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A theoretical investigation of the zero-field splitting parameters for an Mn^{2+} centre in a BiVO_4 single crystal

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Abstract. The zero-field splitting (ZFS) parameters D , E and F for an Mn^{2+} centre in a BiVO_4 single crystal are calculated using the point-charge electrostatic model and the superposition model. The calculated ZFS parameters at the Bi and V sites are compared with the experimental values for Mn^{2+} . The calculated second-order axial and rhombic ZFS parameters at the Bi site turn out to be similar to those from experiment. The superposition model and the point-charge model give similar results. This supports the notion that the Mn^{2+} impurity substitutes for the Bi^{3+} ion in BiVO_4 .

1. Introduction

Ferroelastics have received considerable attention in recent years. Bismuth vanadate (BiVO_4) is a comparatively new crystal belonging to the class of ferroelastic materials and may be promising for acousto-optics (Manolikas and Amelinckx 1980, Akimov *et al* 1982). Intensive investigations of BiVO_4 have been carried out recently (Pinczuk *et al* 1977, 1979, Choh *et al* 1985, Moon *et al* 1987, Lim *et al* 1992).

Electron paramagnetic resonance (EPR) studies of paramagnetic impurities in BiVO_4 single crystals have been reported (Baran *et al* 1985a, b, 1986, Yeom *et al* 1992). There are three possibilities for the site of the Mn^{2+} centre in this crystal, namely Bi^{3+} , V^{5+} and a structural vacancy. It is interesting and worthwhile to determine the site of this particular impurity. It was proposed that there are two kinds of Mn^{2+} centre (Baran *et al* 1985b): one is just a replacement of the Bi^{3+} ion with the Mn^{2+} ion without nearby charge compensation (Mn_I^{2+} centre), and the other is the same substitution accompanied by a vacancy in the immediate environment (Mn_II^{2+} centre). Recently, Yeom *et al* (1992) reported that the Mn^{2+} ion substitutes for Bi^{3+} without nearby charge compensation. In addition, the Er^{3+} ion may replace either Bi^{3+} or V^{5+} (Baran *et al* 1985b).

In this paper, we present the calculated zero-field splitting (ZFS) parameters for the Mn^{2+} ion under the assumption that this ion is present at the Bi^{3+} site and the V^{5+} site, respectively, using the superposition model as well as the point-charge model. Possible Mn^{2+} sites in the BiVO_4 crystal are considered. The results derived from these two models are found to be consistent with experimental observations.

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2. Crystal structure

BiVO_4 was first shown to be ferroelastic by Bierlein and Sleight (1975). The crystal undergoes a reversible second-order phase transition between the monoclinic fergusonite structure (space group, $I2/a$ (C_{4h}^6)) and the tetragonal scheelite structure (space group, $I4_1/a$ (C_{4h}^6)) (David 1983). The structural parameters at room temperature are $a = 5.1966 \text{ \AA}$, $b = 5.0921 \text{ \AA}$, $c = 11.704 \text{ \AA}$ and $\gamma = 89.616^\circ$, and the lattice parameters at 573 K are $a = b = 5.1509 \text{ \AA}$, $c = 11.730 \text{ \AA}$ and $\gamma = 90.0^\circ$ (David *et al* 1979). In the ferroelastic phase, the vanadium ions are located in a distorted tetrahedron of oxygen ions with different bond lengths, and the bismuth atom is coordinated with eight distorted VO_4 tetrahedra. The displacements of Bi^{3+} and V^{5+} are along the b axis, and both cations move in the same direction (Sleight *et al* 1979). The displacement of the Bi^{3+} ions plays a major role in the ferroelastic-to-paraelastic phase transition (Wood and Glazer 1980).

