all these equations pressure \( P \) and the corresponding elastic parameters are expressed in GPa.

It can be noted that the pressure coefficients of the bulk moduli obtained from these linear fits are very close to those estimated from the Murnaghan equation of state.

3.3. Elastic anisotropy of KZnF3

The cubic crystals - even in spite of their highly symmetric structural properties - possess, nevertheless, certain elastic anisotropy, which can be visualized by plotting a three-dimensional surface representing dependence of the Young’s modulus \( E \) on a chosen direction in a crystal. For cubic materials, it is described by the following equation [42]:

\[
E(\vec{n}) = \frac{1}{S_{11} - \beta_1 (n_1^2 n_2^2 + n_1^2 n_3^2 + n_2^2 n_3^2)}
\]

where \( \beta_1 = 2S_{11} - 2S_{12} - S_{44} \), and \( n_1, n_2, n_3 \) are the direction cosines, which determine the angles between the \( a, b, c \) axes of a crystal and a given direction. The \( S_{ij} \) values in Eq. (4) are the elastic compliance constants (measured in GPa\(^{-1}\)), which form the matrix inverse to the matrix of elastic constants \( C_{ij} \); their numerical values are given in Table 4. Eq. (4) determines in general a three-dimensional closed surface, and the distance from its center to the surface equals to the Young’s modulus in a given direction, determined by \( n_1, n_2, n_3 \). For an ideal isotropic medium this surface would be a perfect sphere, but, this is often not a case even for cubic crystals [42].

| Table 4 | Calculated elastic compliance constants (all in GPa\(^{-1}\)) for KZnF3. |
|---------|-----------------|-----------------|-----------------|
|         | \( S_{11} \)   | \( S_{12} \)   | \( S_{44} \)   |
| This work, GGA | 0.0128000 | -0.0035474 | 0.0344230 |
| This work, LDA | 0.0074449 | -0.0018421 | 0.0303566 |

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Fig. 9 shows the result of application of Eq. (4) to the considered case of KZnF₃ crystal. The shape of the three-dimensional surface is not spherical, this is also illustrated by its xy (or ab, if the crystallographic axes are used) cross-section. The maximal value of the Young’s modulus (78.13 GPa (GGA) and 134.32 GPa (LDA)) is realized, when the stress is applied along the a,b,c axes, and the minimal value (74.76 GPa (GGA) and 87.93 GPa (LDA)) is achieved with the stress applied along the diagonals in each of the coordinate planes. Such a well-pronounced difference between the maximal and minimal values of the Young’s modulus should be taken into account when performing the experimental measurements of the Young’s modulus with subsequent comparison with other experimental and theoretical data.

3.4. Calculations of the sound velocities, Debye temperature and specific heat capacity for KZnF₃

The calculated values of the elastic constants allow for estimations of the sound velocities in a solid and its Debye temperature θ₀ related to the maximum phonon energy, by using the following equation [43]

\[
\theta_0 = \frac{\hbar}{k} \left( \frac{3n}{N_A} \right)^{1/3} v_{in}.
\]

where \(\hbar\) and \(k\) are the Planck’s and Boltzmann’s constants, respectively, \(N_A\) is the Avogadro’s number, \(\rho\) is the crystal’s density, \(M\) is the molecular weight, \(n\) denotes the number of atoms per one formula unit (5 for KZnF₃), \(v_{in}\) is the mean sound velocity expressed in terms of the longitudinal \(v_t\) and transverse \(v_l\) sound velocities as

\[
v_{in} = \left( \frac{2}{3} \left( \frac{1}{v_l} + 1 \right) \right)^{-1/3}.
\]

