

ENERGY LEVELS SCHEME FOR CrF₂

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Abstract

The parameters of the crystal field acting on the Cr²⁺ ion in the triclinic site symmetry of monoclinic CrF₂ crystal are modeled in the Exchange Charge Model (ECM). With these parameters the Hamiltonian of the crystal has been diagonalized and the low-lying energy levels scheme is calculated. The comparison of calculated values of the energy level with experimental data demonstrates a satisfactory agreement.

1. Introduction

CrF₂ crystal presents interesting optical and spectroscopic properties and had been investigated during the last years [1-5], both experimental and theoretical point of view. In reference [4,5] the fine structure of the energy levels of the crystal was calculated taken into account the site symmetry D_{4h} of the chromium ions [4], respectively D_{2h} [5]. In both cases the local symmetry is far from actual triclinic C_i site symmetry of the chromium ion [6]. The objective of this paper is to model the Crystal Field Parameters (CFPs) for the title crystal with actual triclinic site symmetry of the Cr²⁺(3d⁴) ions and to simulate the low-lying energy levels scheme for these ions in order to give a reliable explanation for experimental data [3].

The parameters of the crystal field acting on the Cr²⁺ ion are calculated in the frame of Exchange Charge Model (ECM) [7], from the crystal structure data [6]. With these parameters we have been diagonalized the crystal field Hamiltonian and the obtained values of the energy level were compared with experimental data. The fine interactions and the standardization of the CFPs are neglecting in this paper. They will be taken into account in next paper which is in progress.

2. Crystal structure of CrF₂

CrF₂ is a monoclinic crystal with a distorted rutile structure belongs to the group No.14 in the International Tables for Crystallography [8]. The tetragonal rutile structure has two CrF₂ in a tetragonal unit cell and each site the Cr²⁺ is surrounded by a distorted octahedron of six F⁻ ions with triclinic C_i site symmetry[6] (Figure 1).

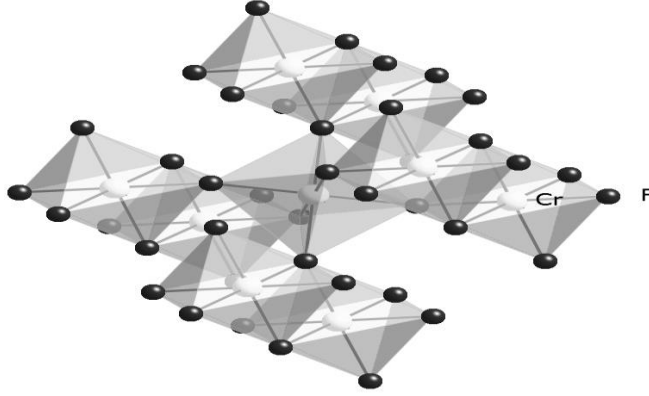


Figure 1. Crystal structure of CrF₂ [6]. Drawn with VESTA [9].

3. Modeling of CFPs

In the framework of the Exchange Charge Model (ECM) [7] of crystal field, the energy levels of an impurity ion are considered as the eigen values of the Hamiltonian:

$$H = \sum_{p=2,4} \sum_{k=-p}^p B_p^k O_p^k \quad (1)$$

where O_p^k are the linear combinations of spherical operators (which act on the angular parts of a $3d$ ion wave functions), and B_p^k are CFPs containing all information about geometrical structure of an impurity center. In ECM the CFPs are given by

$$B_p^k = B_{p,q}^k + B_{p,S}^k \quad (2)$$

The first contribution arises from the electrostatic interaction between a $3d$ ion and ions of crystal lattice (treated as the point charges, without taking into account their electron structure), and the second one is proportional to the overlap of the wave functions of a central ion

and ligands. This term accounts for all effects of the covalent bond formation and exchange interaction, and inclusion of these effects significantly improves agreement between the calculated and experimentally observed energy levels. Expressions for calculating both contributions to the CFPs in the case of $3d$ -ion are as follows [7]

$$B_{p,q}^k = -K_p^k e^2 \langle r^p \rangle \sum_i q_i \frac{V_p^k(\theta(i), \varphi(i))}{R(i)^{p+1}}, \quad (3)$$

$$B_{p,S}^k = K_p^k e^2 \frac{2(2p+1)}{5} \sum_i \left(G_s S(s)_i^2 + G_\sigma S(\sigma)_i^2 + \gamma_p G_\pi S(\pi)_i^2 \right) \frac{V_p^k(\theta_i, \varphi_i)}{R_i} \quad (4)$$

The sums in Eqs. (3) and (4) 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. [10]. The values of the numerical factors K_p^k, γ_p and expressions for the polynomials V_p^k are given in Ref. [7].

