JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 4, April 2008, p. 819 - 822

Comparative study of the energy levels structure of Cr^{3+}:$MIn(WO_4)_2$ with M=Na, K, Rb

N. M. AVRAM[a,*], M. G. BRIK[b], C. N. AVRAM[a]
[a]*Department of Physics, West University of Timisoara,Bd.V.Parvan,300223 Timisoara, Romania*
[b]*Institute of Physics, University of Tartu, Riia Street 142,51014 Tartu, Estonia*

The crystal field parameters and the energy level structure of Cr^{3+} ion are calculated in the exchange charge model of crystal field using the actual symmetry of the chromium positions. The trivalent chromium ion replaces the In cation in each host matrix and occupies the low site symmetry The calculated energy level schemes for each crystal are compared with each other and with experimental results. The obtained results are in good agreement with experimental data. Covalent effects were shown to play an important role in all considered crystals.

(Received February 25, 2008; accepted April 2, 2008)

Keywords: Molybdates, Crystal field, Energy levels, Covalence

1. Introduction

Double molybdates and tungstates have been studied extensively for many years because of interesting optical, antiferroelectric and ferroelastic properties [1-4]. They are suitable as host materials for a variety of inorganic active ions, transition metal and lanthanides, in view of their development of tunable solid-state lasers and new luminescence materials [5, 6]. Recently, Hermanowicz [7], had experimentally investigated the optical properties of Cr^{3+} doped in $MIn(WO_4)_2$ hosts, where M=Na, Ka, Rb. There are a lot of studies in the literature [8 – and references therein] regarding various aspects related to the Cr^{3+}–doped crystals. Nevertheless, it should be pointed out that the reports on the consistent crystal field analysis of Cr^{3+}–doped $MIn(WO_4)_2$ crystals with calculations of crystal field parameters (CFPs) from the structural data are scarce. In this paper we present the results of application of the exchange charge model (ECM) of crystal field [9] to the calculation of the CFPs values and energy levels for Cr^{3+} ion in $MIn(WO_4)_2$.

2. Crystal structure of $MIn(WO_4)_2$; M=Na, Ka, Rb

$NaIn(WO_4)_2$ crystallizes in the monoclinic space group C_{2h}^5 (Z=4) with the lattice parameters a = 10.077 Å, b = 5.808 Å, c = 5.027 Å, β = 91.10˚ [10]. The trivalent chromium ions replace the In^{3+} cationic sites of the C_1 symmetry.

The potassium – indium double tungstate crystal ,at ambient temperature , crystallizes in the monoclinic space group C_{2h}^6 (Z=1) with a = 10.11 Å, b = 5.78 Å, c = 14.49 Å, β = 94˚ [11].The trivalent chromium ions in this crystal are doped into the In^{3+} cationic sites of C_2 symmetry. $RbIn(WO_4)_2$ crystal at ambient temperature has a trigonal symmetry with In^{3+} cation occupies the D_{3d} site symmetry [12]. The trivalent chromium ions in this crystal are substituting the In^{3+} ions.

3. Exchange charge model of crystal field

The energy levels of the Cr^{3+} ions in a crystal field will be calculated using the following crystal field Hamiltonian [9]:

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

where O_p^k are the linear combinations of spherical operators (which act on the angular parts of a 3*d* ion wave functions), and B_p^k are CFPs containing all information about geometrical structure of an impurity center. Salient feature of the ECM is that these parameters can be written as a sum of two terms [9]:

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

The first contribution arises from the electrostatic interaction between a 3*d* 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 3*d*-ion are as follows [9]

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

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

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 central ion. The averaged values $\langle r^p \rangle$ of p-th power of the central ion electron radial coordinate can be found in the literature or calculated numerically. The values of the numerical factors K_p^k, γ_p and expressions for the polynomials V_p^k are given in [9]. $S(s), S(\sigma), S(\pi)$ corresponds to the overlap integrals between the d-functions of the central ion and p- and s-functions of the ligands:

$$S(s) = \langle d0 | s0 \rangle, S(\sigma) = \langle d0 | p0 \rangle, S(\pi) = \langle d1 | p1 \rangle$$

G_s, G_σ, G_π are the 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 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.