The \(v_l\) and \(v_t\) sound velocities are calculated as [44]

\[
v_l = \sqrt{\frac{3B + 4G}{3\rho}}, \quad v_t = \sqrt{\frac{G}{\rho}}
\]

with \(B\) being the bulk modulus and \(G = (G_v + G_R)/2\) the isotropic shear modulus, which is calculated as the average value of the Voigt’s shear modulus \(G_v\) (an upper limit for G values) and the Reuss’s shear modulus \(G_R\) (a lower limit for G values). The analytical expressions for \(G_v\) and \(G_R\) are as follows:

\[
G_v = \frac{C_{11} - C_{12} + 3C_{44}}{5}, \quad \frac{G}{G_R} = \frac{4}{C_{11} - C_{12} + \frac{3}{C_{44}}}
\]

Table 5 below summarizes the results of the sound velocities and Debye temperature calculations (at ambient pressure), performed in the present work, in comparison with the experimental data and other theoretical estimations. The calculated values of the sound velocities and Debye temperatures agree very well with the experimental measurements and other theoretical data.

After the elastic constants and equilibrium volume at different pressures are calculated, one can easily plot dependence of the Debye temperature on both pressure and volume (Fig. 10). The calculated values of the Debye temperature grow up linearly with increased pressure, and decrease with increased volume. The volume (pressure) derivatives of the Debye temperature are \(-6.34 \text{K} \cdot \text{A}^{-3} (3.95 \text{ K GPa}^{-1})\) and \(-10.31 \text{ K} \cdot \text{A}^{-3} (4.56 \text{ K GPa}^{-1})\) for the GGA and LDA calculations, respectively.

With the calculated volume derivatives of the Debye temperature, one can proceed further with estimations of the Grüneisen parameter \(\gamma\), which indicates how the change of the crystal lattice
volume affects the vibrational properties. It can be found by using the following equation:

\[
\frac{d}{d \ln V}\frac{d \ln q}{d \ln V} = \frac{C_0}{V} q D \frac{d q}{d V},
\]

(9)

and the calculated values of \( \gamma \) as a function of the hydrostatic pressure are collected in Table 6. The overall trend for \( \gamma \) is to decrease with increasing pressure. The ambient pressure values 1.179 (GGA) and 1.482 (LDA) are reasonably close to the result of Ref. [45], where the Grüneisen constant for a similar material KMgF3 was estimated to be 1.35.

A deeper look into the thermophysical properties of a solid can be achieved by calculating its specific heat capacity, which in the framework of the Debye model is expressed as [46]

\[
C_p^\text{ph} = \frac{9kN_A}{\omega_D^3} \int_0^{\theta_D} \frac{x^4 \exp(x)}{x(x-1)^2} dx,
\]

(10)

with all quantities already defined previously. In the case of KZnF3 the calculated result from Eq. (10) should be multiplied by 5, since there are five atoms in a formula unit. Fig. 11 shows comparison between the theoretical (this work) and experimental [22] specific heat capacity for KZnF3. Since the temperature range covered in Ref. [22] was only until 300 K, it is not possible to perform comparison of the calculated and measured heat capacity above the room temperature. However, in the whole range from 0 to 300 K agreement between the calculated and experimental heat capacities is very good, which serves as another justification of the performed calculations of the elastic properties of KZnF3.

4. Results of \textit{ab initio} calculations: KZnF3: Ni2+

4.1. Electronic and optical properties

Presence of impurity ions drastically modifies the electronic and optical properties of a crystal, as is illustrated by Fig. 12, which shows the GGA-calculated band structure of KZnF3: Ni2+ (the details of calculations are described in Section 2).

As seen from Fig. 12, the indirect character of the band gap for the KZnF3: Ni2+ system is kept - as for the pure crystal. But an
important different feature is that the host’s band gap contains now
the Ni 3d states. They are mostly flat in the k-space, which indicates
their high degree of localization. The lowest 3d state of the nickel
ions is located at about 1.0 eV above the valence band. The gap
between the highest occupied Ni 3d state and the conduction band
is about 1.4 eV.

