

ENERGY LEVELS SCHEME FOR $\text{K}_2\text{SiF}_6:\text{Mn}^{4+}$ NANOPHOSPHOR

R. Nistora, S. Ivascu, C. N. Avram

Department of Physics, West University of Timisoara, Bd. V. Parvan, No. 4, 300223, Timisoara, Romania

Abstract

Luminescent materials using manganese ion as activator have become popular due their superb properties. The energy level structure of this ion can be well described by the standard crystal field theory. The objective of this paper is to report on detailed crystal field calculation of the Mn^{4+} energy levels in order to give a reliable explanation for experimental data. The parameters of the crystal field acting on the Mn^{4+} ion are calculated in the frame of Exchange Charge Model, from the crystal structure data. With these parameters we have been diagonalized the crystal field Hamiltonian. The obtained energy level schemes were compared with experimental data, and a good agreement is demonstrated.

Keywords: energy levels scheme, crystal field theory, 3d-ions, nanophosphor.

1. Introduction

The recent development of white light-emitting diodes relies on the use of phosphors for converting blue or UV light into longer wavelength complementary colors [1, 2]. Many phosphors were synthesized by firing host and activated, at high temperatures, with rare earth or transitional metals [3].

Luminescent materials using manganese ion as activator have become popular due their superb properties [3]. In order to explain experimental data concerning the luminescent properties of K_2SiF_6 phosphor, doped with Mn^{4+} ion, is necessary to investigate the electronic structure of this ion doped in host lattice. The Mn^{4+} ion has the same electronic configuration, with $3d^3$ electrons, as Cr^{3+} ion. The energetic structure of this ion can be well described by the standard crystal-field theory [4, 5]. The sequence of the energy levels is determined by the symmetry of ion sites, by interelectronic interactions determined by the Racah parameters B and C and by the crystal-field parameters. Although, the system $\text{Mn}^{4+}:\text{K}_2\text{SiF}_6$ have been

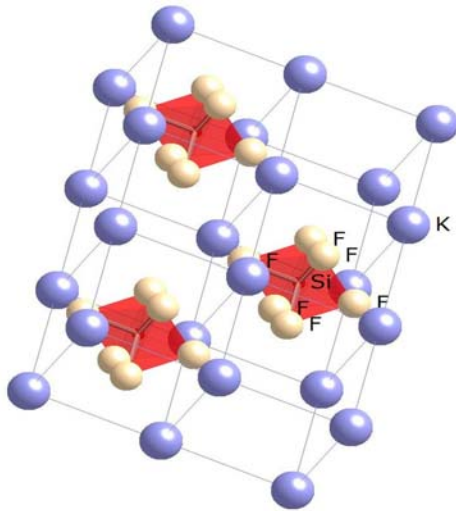
experimentally investigated [6-9], a consistent theoretical analysis on the crystal field parameters and the energy levels scheme have been not yet done.

The objective of this paper is to report on detailed crystal field calculation of the Mn^{4+} energy levels in order to give a reliable explanation for experimental data [6].

2. Method and samples

After doping Mn^{4+} in K_2SiF_6 crystal this ion will substitutes the Si^{4+} with octahedral coordination formed by F^- ions. These phosphors have a cubic structure space group Oh^5 ($Fm3m$), with one formula unit per primitive cell and a lattice constant of $a = 8.13 \text{ \AA}$.

The parameters of the crystal field acting on the Mn^{4+} ion are calculated in the frame of Exchange Charge Model [3], from the crystal structure data. With these parameters we have been diagonalized the crystal field Hamiltonian. The obtained energy level schemes were compared with experimental data, and a good agreement is demonstrated.



K_2SiF_6 (potassium hexafluorosilicate) space group = $Oh^5 - Fm3m$ with the lattice constant of $a = 8.13 \text{ \AA}$ [8].

FIGURE1. K_2SiF_6 structure [8]

In order to analysis the crystal field for Mn^{4+} doped in K_2SiF_6 crystal we follow paper [3]. In the framework of the exchange charge model (ECM) of crystal field the energy levels of an impurity ion are considered as the Eigen values of the following Hamiltonian [10]:

$$H = \sum_{p=2,4} \sum_{k=-p}^p (B_{p,q}^k + B_{p,s}^k) O_p^k \quad (1)$$

Here O_p^k are the linear combinations of irreducible tensor operators, and crystal field B_p^k parameters (CFP) are defined as:

$$B_{p,q}^k = -K_p^k e^2 \langle r^p \rangle \sum_i q_i \frac{V_p^k \langle \theta(i), \varphi(i) \rangle}{R(i)^{p+1}} \quad (2)$$

$$B_{p,S}^k = K_p^k e^2 \frac{2(2p+1)}{5} \sum_i (G_s S(S)_i^2 + G_\sigma S(\sigma)_i^2 + \gamma_p G_\pi S(\pi)_i^2) \frac{V_p^k(\theta_i, \varphi_i)}{R_i} \quad (3)$$

The last term includes all effects of the covalent bond formation and exchange interaction. The sums are carried out over lattice ions denoted by i with charges q_i ; $R(i), \theta(i), \varphi(i)$ are the spherical coordinates of the i -th ion of crystal lattice in the system of reference centered at the impurity ion. The averaged values $\langle r^p \rangle$ of p -th power of the impurity ion electron radial coordinate can be found in Ref. [11]. The values of the numerical factors K_p^k, γ_p and expressions for the polynomials V_p^k are given in [10].