Originally the ECM was proposed by Malkin [9] for rare earth ions, but later it has also been successfully applied to the transition metal ions in different hosts [13-19 and references therein]. The ECM is an extension of the angular overlap model and it considers both the long –and short-range interactions between an impurity ion and the lattice ions. Numerous applications show this model to be a powerful and reliable tool for analysis and interpretation of the crystal field effects and optical absorption spectra. The main advantages of ECM are connected with the calculation of CFPs from the available crystal structure data; these CFPs are not obtained *a posteriori* as a result of a fitting procedure. Also a small number of phenomenological parameters, only one (if $Gs=G\sigma=G\pi$) is needed for calculation of the energy levels .The 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 that gives a reliability of obtained results. Using the ECM offers the possibility to analyze the covalent effects for different impurity centers by comparing bilinear form constructed from the overlap integrals calculated using the wave functions of the impurity ions and ligands.

4. Results of calculations and discussion

Numerous applications of the ECM to the analysis of rare-earth and transition metal doped crystals [13-19, and references therein] show this model to be a powerful and reliable tool for analysis and interpretation of crystal field effects and optical absorption. The CFPs were calculated using the ionic positions obtained from structural data [10-12]. To ensure convergence of CFPs (especially those ones of the second rank), a large clusters consisting of 41760 ions for Na, 42841 for K and 33965 for Rb was taken into account. The overlap integrals between the Cr^{3+} and O^{2-} ions were calculated numerically using the wave functions from Refs. [20,21]; their dependence on distance between both ions is shown in Table 1. The calculated CFPs values are shown in Table 2.

Table 1. Dependence of the overlap integrals on distance r for Cr^{3+} - O^{2-} ions (r in atomic units).

$$S_s = \langle d0 | s0 \rangle = -1.5941 \exp(-0.74497r)$$
$$S_\sigma = \langle d0 | p0 \rangle = 1.3496 \exp(-0.76490r)$$
$$S_\pi = \langle d1 | p1 \rangle = 1.2614 \exp(-0.86530r)$$

Table 2. Crystal field, Racah parameters (in cm^{-1}),G and β parameters for Cr^{3+} in $MIn(WO_4)_2$ (M = Na, K, Rb).

	$NaIn(WO_4)_2$	$KIn(WO_4)_2$	$RbIn(WO_4)_2$
B_2^{-2}	0.0	-2.8	-2.8
B_2^{-1}	-43.6	-3.8	1.0
B_2^{0}	1513.7	994.5	8367.5
B_2^{1}	-1510.6	-2.6	1.4
B_2^{2}	2042.4	1.4	1.7
B_4^{-4}	0.0	0.8	0.0
B_4^{-3}	0.0	-47213.8	-62598.3
B_4^{-2}	0.0	0.0	0.0
B_4^{-1}	0.0	0.0	0.4
B_4^{0}	-1291.4	-2582.3	-2825.1
B_4^{1}	17353.2	0.0	0.0
B_4^{2}	6838.7	0.5	-0.4
B_4^{3}	44483.0	-53209.5	0.0
B_4^{4}	-9783.7	0.0	0.2
G	5.611	3.964	5.145
B	500	670	535
C	3435	3096	3650
β	0.54	0.72	0.58

The obtained values of CFPs were used to diagonalize the crystal field Hamiltonian (1) in the space spanned by all 120 wave functions of the LS terms of Cr^{3+} ion (^4P, ^4F, $^2PD_1D_2FGH$). Spin-orbit interaction was not considered, since the absorption bands in the experimental spectra are broad and no fine structure is observed. The Racah parameters B, C and G parameter of the model given in the Table 2 are used during diagonalization of the Hamiltonian of the system. The calculated energy levels are shown in Table 3.

Table 3. Calculated energy levels (cm^{-1}) of Cr^{3+} in $MIn(WO_4)_2$ (M = Na, K, Rb). The experimental values [7] are shown in italic in the parenthesis after the calculated barycenters.

