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ENERGY LEVELS FINE STRUCTURE OF Ni^{2+} DOPED IN MgO CRYSTAL

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Abstract

The fine structure of the energy levels of octahedrally coordinated Ni^{2+} ion in MgO single crystal, has been calculated taken into account, besides the spin-orbit interaction, also the spin-spin, orbit-orbit and spin-other-orbit interactions. The parameters of the crystal field acting on the Ni^{2+} ion are calculated in semiempirical Zhao model and the energy level schemes have been obtained by diagonalization the crystal field Hamiltonian. The results were compared with experimental data and a good agreement was demonstrated.

Keywords: Magnesium galate; Ni^{2+}, Crystal field theory, fine structure energy levels scheme.

1. Introduction

It is well known [1] that MgO single crystal doped with transitional metal ions $3d^n$ is a good candidate for tunable laser operation. Well known are the laser crystal MgO: Cr^{3+} [2] and MgO:Ni^{2+} [3], last operating in 1300-1500nm IR spectra. The MgO:Ni^{2+} system has a long history of investigation, in part, because the Ni^{2+} impurity is coordinated by a perfect octahedron of oxygen ions in this crystal, and therefore represents a prototypical system for study and testing of theoretical formalism. In papers [4-6] has been studied experimentally and theoretically the absorption spectra of the MgO:Ni^{2+} system. A more thorough theoretical description of $Ni^{2+}$was been developed by Lhier and Balhausen [7], in which the effects of spin-orbit coupling included, in addition to the crystal field and electron – electron interactions. Notable papers [8-12], represent some of the different objectives of research on this and closely related system. Experimentally only the first ligand field transition $^3A_{2g} \rightarrow {}^3T_{2g}(A_{2g}, E_g, T_{1g}, T_{2g})$ is directly allowed in one phonon absorption by a magnetic dipole operator (the others are vibronically induced), the spin-orbit components of all of the excited states are allowed via two-photon absorption [13]. In that paper the authors investigated

experimentally and calculated the spin-orbit fine structure of the energy levels. In present paper we simulated the energy level scheme of title system ,taken into account, beside spin-orbit interaction, also other fine interaction like, spin-spin, orbit-orbit and spin-other-orbit interactions, due their importance in evaluation the values of energy [14, 15].

2. Method and samples

MgO is a cubic crystal of NaCl structure belonging to the space group F*m*3*m* (O5*h*) [16]. The unit cell consists of four formula units; the lattice constant is *a*=4.213Å. The melting temperature is 2850°C, the density is 3.58gcm^{-3}, the hardness is 5.5 Mohs**,** and the refractive index is 1.726 at 840nm. Te structure of MgO crystal is presented in Fig. 1.

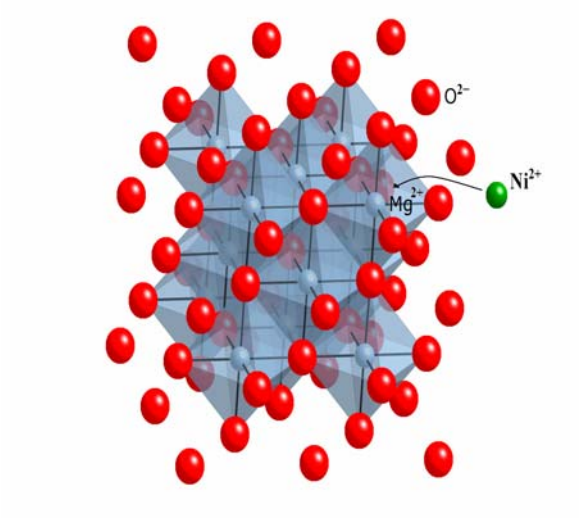

FIGURE 1. Geometric structure of MgO crystal[16]. Ni^{2+} will substitute the Mg^{2+} without charge compensation.

The Ni^{2+} dopant will substitute the isovalent Mg^{2+}, in O_h site symmetry of six O^{2-} ligands and the $[MgO_6]^{10-}$ cluster will appear. The MgO:Ni^{2+} Hamiltonian system is [15]:

$$H=\sum_{k=2,4}F^k f_k+\xi_{3d}A_{SO}+\alpha L(L+1)+\beta G(R_5)+\sum_{k=2,4}m_k M^k+\frac{7}{2}B_0^4\left[C_0^{(4)}+\left(\frac{5}{14}\right)^{1/2}\left(C_4^{(4)}+C_{-4}^{(4)}\right)\right] \quad (1)$$

where: F^k - the Slater parameters,

ξ_{3d} - spin-orbit coupling constant,

α - Tress constant,

β - Racah constant,

M^k - Marvin constants,

B_0^4 - crystal field parameter ,

$C_p^{(k)}$ - operator connected with spherical harmonics.

3. Simulation of the energy levels scheme

In order to diagonalize this Hamiltonian we use the *B* and *C* Racah parameters instead F^k Slater parameters and the *Dq* octahedral crystal field parameter instead B_0^4. Using [17]:

$$E(^3T_{2g}) - E(^3A_{2g}) = 10Dq \quad (2)$$

$$E(^3T_{1g}(F)) - E(^3A_{2g})) = 7.5B + 15Dq - (225B^2 - 180BDq + 100Dq2)^{0.5}/2 \quad (3)$$

and experimental values:

$E(^3T_{2g}) - E(^3A_{2g})=8845cm^{-1}$ and $E(^3T_{1g}(F)) - E(^3A_{2g}))=14700cm^{-1}$ [5],

we obtained $B=954cm^{-1}$ and $Dq=884,5cm^{-1}$.