The enlarged view of the calculated DOS diagrams (in the band
gap region) for KZnF$_3$:Ni$^{2+}$ is depicted in Fig. 13. The position of
the Ni$^{2+}$ 3d states in the band gap is emphasized. There are two
clearly seen maxima in the 3d states distribution, which can be
unambiguously ascribed to the $t_{2g}$ (the lowest in energy) and $e_g$
(the highest in energy) components of the 3d states split in the
octahedral crystal field. The energy separation between their
maxima can be estimated as the crystal field strength 10$Dq$ [47],
whose value from Fig. 13 turns out to be about 1 eV (or
$\approx$ 8000 cm$^{-1}$), which is reasonably close to the experimentally
deduced from the KZnF$_3$:Ni$^{2+}$ absorption spectrum value of about
7000 cm$^{-1}$ [47].

The electron density difference is also changed upon introduction
of the Ni$^{2+}$ ions into the KZnF$_3$ crystal lattice, as shown in
Fig. 14. The changes occur not only at the crystal lattice sites, where
the Zn and Ni ions are located. The electron density difference on
the fluorine ions is also changed and depends on whether the Zn or
Ni ions are their nearest neighbors. The main reason for that is that
although the Zn and Ni ions have the same formal charge +2, their
calculated Mulliken effective charge are considerably
different: +1.15e for Zn and +0.64e for Ni. The charges of the
fluorine ions close to the Zn ions are −0.63e and those close to the
Ni ions are −0.61e. The decreased electric charges and a smaller
difference between them in the case of the Ni−F pair lead to higher
covalency of the Ni−F bond, if compared to the Zn−F bond. Such
a conclusion is in line with the electronic configurations of these
ions: the completely filled 3$d^8$ shell of Zn ions offers no space
for the fluorine 2p electrons density and thus does not participate
in the bonding. The empty 4s states of Zn are located considerably higher in energy than the fluorine 2p states. In the case of the nickel ions, on the contrary, the unfilled 3$d^8$ electron shell can be actively involved into the Ni−F bonding. Besides, the energy gap between the Ni 3d states and the F 2p states is considerably lower, when compared to the difference between the Zn 4s and F 2p states.

Although the 4s states of the Zn$^{2+}$ ions are located higher in
energy than the 2p states of fluorine, still there is an interaction and
electronic charge from between the F$^-$ and Zn$^{2+}$ ions, as was
indicated by the calculated Mulliken charges.

Finally, in Fig. 15 the ab initio calculated absorption spectra of
both pure and Ni$^{2+}$-doped KZnF$_3$ are shown. Drastic difference
between these two spectra is caused by the Ni$^{2+}$ impurities. Non-
zero absorption in the infrared and visible spectra region, which
is absent in the case of the un-doped host, is due to the transitions
within the states arising from the 3$d^8$ electron configuration of the
Ni$^{2+}$ ion. In addition, the transitions between the F 2p and Ni 3d
states also contribute to the calculated absorption of the KZnF$_3$:Ni$^{2+}$.

A proper analysis of the doped crystal absorption spectra
implies consideration of the impurity ion’s multiplets (energy
levels arising from the Coulomb, spin-orbit, magnetic, many-body
and other interactions between the electrons in the unfilled
electron shell). However, the calculations of the multiplet structure and
crystal field splitting of the multi-electron states with subsequent
detailed analysis and assignment of the observed features in the
absorption spectra are not possible in CASTEP.

The crystal field theory (although it does not belong to the ab
initio methods and operates with some fitting parameters) can be
successfully applied in this case, as shown in Section 5.

4.2. Microscopic crystal field effects in KZnF$_3$:Ni$^{2+}$

Before we proceed with detailed analysis of the experimental
absorption spectra with assignment of the observed absorption

![Fig. 15. Calculated absorption spectrum of KZnF$_3$:Ni$^{2+}$ (solid line) in comparison with the calculated absorption spectrum of KZnF$_3$ (dashed line).](image)

**Fig. 15.** Calculated absorption spectrum of KZnF$_3$:Ni$^{2+}$ (solid line) in comparison with the calculated absorption spectrum of KZnF$_3$ (dashed line).
peaks, we present here some additional results of the performed \textit{ab initio} calculations of the electronic properties for KZnF$_3$:Ni$^{2+}$. Namely, the microscopic crystal field effects (in other words, dependence of the crystal field strength 10Dq on the interionic distance and its manifestation in the optical spectra) have been studied in details.

