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Spectral fine structure and electron paramagnetic resonance parameters of $\text{LiNbO}_3:\text{Ni}^{2+}$

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Abstract. Using a phenomenological parametrized crystal-field model, the spectral structure and EPR parameters of the ground state ${}^3A_2(F)$ of $\text{LiNbO}_3:\text{Ni}^{2+}$ are calculated by means of diagonalization of the complete energy matrix. Two parameters A_1 and A_2 are fitted to the experimental spectra. The results agree well with the experimental findings. The theoretical method is suitable for any $C_{3v}(d^8)$ ion.

1. Introduction

Since Macfarlane (1967) suggested the importance of the high-order effect on the properties of the ground state of transition-metal ions, a number of investigations (Fairbank and Klauminzer 1973, Du and Zhao 1985, Yu *et al* 1985) have been carried out to calculate the high-order contribution to the spin-Hamiltonian parameters. Impurity ions of $3d^8$ configuration have been intensively investigated by EPR and optical spectroscopy (Ballhausen 1962, Abragam and Bleaney 1970). In a crystal field of octahedral symmetry the ground state of these ions is the ${}^3A_2(F)$ orbital singlet which is triple spin degenerate. If the crystal field has an axial component (in particular, a trigonal distortion), the ground state is split into the singlet $|0\rangle$ and the doublet $|\pm\rangle$. In the absence of an external magnetic field the zero-field splitting (ZFS) between these levels is equal to the axial parameter D of the spin Hamiltonian. As a rule, a trigonal field also leads to anisotropy of the g -values. However, the attempts to explain the magnitudes of ZFS and g -value anisotropy for Ni^{2+} in some crystals by taking into account the interaction with only the nearest excited 3T_2 level were unsuccessful, since a wrong sign was obtained for both D and $\Delta g = g_{\parallel} - g_{\perp}$ (Ballhausen 1962, Blumberg *et al* 1963, Geschwind and Remeika 1963, Kamimura 1962). Petrosyan and Mirzakhanyan (1986) calculated the ZFS and g -values for d^8 ions in trigonally distorted octahedral complexes within the framework of the crystal-field theory. On the basis of the complete strong-field scheme, Zhou *et al* (1990) reported the spectral fine structure, the EPR parameters of which are incorrect.

This work presents the results using a phenomenological parametrized crystal-field model. The calculation is based on the complete strong-field coupling scheme by diagonalization of the complete energy matrices including the electron–electron interaction, the spin–orbit coupling and the low-symmetry C_{3v} crystal field (Rahman and Runciman 1971). In calculating the energy levels, two adjustable parameters A_1 and A_2 are employed which are fitted to experimental spectra (Arizmendi *et al* 1980). The structure parameters R_1 , R_2 , θ_1 and θ_2 are determined by x-ray diffraction (Abrahams 1966). The results are in good agreement with experimental findings.

2. Theoretical method

The $\text{LiNbO}_3:\text{Ni}^{2+}$ ion has a $3d^8$ electron configuration. The ground state ${}^3A_2(\text{F})$ will be split under the action of the low-symmetry crystal field and spin-orbit coupling. These interactions also lead to anisotropy of the g -values.

Using the irreducible representation basis functions of the C_{3v} group, the Hamiltonian matrix is obtained for the d^8 configuration. The complete energy matrix elements are expressed in terms of the Racah parameters B and C , the cubic crystal-field parameter Dq , the spin-orbit coupling coefficient ζ and the crystal-field parameters V and V' (Rahman and Runciman 1971).

In the strong-field scheme, the crystal parameters Dq , V and V' of $C_{3v}(d^8)$ are defined as follows:

$$\begin{aligned}\langle X_{\pm}|H|X_{\pm}\rangle &= -\frac{1}{3}V - 4Dq \\ \langle X_0|H|X_0\rangle &= \frac{2}{3}V - 4Dq \\ \langle U_{\pm}|H|U_{\pm}\rangle &= 6Dq \\ \langle U_{\pm}|H|X_{\pm}\rangle &= V'\end{aligned}\quad (1)$$

