3d Ions in Solids and Microscopic Crystal Field Effects: Theoretical Analysis and Relations with Experimental Spectroscopic Data

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Abstract. The transition metal ions with unfilled 3d electron shell are important activator ions for solid-state lasing and solid-state lighting. Since their spectroscopic properties depend significantly on the nearest environment, studies of the microscopic crystal field effects (influence of variation of the impurity center geometry) acquire additional importance. In the present paper, methods of calculating the crystal field strength $10Dq$ and its dependence on the interionic distances $R$ are described. Relation between the $10Dq(R)$ functions and experimentally observed quantities such the Stokes shift is highlighted. The results of performed $10Dq(R)$ calculations for several crystals doped with various 3d ions are summarized and discussed.

1. Introduction

It is a well-known fact that the highly degenerated energy levels of free ions with unfilled d- and f-electron shells are split into a number of sublevels, if such ions are placed into crystalline solids. The number of the formed energy levels and their properties are determined by the crystal field created by the crystal lattice ions, whose geometrical arrangement and electrical charges are the most important factors affecting the optical properties of impurity ions [1].

The ions with the unfilled 3d electron shell are excellent probes for the crystal field effects, since their open external 3d shell makes them very sensitive even to small variations of the interionic distances and/or angles between the chemical bonds. In an ideal octahedral crystal field the five-fold degenerated 3d orbitals are split into two sets: three orbitals with the $t_{2g}$ symmetry and two orbitals with the $e_g$ symmetry. The energy interval between them is called the crystal field strength and is denoted by $10Dq$. The value of $10Dq$ increases with shortening interionic separations $R$ and decreases otherwise. The distance dependence of $10Dq$ on $R$ can be written in general as

$$10Dq = \frac{A}{R^n},$$

where $A$ and $n$ are some constants. The value of $n$ if determined from the point charge model (PCM) of crystal field should be 5 [2]. However, numerical estimations of $10Dq$ for real systems with such $n$ value do not yield good agreement with the experimental data because of oversimplified PCM

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assumptions, which completely neglects the quantum nature of the impurity ions and nearest neighbors, overlap of their wave functions etc. Various quantum chemical calculations allow for theoretical estimations of the \( n \) value; it appears to vary in a wide range from 3.5 to 7.3 for various systems [3-7]. It is also possible to estimate the \( n \) value from the experimental measurements of the absorption peaks shifts with pressure [8, 9].

Knowledge of \( n \) gives a deeper insight into the microscopic structure of the impurity ions and relations between the geometry of the impurity center and its energy level scheme. It also allows to estimate the experimentally observed quantities, such as Stokes shift (difference between the maxima of the absorption and emission bands related to the same electronic transition), thus linking together the microscopic crystal field effects with macroscopic characteristics of impurity centers.

In Section 2 the basic theoretical foundations needed for the microscopic crystal field effects studies are described briefly, and a short summary of the calculated results for a number of crystals containing the ions with unfilled 3d shell is given in Section 3. The paper is concluded with a short summary.

2. Calculations of 10\( Dq \) values: theoretical background

If the values of \( A \) and \( n \) in Eq. (1) are known, then it is possible to evaluate the constants of the electron-vibrational interaction with the \( a_{1g} \) and \( e_g \) normal modes of the octahedral complex as follows:

\[
V_{a_{1g}} = - \frac{nA}{\sqrt{6}R^{n+1}}, \quad V_{e_g} = \frac{V_{a_{1g}}}{\sqrt{2}}. \quad (2)
\]

These estimated constants can be used for calculations of the energetical Stokes’ shift \( E_S(i) \), where \( i \) denoted the \( a_{1g} \) and \( e_g \) normal modes:

\[
E_S(i) = 2S_i \hbar \omega_i = \frac{v_i^2}{M\omega_i^2}, \quad (3)
\]

with \( M \) standing for the mass of a single ligand and \( S_i \) being the non-dimensional Huang-Rhys factor for \( i \)th normal mode with the frequency \( \omega_i \). The total Stokes shift, which is a result of interaction with both \( a_{1g} \) and \( e_g \) normal modes can be taken as a simple sum of the Stokes shifts coming from each mode separately [10, 11]. Moreover, if both pressure and distance dependences of 10\( Dq \) are known, it is possible to evaluate the bulk modulus \( B \) of a considered crystal from the following equation:

\[
\left( \frac{\partial 10Dq}{\partial R} \right)_{R=R_0} = - \left( \frac{\partial 10Dq}{\partial P} \right)_{P=P_0} \frac{3B}{R_0}. \quad (4)
\]

It is possible to use the crystal field theory or various ab initio methods for calculations of the 10\( Dq \) values. In the case of the ions with the \( d^1(d^3) \) electronic configurations the 10\( Dq \) value is simply the separation between the \( t_{2g} \) and \( e_g \) states. If the ions with the \( d^2(d^5) \) electronic configurations are considered, 10\( Dq \) equals to the energy interval between the \(^3A_{2g}\) and \(^3T_{2g}\) states originating from the ground \(^3F\) term. If the ions with the \( d^3(d^7) \) electronic configurations are studied, then 10\( Dq \) is the separation between the \(^4A_{2g}\) and \(^4T_{2g}\) states coming from the ground \(^4F\) term [2].