For the values of the others parameters enter in (1) Hamiltonian we adopt the model of Zhao [18], taken into account the covalent effects of the ligands. According this model the parameters of the Hamiltonian (1) are:

$$B=N^2B_0,\ C=N^2C_0,\ \xi_{3d}=N\,\xi_0,\ \alpha=N^2\,\alpha_0,\ \beta=N^2\,\beta_0,\ M^k=NM^k_0 \quad (4)$$

The index zero to parameters corresponds to free ion. For Ni^{2+} these values for the free ion are [14]:

$$B_0=1092cm^{-1};\ C_0=4086cm^{-1};\ \alpha_0=79cm^{-1};\ \beta_0=244cm^{-1};\ M_0^0=1.864cm^{-1};\ M_0^2=1.236cm^{-1} \quad (5)$$

The spin-orbit constant ξ_0 can be calculated as [19]:

$$\xi_0=\xi_{10} - 91M_0^0/7 + 42\,M_0^2/41 \quad (6)$$

where $\xi_{10}=656.5cm^{-1}$ [14].

From Eqs. (3) and (4) it obtained $N=0.93$. With these values the parameters from Eq. (4) are:

$B=954cm^{-1}$;$C=3555cm^{-1}$;$\alpha=73cm^{-1}$; $\beta=227cm^{-1}$; $M^0=1.612cm^{-1}$; $M^2=1.149cm^{-1}$; $\xi_{3d}=589cm^{-1}$.

The crystal field parameter $B_0^4=21Dq=18574.5cm^{-1}$.

The energy levels scheme of Ni^{2+} doped in $MgGa_2O_4$ were obtained by diagonalization of the Hamiltonian (1) and the results are given in Table 1.

TABLE 1.The values of energy levels of Ni^{2+}:MgO

IRR Oh notations	Experimental values [13] (cm^{-1})	Calculated values (cm^{-1})
$^3A_{2g}$(T2)	0	0
$^3T_{2g}$ (E)	8605	8573
$^3T_{2g}$ (T_1)	8783	8726
$^3T_{2g}$ (T_2)	-	9086
$^3T_{2g}$ (A_2)		9242
^1E	13650	13820
$a^3T_{1g}(A_1)$	-	13925
$a^3T_{1g}(T_1)$	14111	14388
$a^3T_{1g}(T_2)$	15150	15101
$a^3T_{1g}(E)$	15580	15632
$^1T_2$	21734	22294
$^1A_1$	-	24094
b^3T1g(E)	24587	25401
$b^3T_{1g}(T_2)$	-	25647
$b^3T_{1g}(T_1)$	-	25824
$b^3T_{1g}(A_1)$	-	26010

$a=^3T_{1g}(F)$; $b=^3T1g(P)$

As can seen from this table the calculated results, taken into account the spin-spin, spin-other-orbit and orbit-orbit interactions, are in good agreement with experimental data. Also the new values for energy levels are predicted.

Conclusions

In this paper the fine structure of the energy levels of octahedrally coordinated Ni^{2+} ion doped in MgO single crystal, has been calculated taken into account, besides the spin-orbit interaction, also the spin-spin, orbit-orbit and spin-other-orbit interactions. The parameters of the crystal field acting on the Ni^{2+} ion are calculated in semiempirical Zhao model, taken into account the covalent effects of the ligands. The energy level schemes have been obtained by diagonalization the crystal field Hamiltonian. The obtained results are in agreement with experimental data.

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References

1. S. Kück, Appl. Phys., B72 (2001)515.
2. M. O. Henry, J. P. Larkin, G.F. Imbusch, Phys. Rev. B 13 (1976) 1893.
3. P. F. Moulton: In *Handbook of Lasers Science and Technology* I, *Lasers and Masers*, ed. by M. J. Weber (Chemical Rubber, Boca Raton) (1982) p.60.
4. W. Low, Phys. Rev., 109 (1958) 247.
5. S. Minomura, H. G. Drickamer, J. Chem. Phys., 35 (1961) 903.
6. R. Papalardo, D. L.Wood, R. C. Linares, Phys. Chem., 35 (1961) 1460.
7. A. D. Liehr and C. J. Ballhausen, Annals of Physics, 2 (1959) 134.
8. D. D. Bird, G. A. Osborne, P. J. Stephens, Phys. Rev., B37 (1972) 1800.
9. N. B. Manson, Phys. Rev., B4 (1971) 2645.
10. N. B. Manson, Phys. Rev., B4 (1971) 2656.
11. R.Moncorge, T.Benyattou, Phys. Rev., B37 (1988) 9186.
12. S. A. Payne, Phys. Rev., B41 (1990) 610.
13. C. Campochiaro, D. S. McClure, P. Rabinowitz, S. Dougal, Phys. Rev. B43 (1991) 14.
14. E. N. Irinyakov, PhD Thesis, Kazan, (2007).
15. A. M. Lenshin, E. N. Irinyakov, Optics and Spectrscopy, 100 (2006) 368.
16. R. M. Hazen, American Mineralogist**,** 61 (1976) 266.
17. Balhausen, Molecular electronic structure of transition metal complex, Mc Graw - Hill, New York, (1979).
18. M. G. Zhao, M. L. Du, G. Y. Sen, J. Phys. C: Solid State Phys. 20 (1987) 5557.
19. E. V. Condon, H. Odabasi, Atomic Structure, Cambridge University Press, Cambridge, (1980).