The theoretical foundation for such a study is as follows. Dependence of the crystal field strength 10Dq on the interionic distance $R$ can be described by the following function:

$$10Dq = \frac{A}{R^3}$$  \hspace{1cm} (11)

where $A$ is a constant, and $n$ should be equal to 5, if the point charge model of crystal field is considered [47]. However, elaborated quantum mechanical calculations [48–57], which take into account various effects left out of consideration in the point charge model (e.g. covalent and exchange interaction, mixture of wave functions of different states, modifications of the electron density of impurity ions and ligands in crystals), show the value of $n$ to be essentially host and impurity ion dependent and varied in a wide range from 3.5 to 7 for different systems. Exact knowledge of the functional dependence described by Eq. (11) is not of only academic interest to check out how significant deviations of the crystal field properties from the point charge model might be in a given doped crystalline material; the values of the $A$ and $n$ constants can be used to estimate essential parameters of an impurity center in a crystalline host, such as the constants of electron–vibrational interaction (EVI), energetic Stokes shifts (differences between the maxima of the first absorption and emission bands), Huang-Rhys factors, compressibility, Grüneisen constants etc. A few useful equations linking the observable spectroscopic characteristics of impurity centers with the 10Dq($R$) dependence are given below.

For example, the EVI constant $V_{ai}g$ of interaction of the impurity ions’ orbital triplet states with the fully-symmetric $a_{1g}$ normal mode of the octahedral complex can be expressed in a way similar to 10Dq [51]

$$V_{ai_{eg}} = -\frac{nA}{\sqrt{6}R^{n+1}}.$$  \hspace{1cm} (12)

with the subsequent estimation of the constant $V_{ei}$ of interaction with the eg normal mode as

$$V_{ei} = \frac{V_{ai_{eg}}}{\sqrt{2}}$$  \hspace{1cm} (13)

One of the most evident experimental observations of EVI is the energetic Stokes shift $E_{S(i)}$ (the difference between the maxima of the lowest absorption and emission bands), if it is caused by the $i$th normal mode, this shift is defined as [52]

$$E_{S(i)} = 2S_i \hbar \omega_i = \frac{V^2}{M \omega_i^2}$$  \hspace{1cm} (14)

where $M$ is the mass of a single ligand, and $S_i$ stands for the non-dimensional Huang-Rhys factor for the $i$th mode with a frequency $\omega_i$ (the vibrational frequencies can be obtained from Raman spectra or analysis of vibronic progressions). It was shown [55] that the total Stokes shift $E_S$ arising from the combined effect of both $a_{1g}$ and $e_g$ modes can be written just as a sum of the individual contributions from each mode:

$$E_S = E_S(a_{1g}) + E_S(e_g)$$  \hspace{1cm} (15)

Since variations of the interionic distances in a solid are directly related to its elastic properties, the 10Dq($R$) dependence can be linked to the local bulk modulus $B$ around an impurity ion by the following equation [56]

$$\left(\frac{\partial 10Dq}{\partial R}\right)_{R=R_0} = -\left(\frac{\partial 10Dq}{\partial P}\right)_{R=R_0} \frac{3B}{R_0^3},$$  \hspace{1cm} (16)

where $R_0$ is the equilibrium interionic distance (usually taken at the ambient pressure), and the derivative $\partial 10Dq/\partial P$ shows how 10Dq depends on variations of pressure.

To apply Eqs. (11)–(16) to KZnF$_3$:Ni$^{2+}$, the following procedure was used: since the Ni$^{2+}$ 3d states DOS diagram clearly exhibits two maxima corresponding to the $e_g$ and $a_{1g}$ states (Fig. 13), the energetic separation between their maxima was assumed to be 10Dq. Then the DOS diagrams were calculated at elevated hydrostatic pressures from 0 to 20 GPa, and every time the 10Dq value was determined from the corresponding DOS plots.

