

Supplementary Material to the article

“Fine structure of ${}^3T_1({}^3H) \rightarrow {}^5E({}^5D)$ intracenter transition for Fe^{2+} ions in ZnSe”

The Fe^{2+} ion has a value of d^6 , the level increase is 5D , the first excited one is 3H . The crystal lattice of ZnSe forms a tetrahedral structure in the cubic syngony. Correspondingly, iron impurities are in the tetrahedral electric field of the ZnSe ligand. In this case, the initial levels are split due to the Stark effect. The tetrahedral distortion splits the 5D ground state into two terms 5E and 5T_2 . Excited terms are also affected by fields: ${}^3H \rightarrow {}^3T_1, {}^3E, {}^3T_2$.

A qualitative assessment of the splitting leads to the number and types of terms in the tetrahedral field. The energy values of levels 5E and 5T_2 are expected in the work. Further, for convenience, zero on the scale will correspond to level 5E . In the study of the crystal field of the state of the system about the development of the Hamiltonian:

$$H = H_0 + H_{ee} + H_{cr} + H_{SO1} + H_{SO2},$$

H_0 is the interaction of the impurity ion with the nucleus, H_{ee} – Coulomb interaction of electrons, Electrostatic interaction operator:

$$V_{ee} = e^2 \sum_{i>k} \frac{1}{|r_i - r_k|},$$

e is the electron charge, r is the set of electron coordinates. $H_{cr}(V_C)$ is the interaction of an impurity ion with ions of the crystal lattice. The crystal field potential for a cubic (tetrahedral) environment has the form:

$$H_{cr}(T_d) = a' \sum_i \left(x_i^4 + y_i^4 + z_i^4 - \frac{3}{5} \right),$$

x, y, z are isolated cases of supposed cubic axes, a – parameter, r is the set of electron coordinates. H_{SO1} – spin-orbit interaction of the first order,

$$\hat{H}_{SO} = \xi(r)(\mathbf{l}s),$$

$$\xi(r) = -\frac{e}{2m^2c^2} \frac{1}{r} \frac{\partial V(r)}{\partial r}.$$

$V(r)$ is the potential of the field in which the electron is located, m – electron mass, c – speed of light, r is the set of electron coordinates. H_{SO2} – spin-orbit interaction of the second order. In view of the complexity of the calculations, which relate to the second-order spin-orbit interaction and the smallness of the corresponding energy corrections, only a qualitative one was taken into account in the work of this H_{SO2} : only additional level splittings associated with this correction were analyzed.

When calculating the electrostatic interaction, radial integrals (Slater integrals) are used that describe the interelectronic interaction. A typical form of the radial Slater integral:

$$F^k = (nl, n'l') = e^2 \int \frac{r_{<}^k}{r_{<}^{k+1}} R_{nl}^2(r_1) R_{n'l'}^2(r_2) r_1^2 dr_1 r_2^2 dr_2.$$

R_{nl} is the radial part of the electron wave function in the nl state, n is the main quantum number, l – orbital quantum number, e is the electron charge, $r_{<}$ and $r_{>}$ – the smaller and larger modules of the vectors \mathbf{r}_1 and \mathbf{r}_2 , r is the set of electron coordinates. Many authors leave these radial integrals as the parameters of the theory, which are determined from experiment. Racah introduced new notation for Slater integrals, which are convenient to use as semi-empirical parameters in solving the problem:

$$B = \frac{9F^2 - 5F^4}{441},$$

$$C = \frac{5F^4}{63}.$$

Corrections V_c are found by solving the characteristic equation in perturbation theory, the matrix elements of the determinant are calculated by formulas. According to the crystal field theory, these calculations can be performed with the crystal field splitting parameter Dq (ligand field splitting) for ZnSe, and the Racah parameters B and C (interelectron interaction) for the Fe^{2+} ion. The parameter Dq determines the distance between the lower levels 5E and 5T_2 ($10Dq \sim 3000 \text{ cm}^{-1}$) and therefore is uniquely determined from the experimental data. The parameters B and C for the free Fe^{2+} ion are given in reference books: $B_0 = 917 \text{ cm}^{-1}$, $C_0 = 4040 \text{ cm}^{-1}$. The experimental data obtained by us made it possible to refine the values of the parameters B and C for the Fe^{2+} ion embedded in the ZnSe lattice. Figure 1 shows the range of allowable values of parameters B and C for our problem, which give an energy shift between ${}^5E({}^5D)$ and ${}^3T_1({}^3H) \sim 1.383 \text{ eV}$. As can be seen, the range of suitable pairs of values is: $B = 2550\text{--}2800 \text{ cm}^{-1}$, $C = 590\text{--}783 \text{ cm}^{-1}$. These values were chosen in accordance with the rule (regularity) of the ratio $C/B = 4\text{--}4.5$. In addition, for ions of the iron group, a more significant decrease in the B parameter is expected than in the C parameter with respect to the values for the free ion. Therefore, $B = 600 \text{ cm}^{-1} (\pm 15)$ and $C = 2733 \text{ cm}^{-1} (+18)$ can be chosen as the most optimal parameters.