Thus we have

$$\begin{aligned}V &= 3D_2 + \frac{20}{3}D_1 \\ V' &= \frac{5}{3}\sqrt{2}[D_1 - \frac{3}{5}D_2] \\ Dq &= -\frac{3}{2}D_3 - \frac{1}{30}V - \frac{1}{20}\sqrt{2}V'\end{aligned}\quad (2)$$

where

$$\begin{aligned}D_1 &= A_1\left\{\frac{1}{56}[(35\cos^4\theta_1 - 30\cos^2\theta_1 + 3) + \frac{1}{8}\sqrt{2}\sin^3\theta_1\cos\theta_1]/R_1^n\right. \\ &\quad \left. + \frac{1}{56}[(35\cos^4\theta_2 - 30\cos^2\theta_2 + 3) + \frac{1}{8}\sqrt{2}\sin^3\theta_2\cos\theta_2]/R_2^n\right\} \\ D_2 &= \frac{3}{14}A_2[(3\cos^2\theta_1 - 1)/R_1^m + (3\cos^2\theta_2 - 1)/R_2^m] \\ D_3 &= -\frac{1}{8}\sqrt{2}A_1[\sin^3\theta_1\cos\theta_1/R_1^n + \sin^3\theta_2\cos\theta_2/R_2^n].\end{aligned}$$

In the phenomenological parametrized crystal-field model, experimental values for Ni^{2+} , Mn^{3+} and Cr^{3+} in oxides and fluorides lead to an exponent n which is close to five (Drickamer 1967, Rodriguez *et al* 1986, Duclos *et al* 1990). A realistic calculation performed within a molecular orbital description gives a similar conclusion (Moreno *et al* 1992). We take $n = 5$ and $m = 3$ to obtain values of A_1 and A_2 from experimental optical spectra for $\text{LiNbO}_3:\text{Ni}^{2+}$.

The diagonalization of the complete energy matrix leads to complete mixing of all terms of ligand-field configurations. From the eigenvalues the spectral fine structures are obtained. The difference between the lowest two eigenvalues $E(|{}^3A_2(\text{F}), \pm 1\rangle)$ and $E(|{}^3A_2(\text{F}), 0\rangle)$ is the ground-state ZFS. The three lowest-lying eigenvectors, namely one belonging to $E(|{}^3A_2(\text{F}), 1\rangle)$, denoted by $|\varphi_+\rangle$, another belonging to $E(|{}^3A_2(\text{F}), -1\rangle)$, denoted by $|\varphi_-\rangle$, and the third belonging to $E(|{}^3A_2(\text{F}), 0\rangle)$, denoted by $|\varphi_0\rangle$, will be produced by diagonalization of the complete energy matrix. Thus we may write

$$\begin{aligned}|\varphi_+\rangle &= |{}^3A_2(\text{F}), 1\rangle \\ |\varphi_-\rangle &= |{}^3A_2(\text{F}), -1\rangle \\ |\varphi_0\rangle &= |{}^3A_2(\text{F}), 0\rangle\end{aligned}\quad (3)$$

and

$$|\varphi_i\rangle = \sum_k C_i(K)\chi_i(K) \quad i = \pm 1, 0$$

where $\chi_i(K)$ is the K th basis function of the complete energy matrix. $C_i(K)$ is the K th component of $|\varphi_i\rangle$, which will be obtained by diagonalizing the energy matrix.

2.1. EPR parameters

The spin Hamiltonian of ${}^3A_2(F)$ is

$$H_s = g_{\parallel}\mu_B H_z S_z + g_{\perp}\mu_B(H_x S_x + H_y S_y) + DS_z^2 \quad (4)$$

where D and g are the spin-Hamiltonian parameters.

Following the spin-Hamiltonian theory,

$$D = E(|{}^3A_2(F), \pm 1\rangle) - E(|{}^3A_2(F), 0\rangle). \quad (5)$$

Thus, D , including its sign, is the result of the interaction of the low-symmetry crystal field and spin-orbit coupling.