The calculated dependences of the 10Dq on pressure and Ni–F distance are shown in Fig. 16. The pressure dependence is linear, with the pressure coefficients practically equal in both GGA and LDA calculations. The approximating linear functions are $10Dq = (1.0033 \pm 0.0069)P + (0.0187 \pm 0.0006)(\text{GGA})$ and $10Dq = (1.1331 \pm 0.0112)P + (0.0197 \pm 0.0009)(\text{LDA})$. In both given equations the pressure is measured in GPa and the calculated 10Dq value is obtained in eV. A higher value of 10Dq in the LDA calculations is explained by the shorter equilibrium distances in comparison with the GGA results. The distance dependence of 10Dq is presented by the following functions: 10Dq = $47.3798 \pm 4.1280 |R^{5.4020 \pm 0.1295}|$ (GGA) and $10Dq = 67.0790 \pm 9.7924 |R^{6.0160 \pm 0.2270}|$ (LDA), with the distance $R$ being measured in Å and calculated result being the value of 10Dq in eV. The value of $n$ determined from the distance dependences of 10Dq deviates from 5, thus indicating that the point charge

\begin{table}[h]
\centering
\caption{Calculated EVI constants $V_{ai}$, $E_S$ (in 10$^{-9}$ cm$^{-1}$), Huang-Rhys factors $S_{ai}$, $S_i$ (non-dimensional), Stokes shifts $E_S(a_{1g})$, $E_S(e_g)$ and total $E_S$ (all in cm$^{-1}$) for KZnF$_3$:Ni$^{2+}$.}
\begin{tabular}{lllllll}

\hline

$V_{ai}$ & $E_S$ & $S_{ai}$ & $S_i$ & $E_S(a_{1g})$ & $E_S(e_g)$ & $E_S$ \\
\hline

GGA & -1.711 & -1.210 & 0.704 & 0.568 & 639 & 440 & 1139 \\
LDA & -2.206 & -1.560 & 1.169 & 0.944 & 1062 & 731 & 1793 \\
\hline
\end{tabular}
\end{table}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig17.png}
\caption{Comparison between the experimental absorption (solid line) and emission (dashed line) spectra of KZnF$_3$:Ni$^{2+}$. The value of the Stokes’s shift is given in the figure.}
\end{figure}
approximation is too crude for KZnF$_3$:Ni$^{2+}$ and the covalent effects should not be left out of consideration.

The calculated pressure and distance dependences of 100q together with Eq. (16) and calculated Ni–F distances of 2.04605 A/1.977775 A (GGA/LDA) give the following estimations of the local bulk modulus $B$: 95.4 GPa (GGA) and 112.9 GPa (LDA). Although both estimated $B$ values may seem to be somewhat overestimated when compared to the experimental data and other calculated values in Table 3, it should be kept in mind that this is the local bulk modulus around impurity ions, which is not necessarily equal to the bulk modulus of a pure host material.

Finally, Table 7 collects the calculated values of the EVI constants, Huang-Rhys factors and Stokes shifts for KZnF$_3$:Ni$^{2+}$. From these values, one can conclude that the infrared emission peak, corresponding to the $^1T_2g(1S)\rightarrow^3A_2g(1F)$ transition, would occur at about 6200–6700 cm$^{-1}$. Fig. 17 shows the experimental low-temperature emission and absorption spectra of KZnF$_3$:Ni$^{2+}$ plotted in one system of reference for easier comparison. The experimentally measured Stokes shift, which is shown in the figure as the energy separation between the IR emission maximum and the lowest in energy absorption peak, is about 1400 cm$^{-1}$. This experimental value is between the LDA and GGA estimations (Table 7).

5. Samples preparation, experimental spectroscopy and crystal field calculations for KZnF$_3$:Ni$^{2+}$

Prior to the description of the crystal field calculations, a short comment on the samples preparation and spectroscopic measurements is given.