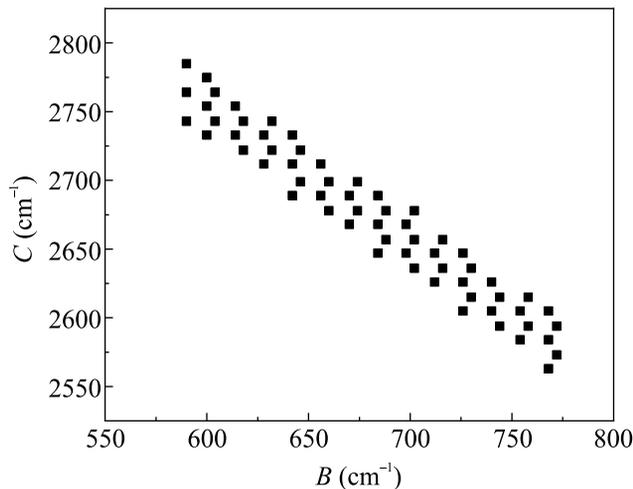


Fig. S1. Range of values of parameters B and C , at which the desired value of 1.383 eV is obtained for the 3T_1 level

The corrections taking into account the spin-orbit interaction of the first order (1st SO) were calculated according to the work, the value of the spin-orbit interaction constant $\lambda = -100 \text{ cm}^{-1}$. The results are shown in Table 1 of the article. In the first order, the term 5E does not change. The 3T_1 term is split into three levels, which give corrections to the energy values: -2λ , $-\lambda$, $+2\lambda$.

Table 1. Energy values for split levels with allowance for the first-order spin-orbit interaction.

Energy (eV)	Position relative to 3T_1 (eV)
1 st SO	
1.4081665	+0.025
1.3957685	+0.012
1.3709725	-0.012

The two upper terms lie much higher in energy than the fine structure lines observed by us in low-temperature luminescence spectra. Thus, only the lower sublevel corresponding to the splitting of 3T_1 by the spin-orbit interaction of the 1st order should be taken into account. The second-order spin-orbit interaction further splits this sublevel into two components, the energy shift between which is on the order of several meV. We considered two given sublevels corresponding to the irreducible representations Γ_3 and Γ_5 when identifying the fine structure of zero-phonon transitions (Fig. 5 of the manuscript).

The corrections associated with H_{SO1} and H_{SO2} for the 5E and 5T_2 levels were calculated by many authors. Since the considered transitions occur from 3T_1 to the 5E ground state, we present a detailed splitting scheme

for this level (Fig. 2) indicating the difference in energy from the upper level, which in this scheme has a value of 0 eV for the convenience of splitting estimation. The observed transitions are described in the text of the article.

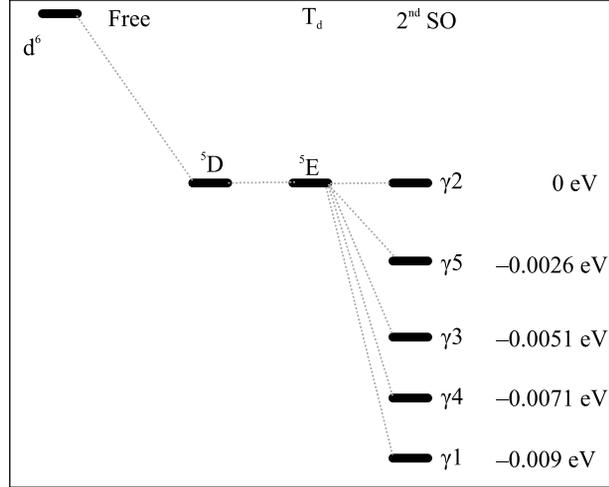


Fig. S2. Splitting of the 5E level in a crystal field and taking into account the second-order spin-orbit interaction

Certain values of the Racah parameters (B, C) made it possible to further calculate the magnitude of the nephelauxetic effect, which describes the degree of weakening of the rigidity of bonds in an ion (transition from covalent bonds to ionic ones). Quite consistently this effect (the effect of an expanding cloud), which is most significant for d -transition elements, was considered by Jorgensen. For these ions, the size of d -orbitals increases due to their shielding by unshared electron pairs of ligands. An increase in the nephelauxetic effect approximately corresponds to an increase in the covalence of the ligand-metal bond.

To assess nephelauxetic effect, the formula was previously used $\beta = B/B_0$.

In this case, $\beta = 0.65(\pm 0.09)$. Recently, new approaches to assessing the nephelauxetic effect of ?1 have begun to appear:

$$\beta_1 = \sqrt{\left(\frac{B}{B_0}\right)^2 + \left(\frac{C}{C_0}\right)^2} = 0.941(\pm 0.04).$$

Thus, the covalent nature of the bonds is preserved in the sample under study.