When a magnetic field is applied, the perturbation Hamiltonian has to be extended by the Zeeman term:

$$H = H_e(B, C) + H_{\text{cub}}(Dq) + H_{\text{trig}}(V, V') + H_{\text{so}}(\zeta) + H_m. \quad (6)$$

Following the perturbation theory, we have

$$g_{\parallel} = (1/\mu_B H_z)\langle\varphi_+|H_{mz}|\varphi_+\rangle \quad H \parallel Z \text{ axis} \quad (7)$$

$$g_{\perp} = (\sqrt{2}/\mu_B H_x)\langle\varphi_+|H_{mx}|\varphi_0\rangle \quad H \parallel X \text{ axis} \quad (8)$$

with

$$H_{mz} = \mu_B H_z(kL_z + g_e S_z)$$

$$H_{mx} = \mu_B H_x(kL_x + g_e S_x)$$

where $g_e = 2.0023$ is the free-electron g -values and $k = 0.85$ is the orbit reduction factor.

3. Numerical results

In the calculation, A_1 and A_2 are fitted to experimental spectra, taking $A_1 = -3750927.29 \text{ cm}^{-1} \text{ au}^5$ and $A_2 = -528990.92 \text{ cm}^{-1} \text{ au}^3$. The crystal-field parameters can be obtained as long as the structure parameters R_1 , R_2 , θ_1 and θ_2 are known. By the diagonalization of the complete energy matrix the spectral fine structure (see table 1), D -values and g -values (see table 3) are obtained.

It can be seen from tables 1–3 that the high-order perturbation formula is suitable for calculating the ZFS parameters. The strong-field scheme employed by Zhou *et al* (1990) gives incorrect results.

(1) The D obtained by Zhou *et al* (1990) is 5.073 19, but the sign of D determined by the EPR experiment is negative (Petrosyan and Mirzakhanyan 1986).

(2) Δg in the work of Zhou *et al* (1990) is -0.0057 ; it contradicts the Δg value of 0.04 obtained by Petrosyan and Mirzakhanyan (1986).

(3) If the parameters obtained by Zhou *et al* (1990) ($B = 790$, $C = 3270$, $Dq = 830$, $V = -2400$, $V' = 565.69$ and $\zeta = 530.5$) are substituted into the complete Hamiltonian matrices used in this paper, the calculated values do not agree with their results (shown in table 2).

Table 1. The spectral fine structure of $\text{LiNbO}_3:\text{Ni}^{2+}$. The parameters are

c	d	a	b
$A_1 = -3750927.29$	$A_1 = -3.750927.29$	$\zeta/\zeta_0 = 0.83$	$B = 790$
$A_2 = -528990.92$	$A_2 = -528990.92$	$B = 816$	$C = 3270.$

The structure data are (Abrahams 1966)

c	d	a	b
$\theta_1 = 62.9^\circ$	$\theta_1 = 61.65^\circ$	$C = 3224$	$Dq = -830$
$\theta_2 = 49.2^\circ$	$\theta_2 = 47.99^\circ$	$Dq = -792$	$V = 2400$
$R_1 = 1.889 \text{ \AA}$	$R_1 = 1.889 \text{ \AA}$	$V = 950$	$V' = 565.69$
$R_2 = 2.112 \text{ \AA}$	$R_2 = 2.112 \text{ \AA}$	$V' = -600$	$\zeta = -530.5.$

Calculated in this paper (C_{3v})			Observed by Arizmendi <i>et al</i> (1984) (O_h)		Calculated ^a (C_{3v})	Calculated ^b (C_{3v})	
Assignment	Band ^c (cm^{-1})	Band ^d (cm^{-1})	Assignment	σ (cm^{-1})	π (cm^{-1})	Band (cm^{-1})	Band (cm^{-1})
A'	0	0	3A_2		0	0	0
E'	-4.33	-2.00				-4.14	-6.07
A'	7712	7821				7636	7549
A'	7731	7829	$^3T_{2g}$		7810	7648	7577
E'	7865	7865				8036	8500
E'	7958	7901	$^3T_{2g}$	7970		8073	8516
E'	8065	8066				8228	8757
A'	8070	8122				8240	8768
E'	12338	12482	1E_g	12120		12345	12438
A'	12818	12978	$^3T_{1g}$		12990	13036	13397
A'	13027	13249			13773	13269	13784
E'	13291	13384	$^3T_{1g}$			13273	13792
E'	13300	13391		13330		13393	14137
E'	14459	14171	$^3T_{1g}$			13822	14143
A'	14465	14181				13835	14354
E'	19454	19972	$^1T_{2g}$	20450		19350	19326
A'	20510	20403	$^1T_{2g}$		19420	20237	20521
A'	21607	21496	$^1A_{1g}$		20620	20782	20777
E'	22221	23026				21776	21394
E'	22286	23050				21832	21437
A'	24227	23848	$^3T_{1g}$		22220	23495	23625
A'	24466	24139				23746	24255
E'	24466	24139	$^3T_{1g}$	23260		23746	24300
A'	24814	24423	$^3T_{1g}$			24056	24612
E'	24913	24932				24448	25079
A'	30384	30739	1E_g			29712	29431