The KZnF$_3$:Ni$^{2+}$ single crystals were grown from the melt in graphite crucibles by the Bridgman–Stockbarger method using KF, NiF$_2$ and ZnF$_2$ as starting materials. The concentration of NiF$_2$ in the melt was 0.1 mol%. The crystals were grown in a furnace atmosphere. The samples grown were of good optical quality and free from NiF$_2$ and ZnF$_2$ as starting materials. The concentration of NiF$_2$ in the melt was monitored by the Bridgman Stockbarger method using KF, NiF$_2$ and ZnF$_2$ as starting materials. The concentration of NiF$_2$ in the melt was 0.1 mol%. The crystals were grown in a furnace atmosphere. The samples grown were of good optical quality and free from NiF$_2$ and ZnF$_2$ as starting materials. The concentration of NiF$_2$ in the melt was monitored by the Bridgman Stockbarger method using KF, NiF$_2$ and ZnF$_2$ as starting materials.

The experimental absorption spectrum of KZnF$_3$:Ni$^{3+}$ shown in Fig. 17 was recorded at 8 K using a spectrophotometer (Cary, Model 14R). This spectrum was analyzed by using the crystal field theory, namely, the exchange charge model (ECM) [58] of crystal field, which allowed for calculations of the Ni$^{2+}$ energy levels and comparison with the experimental spectrum. In the ECM framework the crystal field Hamiltonian of an ion with unsplit 3d electron shell can be written as follows:

$$H = \sum_{p=-2,4}^{p} \sum_{k=-p}^{p} V_{kp}^{k} O_{kp}^{k}. \quad (17)$$

where $O_{kp}^{k}$ are the linear combinations of the spherical operators acting on the angular parts of the impurity ion’s wave functions (exact definition of the operators used in the ECM can be found in Ref. [58]), and $V_{kp}^{k}$ are the crystal field parameters (CFPs), which can be calculated from the crystal structure data. They include all the structural and geometrical information about the host lattice and in particular reflect in a certain sense arrangement of the host lattice ions around the impurity site. The Hamiltonian (Eq. (17)) is defined in the space spanned by all wave functions of the free ion’s LS terms (which arise due to the Coulomb interaction between electrons of an impurity ion). In the ECM, the CFPs are written as a sum of two terms [58]:

$$b_{kp}^{k} = b_{kp,q}^{k} + b_{kp,s}^{k}. \quad (18)$$

where

$$b_{kp,q}^{k} = -K_{kp}^{k} \frac{2}{R_{k}^{p+1}} \sum_{\ell} \frac{V_{kp}^{k}(\ell, q_{\ell})}{R_{k}^{p+1}}. \quad (19)$$

$$b_{kp,s}^{k} = K_{kp}^{k} \frac{2(2p+1)}{5} \sum_{\ell}(G_{p}S(\ell)^{2} + G_{p}S(\ell)^{2} \gamma_{p}G_{p}\pi(\ell)^{2}) \frac{V_{kp}^{k}(\ell, q_{\ell})}{R_{k}}. \quad (20)$$

The $b_{kp,q}^{k}$ term is the point charge contribution to the CFPs, which describes the electrostatic interaction between the central ion and the lattice ions enumerated by index $i$ with charges $q_{i}$ and spherical coordinates $R_{k}, \theta_{k}, \phi_{k}$ (with the reference system centered at the impurity ion itself). The averaged values ($\bar{p}$), where $r$ is the radial coordinate of the $d$ electrons of the optical center, can be obtained either from the literature or calculated numerically, using the radial parts of the corresponding ion’s wave functions. The values of the numerical factors $K_{kp}^{k}, \gamma_{p}$, the expressions for the polynomials $V_{kp}^{k}$ and the definitions of the operators $O_{kp}^{k}$ can all be found in Ref. [58] and thus are not shown here for the sake of brevity. The $b_{kp,s}^{k}$ term is proportional to the overlap between the wave functions of the central ion and ligands and thus includes all covalent effects.