$S(s), S(\sigma), S(\pi)$ correspond to the overlap integrals between d -functions of the central ion and p - and s -functions of the ligands: $S(s) = \langle d0|s0 \rangle, S(\sigma) = \langle d0|p0 \rangle, S(\pi) = \langle d1|p1 \rangle$. These integrals are numerical evaluated. G_s, G_σ, G_π are dimensionless adjustable parameters of the model, whose values can be determined from the positions of the first three absorption bands. We assume that they can be approximated to a single value, i.e. $G_s = G_\sigma = G_\pi = G$, that can be estimated from only one (the lowest in energy) absorption band. This is usually a reasonable approximation.

The dependence of the overlap integrals on distance between both ions is described by the following exponential functions [12]:

$$\begin{aligned} S_s &= \langle d0|s0 \rangle = 2.9481 \exp(-1.1738R) \\ S_\sigma &= \langle d0|p0 \rangle = 1.2177 \exp(-0.8233R) \\ S_\pi &= \langle d0|p0 \rangle = 1.9908 \exp(-1.1314R) \end{aligned}$$

The strong advantage of the ECM is that if the G parameter is determined to fit the first absorption band, the other energy levels, located higher in energy, will also fit experimental spectra fairly well. Another advantage of this model is connected with the fact the all CFP can be calculated from available crystal structure data, but not obtained *a posteriori* as a result of a fitting procedure. Also the obtained results are reliable (deviation between the calculated and observed energy levels is about several hundred cm^{-1} for $3d$ ions and several tens cm^{-1} for $4f$ ions). The ECM gives possibility to analyze covalent effects for different impurity centers

by comparing bilinear form constructed from the overlap integrals calculated using wave functions of the impurity ions and ligands.

The ECM has been successfully applied for the calculations of the energy levels of both rare earth [13-15] and transition metal ions in different hosts as well [16–18].

The obtained energy levels were compared with results of experimental data and discussed. During the diagonalization of the Hamiltonian the estimated Racah parameters B, C and G parameter of the exchange charge model have done.

3. Results and Discussions

The calculated CFPs values of Mn^{4+} doped in K_2SiF_6 are shown in Table 1. (the point charge and exchange charge contributions are denoted by PCC and ECC, respectively, and shown separately).

The value of the ECM fitting parameter G was determined from the position of the first absorption band in the corresponding absorption spectra and is equal to 4.825.

The Racah parameters $B = 413\text{cm}^{-1}$, $C = 4264\text{cm}^{-1}$ are used during diagonalization of the Hamiltonian of the system. Calculated energy levels are shown in Table 2.

TABLE 1. Crystal field parameters for $\text{Co}^{2+}:\text{MgF}_2$

Parameter	PCC	ECC	Total value
B_2^{-2}	-14	-18	-32
B_2^{-1}	0	0	0
B_2^0	4	1	5
B_2^1	13	28	41
B_2^2	9	23	32
B_4^{-4}	-98	-627	-725
B_4^{-3}	-2220	-14203	-16423
B_4^{-2}	431	2758	3189
B_4^{-1}	-1538	-9840	-11378
B_4^0	-188	-1201	-1389
B_4^1	-1252	-8010	-9262
B_4^2	-2937	-18790	-21727
B_4^3	5841	37368	43209
B_4^4	2479	15865	18344

TABLE 2. Observed and calculated (this work) energy levels (in cm^{-1}) of Mn^{4+} ion in K_2SiF_6 .

Energy levels (Oh group rotations)	This work		Experimental values [6]	Calculated Tanabe Sugano diagram
	Calculated ECM	Averaged ECM		
$^4\text{A}_2$	0	0	0	0
^2E	16100 16100	16100	16100	16126
$^2\text{T}_1$	16334 16336 16336	16335	-	16798
$^4\text{T}_2$	20292 20304 20307	20301	20300	20300
$^2\text{T}_2$	24395 24397 24402	24398	-	24416
$^4\text{T}_1$	24885 24886 24913	24895	24900	28099
$^2\text{A}_1$	34745	34745	-	33790

Conclusions

The crystal field parameters and energy for lowest levels of Mn^{4+} doped in K_2SiF_6 crystal have been calculated and the obtained results are compared with experimental data. The calculations have been performed in the frame of ECM of crystal field, taken into account site symmetry of the impurity ion, the contributions from ions charges of lattices and covalent effects from doped lattice. For this system the covalent effects are strong and obtained results for energy level schemes are in satisfactory agreement with experimental data.

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