^{a,b} Calculated by substituting the two sets of the spectral parameters used by Zhou *et al* (1990) into the complete energy matrix used in this paper.

^c The structure parameters deviate from those of Abrahams (1966) by $\Delta\theta_1 = 1.25^\circ$ and $\Delta\theta_2 = 1.21^\circ$.

Table 2. A comparison between the work of Zhou *et al* (1990) and the work in this paper (transition, ${}^3A_2(F) \rightarrow$).

	Band (cm^{-1})	
	Present work	From table 1 in Zhou <i>et al</i> (1990)
E'	-6.07	5.0734
A'	7549	7560
A'	7577	7611
E'	8500	7704
E'	8516	7823
E'	8757	9173
A'	8768	9216
E'	12 438	12 521
A'	13 397	12 754
A'	13 784	12 841
E'	13 792	13 050
E'	14 137	13 317
E'	14 143	15 627
A'	14 354	15 629
E'	19 326	19 875
A'	20 521	20 303
A'	20 574	20 907
E'	21 394	22 680
E'	21 437	22 881
A'	23 625	23 082
A'	24 255	23 329
E'	24 330	23 742
E'	25 079	24 707
A'	29 431	225 337

Table 3. The values of EPR parameters of $\text{LiNbO}_3:\text{Ni}^{2+}$. The parameters are

c	a	b
$A_1 = -3\,750\,927.29$	$\xi/\xi_0 = 0.83$	$B = 790$
$A_2 = -528\,990.92$	$B = 816$	$C = -3270$
$\Delta\theta_1 = 1.25^\circ$	$C = 3224$	$Dq = -830$
$\Delta\theta_2 = 1.21^\circ$	$Dq = -792$	$V = 2400$
	$V = 950$	$V' = -565.69$
	$V' = -600$	$\xi = -530.5.$

	D (cm^{-1})	g_{\parallel}	g_{\perp}
Calculated in this paper ^c	-4.33	2.25	2.21
Calculated ^a	-4.14	2.239	2.199
Calculated ^b	-6.07	2.29	2.22
From table 2 of Zhou <i>et al</i> (1990)	5.073 19	2.246 81	2.252 51
Experimental data from Mirsahanin (1981)	-5.06	2.24 ± 0.02	2.20 ± 0.02

^{a,b} Calculated by substituting the two sets of the spectral parameters used by Zhou *et al* (1990) into the complete energy matrix used in this paper.

4. Conclusion

The calculated results agree well with the experimental findings obtained by diagonalization of the complete energy matrix of symmetry C_{3v} of Ni^{2+} which is at the Li^+ site. There is no charge compensation in the calculation; it is found that, when $\theta_1 = \theta_2 = \sin^{-1}(\frac{1}{3}\sqrt{2})$, the formula is degenerate for O_h symmetry; when $\theta_1 = \theta_2 < \sin^{-1}(\frac{1}{3}\sqrt{2})$, $D > 0$ and $g_{\perp} > g_{\parallel}$; when $\theta_1 = \theta_2 > \sin^{-1}(\frac{1}{3}\sqrt{2})$, $D < 0$ and $g_{\perp} < g_{\parallel}$.

For impurities in the cubic lattices, the impurity–ligand distance is different from that corresponding to the host lattice (Drickamer 1967, Rodriguez *et al* 1986, Duclos *et al* 1990, Moreno 1990, Barkyoumd *et al* 1992, Moreno *et al* 1992). However, if R_1 varies directly as R_2 , they will have little influence on the optical and EPR parameters. In the calculation, it is found that it is the variation in angles in the vicinity of the host lattice geometry that gives rise to the changes in optical and EPR parameters, as shown in tables 1 and 3.

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