The $S(\ell)$, $S(\ell)$, $S(\ell)$ entries in Eq. (20) correspond to the overlap integrals between the $d$-functions of the central ion and $p$- and $s$-functions of the ligands: $S(d\ell)$ (d$\ell$) (d$\ell$) (d$\ell$) (d$\ell$) (d$\ell$) (d$\ell$) (d$\ell$). The $G_{p}, \gamma_{p}, G_{p}$ entries are dimensionless adjustable parameters of the model, whose values are determined from the positions of the first three absorption bands in the experimental spectrum. They can be approximated to a single value, i.e. $G_{p} = G_{p} = G_{p} = G_{p}$, which can then be estimated from one absorption band only [58], usually the lowest in energy. This $G_{p}$ parameter also effectively takes into account the lattice relaxation processes which take place in a crystal lattice due to the different properties (ionic radii, electronegativities etc) of the substituting and substituted ions.

### Table 8

Crystal field (in Stevens normalization) and Racah parameters $B$, $C$ (in cm$^{-1}$) for Ni$^{2+}$ in KZnF$_3$. $G$ is the dimensionless ECM parameter.

<table>
<thead>
<tr>
<th>$B_{p}$</th>
<th>$B_{ps}$</th>
<th>$B_{p}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_{0}$</td>
<td>350.0</td>
<td>1720.1</td>
</tr>
<tr>
<td>$B_{1}$</td>
<td>1750.0</td>
<td>860.5</td>
</tr>
<tr>
<td>$G$ (ECM parameter)</td>
<td>3.95</td>
<td>3.95</td>
</tr>
<tr>
<td>$B$</td>
<td>880</td>
<td>880</td>
</tr>
<tr>
<td>$C$</td>
<td>3696</td>
<td>3696</td>
</tr>
</tbody>
</table>

### Table 9

Calculated and experimental energy levels (in cm$^{-1}$) of Ni$^{2+}$ in KZnF$_3$.

<table>
<thead>
<tr>
<th>Energy levels (O$_{i}$ group notation and “parent” LS term)</th>
<th>Calculated</th>
<th>Exper. (this work)</th>
<th>Exper. [58]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^1A_2g$ ($^3P$)</td>
<td>7886</td>
<td>7700–8400</td>
<td>A broad band (7000–8000)</td>
</tr>
<tr>
<td>$^3T_2g$ ($^3F$)</td>
<td>11149</td>
<td>~11000–13600</td>
<td>A broad band (12000–14000)</td>
</tr>
<tr>
<td>$^1T_1g$ ($^3F$)</td>
<td>23709</td>
<td>A broad band</td>
<td>A broad band (21700–26000)</td>
</tr>
<tr>
<td>$^1T_2g$ ($^3F$)</td>
<td>25838</td>
<td></td>
<td>A broad band (23000–25000)</td>
</tr>
<tr>
<td>$^1E_2$ ($^3G$)</td>
<td>31624</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^3T_2g$ ($^3G$)</td>
<td>32040</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^1A_1g$ ($^3G$)</td>
<td>56544</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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The ECM has been successfully applied to a number of crystals doped by both rare earth and transition metal ions. Since it explicitly takes into account the overlap effects, which involve the electrons of both impurity ions and ligands, and distinguishes between the overlap integrals of the wave functions with different quantum numbers, this model represents significant improvement and development of the point charge model. Additionally, since the point charge contributions to the crystal field parameters in the ECM framework can be calculated by taking into account as many crystal lattice ions as possible, the ECM is a further development of the superposition model of crystal field as well [58]. Importance of the overlap effects for precise calculations of the crystal field splitting has been emphasized recently [54], by demonstrating that the dominant contribution to the 10Dq value comes from the raise of the transition metal’s e_g orbital due to its effective mixture with the ligands’ s-states. Such a mixture of the 3d states of the transition metal ions with the ligands s- and p-states is also taken into account in the ECM, when calculating the CFPs in Eq. (20).