	$NaIn(WO_4)_2$		$KIn(WO_4)_2$		$RbIn(WO_4)_2$	
$^4A_{2g}$	0		0		0	
$^4T_{2g}$	12251 13742 13970	13321 *(13320)*	14360 14361 14718	14480 *(14480)*	12641 12641 16894	14059 *(14050)*
^2E_g	13930 14002	13966 *(13980)*	14141 14141	*(14140)*	13540 13540	*(14130)*
$^2T_{1g}$	14256 14496 14628	14460 *(14390)*	14706 14706 14888	14767 *(14700)*	14391 14391 16223	15002 *(14870)*
$^4T_{1g}$	17670 18953 19310	18645 *(18650)*	20735 21020 21022	20926 *(20920)*	19634 21314 21314	20754 *(20745)*
$^2T_{2g}$	20187 20795 21174	20719 *(20120)*	20716 21130 21130	20992 *(20160)*	20343 24787 24787	23306 *(20325)*

As is seen from Table 2, the calculated values are in good agreement with experimental data .The higher energy levels (though they also were obtained) are not shown here for the sake of brevity.

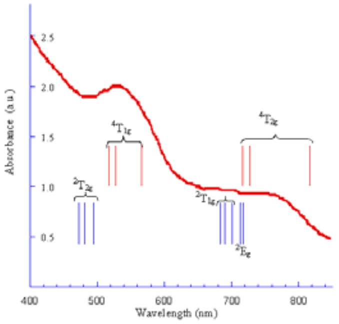

Fig. 1. Absorption spectra [7] of $NaIn(WO_4)_2$:Cr^{3+}. The calculated in this work Cr^{3+} energy levels are shown by vertical lines.

Figs. 1-3 illustrate how the calculated energy levels (including splitting of the orbital triplets) are related to the experimental absorption spectra [7].

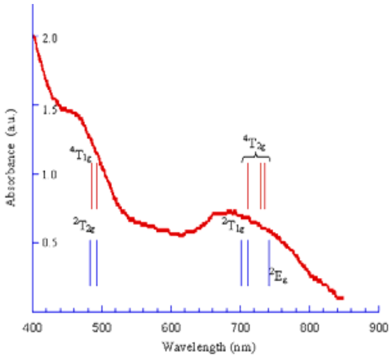

Fig. 2. Absorption spectra [7] of $KIn(WO_4)_2$:Cr^{3+}. The calculated in this work Cr^{3+}energy levels are shown by vertical lines.

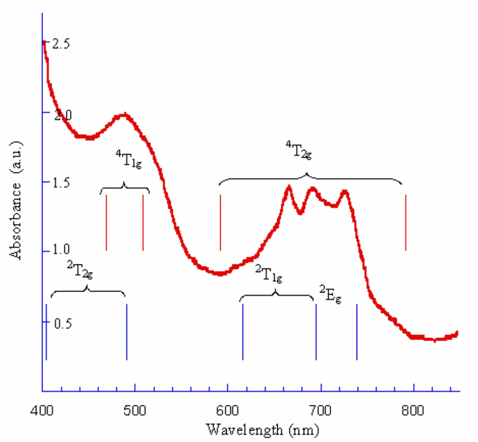

Fig. 3. Absorption spectra [7] of $RbIn(WO_4)_2$:Cr^{3+}. The calculated in this work Cr^{3+} energy levels are shown by vertical lines.

As can be seen from Table 2, comparison of the Racah parameters for Cr^{3+} in crystals with values for free Cr^{3+} ion (B=918 cm^{-1},C=3850 cm^{-1} [22]) shows that there is significant reduction of these parameters due to covalence. To analyze this reduction we introduce a non-dimensional quantity [17], $\beta = (B_1/B_0 + C_1/C_0)^{1/2}$,where subscript „1” and „0” are related to the values of the Racah parameters in a crystal and in a free state, respectively. The values of covalence parameters are given in Table 2.