$S(s), S(\sigma), S(\pi)$ 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.

4. Results of calculations

According the geometrical data of CrF_2 [6], from the equations (2-4), and the overlap integral calculated all the CFPs are calculated and given in Table 1. The contribution from point charge (PCC), Exchange charge (ECC) and total values (TOTAL) are presented separate in Table 1.

Table 1. The crystal field parameters for CrF₂(cm⁻¹)

Parameter	PCC	ECC	TOTAL
B_2^{-2}	-5317	-23983	-29300
B_2^{-1}	3519	16092	19611
B_2^0	1095	4849	5944
B_2^1	2361	14104	16465
B_2^2	410	1516	1926
B_4^{-4}	-320	-2176	-2496
B_4^{-3}	-834	108	-726
B_4^{-2}	1975	14910	16885
B_4^{-1}	1781	11790	13571
B_4^0	408	3258	3666
B_4^1	2105	13800	15905
B_4^2	-84	-475	-559
B_4^3	1827	5167	6994
B_4^4	-2398	18520	-20918
G=9.885	B=780 cm ⁻¹	C=3306 cm ⁻¹	

As can see from the table 1 the contributions to CFPs from ECC is significant and the parameter

$$\beta = \frac{1}{2} \sqrt{\left(\frac{B_1}{B_0}\right)^2 + \left(\frac{C_1}{C_0}\right)^2}$$

which serves as a qualitative measure of the nephelauxetic effect (significant decrease of the Racah parameters for 3d ions in a crystal with respect to those in a free state) has the value 0.67 (for free Cr^{2+} ion [11] $B_0 = 780\text{cm}^{-1}$, $C_0 = 3430\text{cm}^{-1}$). The obtained values of CFPs were used to diagonalize the crystal field Hamiltonian (1) in the space spanned by all 100 wave functions of Cr^{2+} ion (${}^1\text{S}_2\text{D}_2\text{F}_2\text{G}_1\text{ }^3\text{P}_2\text{DF}_2\text{GH }^5\text{D}$). The Racah parameters B, C and G parameter of the model, given in the Table 1, are used during diagonalized of the Hamiltonian of the system. The calculated low-lying energy levels are shown in Table 2.

Table 2. The values of low-lying energy levels of CrF_2

IRR Oh notations	Experimental values 3] (cm^{-1})	Calculated this work (cm^{-1})
${}^5\text{E}_g$	0	0
${}^3\text{T}_{2g}$	8081	8081
${}^3\text{T}_{1g}$	13277	11713
${}^3\text{E}_g$	18705	18079
${}^3\text{T}_{1g}$	18777	18569
${}^3\text{T}_{2g}$	19283	19204

The satisfactory agreement between calculated values and experimental data is obtained.

4. Conclusions

The crystal field parameters and energy for lowest levels of CrF_2 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 low site symmetry of the impurity ion (C_i), 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 low-lying energy level schemes are in satisfactory agreement with experimental data. This means the validity of the ECM, the method used for modeling the CFPs, and the simulation of low-lying energy levels of the Cr^{2+} in CrF_2 crystal.

References

1. W. W. Holloway Jr., M. Kesgian, *Spectrochim. Acta* **22** (1966) 1381.
2. D. Oelkrug Von and Ber. Bunsenges, *Phys. Chem.* **70** (1966) 736.

3. P. E. Lim , J. W. Atout, J. Chem. Phys. **63** (1975) 4886.
4. Li Cui-Lian et al., Physica B **205**, (1995) 335.
5. Xiai-Mig Tan, Xiao-Yu Kuang, Kuang-Wei Zhou, Cheng-Lu and Qin-Sheng Zhu, J. Phys. Condens. Matter, **18** (2006) 1705.
6. K. H. Jack, R. Maitland, Proc. Chem. Chem. Soc. (1957) 232.
7. B. Z. Malkin, “Crystal field and Electron-Phonon Interaction in Rare-Earth Ionic Paramagnets” in *Spectroscopy of solids containing rare-earth ions*, edited by A. A. Kaplyanskii, B. M. Macfarlane, North Holland, Amsterdam, pp. 33-50 (1987).
8. International Tables for Crystallography, edited by Theo Hahn, Fifth edition, Vol. A, (2006), Springer Verlag, Berlin.
9. K. Momma, F. Izumi, J. Appl. Crystallogr. **41** (2008) 653.
10. A. G. Abragam, B. Bleaney, Electron Paramagnetic Resonance of Transition Ions (Oxford, Clarendon, 1970), chap.7.
11. J. S. Griffith, The Theory of Transition – Metal Ions, Cambridge University Press, Cambridge, 1961.