The crystal structure data [26] were used to calculate the CFPs values for Ni^{2+} in KZnF_3. The overlap integrals between the Ni^{2+} and F^- ions were calculated numerically using the radial wave functions of the nickel and fluorine ions [59]. The ideal octahedral symmetry of the Ni^{2+} position is confirmed by the structure of the crystal field Hamiltonian: only two CFPs are not equal to zero (Table 8): R_0^2 and R_0^4, which are related by the following equation R_0^2 = 5R_0^4 if the Stevens normalization is used. The crystal field Hamiltonian of Ni^{2+} with parameters from Table 8 was diagonalized in the space spanned by 25 wave functions of 5 LS terms (3^F, 3^P, 1^D, 1^G, 1^S) of the 3d^8 configuration. The Racah parameter B, which defines the energy gap between the ground term ^2P and the first excited term ^3P (it equals to 158), was taken as 880 cm^-1. This value is close to that one (990 cm^-1) reported for Ni^{2+} in a similar host KmgF_3 [60]. The second Racah parameter C was determined from the ratio C/B = 4.2, which is typical for the transition metal ions in crystals. The spin-orbit interaction was left out of consideration, since the experimental absorption bands are broad, and no fine structure produced by the spin-orbit splitting can be determined in a reliable and unambiguous way.

Table 9 shows the list of the calculated Ni^{2+} energy levels. All energy levels—even those lying out of the experimentally studied spectral range and located presumably in the conduction band of the host material—are given for the sake of completeness.

Three most noticeable features in the absorption spectrum - at about 7500 cm^-1, 15,000 cm^-1, and 27,000 cm^-1—are assigned as the transitions from the ground ^3A_2g state of Ni^{2+} ions to the ^3T_2g, ^3T_1g(^3F) and ^3T_1g(^3P) states, correspondingly. Comparison of the calculated energy levels (Table 9) with the experimental data (Fig. 18) and results of other measurements [48] shows reasonable agreement between all those data sets.

6. Conclusions

The pure and Ni^{2+}-doped KZnF_3 single crystals were studied in details using the combination of ab initio and crystal field calculations together with the experimental absorption spectra measurements. The plane wave based CASTEP method allowed to investigate the structural, electronic, optical and elastic properties, whereas the crystal field analysis permits to calculate the crystal field parameters and crystal field splitting of the Ni^{2+} LS terms. Using the ab initio calculations, the elastic constants were all calculated; elastic anisotropy of the Young’s modulus was visualized using the three- and two-dimensional plots. The pressure effects were modeled by optimizing the crystal structure and calculating the band gaps at elevated hydrostatic pressures. The pressure coefficients of the band gap and lattice constants were all evaluated. It was shown that the Zn–F bond is more covalent than the K–F one. Estimations of the sound velocities, Grüneisen parameters and specific heat capacity from the obtained values of the elastic constants were performed with very good agreement with the experimental data. Successive ab initio calculations for the neat and doped compound allowed for highlighting the differences in the electronic and optical properties, which are due to incorporation of Ni^{2+} ions. In particular, location of the nickel 3d states in the KZnF_3 band gap was determined from the band structure and density of states calculations. Noticeable changes of the electron density distribution in the space around the Zn and Ni ions were visualized using the contour diagrams.

A new feature of the performed analysis is that the microscopic crystal field effects for KZnF_3:Ni^{2+} have been modeled using the ab initio calculated density of states for the Ni^{2+} at different pressures. The obtained pressure and distance dependences of the Dq parameter have been used to estimate the values of the Huang–Rhys factors and Stokes shifts separately for the a_{1g} and e_g modes of the Ni^{3+} octahedral complex. In addition, the local bulk modulus B around that complex has been also evaluated from the results of ab initio calculations.

The KZnF_3:Ni^{2+} absorption spectrum has been analyzed and assigned using the exchange charge model of crystal field; all Ni^{2+} energy levels in crystal field were calculated and compared to the experimentally observed spectral features.

We believe that such application of different approaches—DFT based ab initio technique and crystal field theory—is useful for getting a deeper insight into the physical properties of doped crystals.

Acknowledgments

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