5. Conclusions

Consistent calculations of the CFPs values and energy levels for Cr^{3+} ions in $MIn(WO_4)_2$ (M = Na, K, Rb), the Racah parameters B and C, the G model parameter and covalency parameters were performed in the present paper using the ECM of crystal field. For the first time for the considered crystals the CFPs values were calculated from crystal structure data, with taking into account low symmetry component of crystal field. The calculated energy levels (including splitting of the orbital triplets) match well the available absorption spectra. The calculated complete energy level schemes can be used for analysis of the Cr^{3+} excited state absorption in the considered materials, and the sets of CFPs can be used as initial (starting) sets for analysis of Cr^{3+} energy levels in other isostructural crystals. The strong covalence for all crystals doped with trivalent chromium ions pointed out the justification of ECM use.

Acknowledgements

C. N. Avram is grateful for the financial support from Romanian National Authority for Research in the frame of CEEX program (Project No.3/2005/MANANTECH).

References

[1] M. Maczka, J. Hanuza, J-H Kao, S. Kojima, Phys. Rev. **B 68**, 174101 (2003).

[2] W. Zapart, Phys. Status Solidi a **118**, 447 (1990).

[3] J. Hanuza, M. Maczka, K. Hermanowicz, P. J. Deren, W. Strek, L. Folcik, H. Drulis, J. Solid State Chem. **148**, 468 (1999).

[4] M. Maczka, J. Hanuza, A.F. Fuentes, U. Amador, J. Raman Spectrosc. **33**, 56 (2002).

[5] L. Macalik, P. J. Deren, J. Hanuza, W. Strek, A. A. Demidovich, A. N. Kuzmin, J. Mol. Struct. **450**, 179 (1998).

[6] K. Hermanowicz, J. Hanuza, M. Maczka, P. J. Deren, E. Mugenski, H. Drulis, I. Sokolska, J. Sokolnicki, J. Phys.: Condens Matter **13**, 5807 (2001).

[7] K. Hermanowicz, J. Phys.: Condens.Matter **18**, 10601(2006).

[8] S. Kück, Appl.Phys.B**72**, 515 (2001).

[9] B. Z. Malkin, in : A. A. Kaplianskii, B. F. Macfarlane (Eds), Spectroscopy of Solids Containing Rare-Earth Ions, North Holland, Amsterdam, 1987, pp.133.

[10] V. B. Kravchenko, Zh. Neorg. Khim. **12**, 1108 (1971).

[11] V. P. Klevtsov, R. F. Klevtsovaand, A. V. Demenew, Kristallografiya, **17**, 545 (1972).

[12] V.A. Efremov, V. K. Trunov, Yu. A. Velikodnyi, Zh. Struct. Khimii, **12**, 731 (1971).

[13] C. Jousseaumene, D. Vivien, A. Kuhn-Harari, B. Z. Malkin, Opt. Mater**. 24**, 143 (2003).

[14] S. I. Klokishner, B. S. Tsukerblat, O. S. Reu, A. V. Palii, S. M. Ostrovsky, Opt. Mater. **27**, 1445 (2005).

[15] M. G. Brik, N. M. Avram, C. N. Avram, Central Europ. J. Phys. **3**, 508 (2005).

[16] M. G. Brik, N. M. Avram, C. N. Avram, Spectr. Chim. Acta, Part A**63**, 759 (2006).

[17] M. G. Brik, N. M. Avram, C. N. Avram, Physica B**371,** 43 (2006).

[18] C. Rudowicz, M. G. Brik, N. M. Avram, Y. Y. Yeung, P.Gantek, J.Phys.: Condens. Matter. **18**, 5221 (2006).

[19] M.G. Brik, N. M. Avram, C. N. Avram, C. Rudowicz, Y. Y. Yeung, P. Gnutek, J. Alloys Comp. **432**, 61 (2007).

[20] E. Clementi, C. Roetti, Atomic Data and Nuclear Data Tables **14**, 177 (1974).

[21] M. V. Eremin, in: Spectroscopy of Laser Crystals, Ed. A. A. Kaplianskii, Leningrad, Nauka, 1989, p. 30 (in Russian).

[22] A. G. Abragam, B. Bleaney, Electron Paramagnetic Resonance of Transition Ions (Oxford, Clarendon, 1970) chap. 7.

---

[a] Corresponding author: avram@physics.uvt.ro