The method of finding the distance dependence of 10\( Dq \) in Eq. (1) can be formulated as follows:

i) The energy levels of an impurity ion in a given crystal are calculated for different interion distance with a small step (it is sufficient to take an equilibrium “impurity ion – ligand distance” \( R_0 \) and consider the interval from 0.9\( R_0 \) to 1.1\( R_0 \) with a step of 0.01\( R_0 \).  

ii) The extracted 10\( Dq \) values are plotted as a function of distance and then are fitted to the power law given by Eq. (1).  

iii) Eqs. (2)-(4) can be used to estimate the Stokes shift and the bulk modulus, which then can be compared with the experimental data (if available) to check the validity of the performed calculations.
3. Results and discussion

The results of calculations of the $10Dq$ dependence on distance for a number of solids doped with the 3d transition metal ions are presented in this section. Different calculating techniques have been employed, e.g. discrete variational multielectron method (DVME) [12], exchange charge model (ECM) of crystal field [13], and plane-wave based CASTEP software [14]. The calculations were performed for varying interionic distances and the obtained $10Dq$ numerical values were approximated to the power laws, like in Eq. (1). The calculated $10Dq(R)$ distances are summarized below in Table 1. In all equations the distance $R$ should be taken in Å, then the $10Dq$ value will be in cm$^{-1}$.

### Table 1. Distance dependence of the $10Dq$ parameter for various solids and impurity ions.

| Crystal and impurity ion | 3d ion electron configuration | Calculated $10Dq(R)$ function, cm$^{-1}$ | Method | Stokes shift, cm$^{-1}$ (calc./exp.) | Reference |
|--------------------------|-------------------------------|-----------------------------------------|--------|--------------------------------------|-----------|
| Al$_2$O$_3$::T$^{3+}$    | $d^1$                         | $861347/R^{4.671}$                     | CASTEP | -                                    | [7]       |
| Rb$_2$CrF$_6$            | $d^2$                         | $706048/R^{5.863}$                     | CASTEP | -                                    | [15]      |
| Cs$_2$NaYF$_6$::Cr$^{3+}$| $d^3$                         | $294650/R^{4.463}$                     | DVME   | 3652/3721                           | [5]       |
| Cs$_2$NaYCl$_6$::Cr$^{3+}$| $d^3$                         | $557820/R^{4.374}$                     | DVME   | 1663/1612                           | [5]       |
| Cs$_2$NaYBr$_6$::Cr$^{3+}$| $d^3$                         | $664190/R^{4.353}$                     | DVME   | 2256/2218                           | [5]       |
| SrTiO$_3$::Cr$^{3+}$     | $d^3$                         | $430120/R^{4.905}$                     | ECM    | 1706/-                              | [6]       |
| SrTiO$_3$::Mn$^{4+}$     | $d^3$                         | $880120/R^{5.799}$                     | ECM    | 3020/-                              | [6]       |
| SrTiO$_3$::Fe$^{5+}$     | $d^3$                         | $1612800/R^{6.550}$                    | ECM    | 4737/-                              | [6]       |
| K(Al(MoO$_4$)$_2$::Cr$^{3+}$| $d^3$                         | $477780/R^{5.623}$                    | ECM    | 3600/2800                           | [16]      |
| MgO::Cr$^{3+}$           | $d^3$                         | $1890500/R^{6.401}$                    | ECM    | 5200/4500                           | [17]      |
| ZnS::V$^{2+}$            | $d^3$                         | $193830/R^{4.421}$                     | ECM    | 667/-                               | [17]      |
| KZnF$_3$::Ni$^{2+}$     | $d^8$                         | $541029/R^{6.016}$                     | CASTEP | 1793/1395                           | [18]      |

Figure 1. Calculated dependences of $10Dq$ on distance for a number of crystals from Table 1.

Figure 1 illustrates the calculated $10Dq(R)$ dependences for some of systems from Table 1. The decreasing trend of the crystal field strength with increasing interionic separation is clearly seen. The calculated $10Dq$ values are shown by symbols, they were approximated by the power law functions, whose equations can be found in Table 1 as well. The vast majority of the considered systems are the Cr$^{3+}$-bearing materials, which is explained by their importance for many applications (such as solid-state lasers, phosphors for the solid-state lighting etc) and availability of the experimental data on the absorption and emission spectra of these crystals.
The data in Table 1 show considerably wide range of the obtained $n$ values, from about 4.3 to about 6.55. The deviation of $n$ from the point charge value of 5 is explained by the influence of covalent effects, overlap of the wave functions of the impurity ions and ligands, formation of the molecular orbitals (rather than pure atomic states) etc. The distance dependence of $10Dq(R)$ appears to be essentially host- and impurity ion-dependent. It can be also seen from Table 1, that the value of $n$ increases with increased charge of an impurity ion. This fact can be attributed to more pronounced variations of the electron density around highly charged ions, since they stronger attract the electron density of the s- and p-states of ligands.

The calculated Stokes shifts in Table 1 agree well with the experimental data. Additionally, using the $10Dq(R)$ dependence for Cs$_2$NaYCl$_6$:Cr$^{3+}$, its compressibility was estimated to be $9.88 \times 10^{-4}$ kbar$^{-1}$, that is very close to the experimental value of $9.70 \times 10^{-4}$ kbar$^{-1}$ [19], which serves as an additional argument confirming validity of the performed analysis of the microscopic field effects.

4. Conclusions

Several examples of calculations of the crystal field strength $10Dq$ for the transition metal ions with the unfilled 3d electron shell are given in the present paper. Importance of knowledge of the $10Dq(R)$ dependence is emphasized by the possibility of extracting the experimentally observed value of the Stokes shift and host’s crystal compressibility. If the experimental and theoretical Stokes shifts are in good agreement, this circumstance can give an opportunity of predicting the Stokes shift for other systems, which may be of high importance for assessing the application perspectives of optical materials.

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