3. Theoretical model

Theoretical studies on the spin-Hamiltonian parameters of d^5 ions have been the subject of a considerable amount of work (Powell *et al* 1960, Watanabe 1960a,b, Gabriel *et al* 1961, Low and Rosengarten 1964, Sato *et al* 1976, Du and Zhao 1985, Kuang and Chen 1987, Yu 1989). The lack of orbital angular momentum in the ^6S ground state leads to considerable difficulty in explaining the observed effects of the crystal field. Various mechanisms have been suggested to contribute to the ground-state splitting of the magnetic ions interacting with the lattice.

The experimental results for the resonance fields of Mn^{2+} in BiVO_4 single crystals can be analysed with the usual spin Hamiltonian (Rudowicz 1987):

$$H_s = \beta B \cdot gS + D[S_z^2 - S(S+1)/3] + E(S_+^2 + S_-^2)/2 \\ + F[35S_z^4 - 30S(S+1)S_z^2 + 25S_z^2 - 6S(S+1) + 3S^2(S+1)^2]/180 \\ + a[S_x^4 + S_y^4 + S_z^4 - S(S+1)(3S^2 + 3S - 1)]/5 \quad (1)$$

where $S = \frac{5}{2}$. The ZFS parameters for the Mn^{2+} ions in BiVO_4 have been obtained using only the three conventional ZFS parameters D , E and F , without any fourth-order term a (Yeom *et al* 1992). The spin Hamiltonian used by Yeom *et al* (1992) has provided a satisfactory description of the experimental rotation patterns and evidence that the Mn^{2+} ions are located at the Bi sites. However, it is necessary to obtain a if we wish to compare the fourth-order terms of the experimental and calculated values.

The effect of the spin-orbit interaction is considered as a part of the perturbation to the free-ion Hamiltonian. However, the spin-spin interaction is neglected because its contribution to the spin-Hamiltonian parameters is much smaller than that due to the spin-orbit interaction (Sharma *et al* 1966, 1967, Sharma 1968). In rhombic symmetry, the ZFS parameters D and E are expressed as (Yu and Zhao 1987b, 1988)

$$D^{(4)}(\text{SO}) = (3\zeta^2/70P^2D)(-B_{20}^2 - 21\zeta B_{20} + 2B_{22}^2) \\ + (\zeta^2/63P^2G)(-5B_{40}^2 - 4B_{42}^2 + 14B_{44}^2) \quad (2)$$

$$E^{(4)}(\text{SO}) = (\sqrt{6}\zeta^2/70P^2D)(2B_{20} - 21\zeta)B_{22} \\ + (\zeta^2/63P^2G)(3\sqrt{10}B_{40} + 2\sqrt{7}B_{44})B_{42} \quad (3)$$

where $P = 7B + 7C$, $G = 10B + 5C$ and $D = 17B + 5C$, B and C being the Racah parameters. Since the first-, second-, third- and fifth-order perturbations of D and E are zero, only the fourth-order perturbation is considered. The sixth-order term is so small that it is usually negligible. The formula of the fourth-order ZFS parameter F is given by Yu (1990).

The two-particle operator parameters B and C describe electron–electron repulsion. By considering the covalency effect and by introducing the average covalency parameter N , we can express the Racah parameters B and C in terms of N (Jorgensen 1971, Zhao and Zhang 1983, Zhao *et al* 1987):

$$B = N^4 B_0 \quad C = N^4 C_0 \quad (4)$$

where B_0 and C_0 denote the Racah electrostatic parameters in the free state. Also the spin–orbit coupling would be reduced in a crystal (Zhao and Zhang 1983, Zhao *et al* 1987) i.e.

$$\zeta_d = N^2 \zeta_d^0 \quad (5)$$

where ζ_d^0 is the value in the free state.

The crystal-field parameters B_{kq} are related to the crystal structure. The point-charge model and the superposition model are used to calculate the ZFS parameters for Mn^{2+} at the Bi^{3+} site and the V^{5+} site, respectively.

3.1. Point-charge model

If we consider the point-charge model, the crystal-field parameter can be written as

$$B_{kq} \equiv (-1)^q \sum_i \frac{eq_i \langle r^k \rangle}{R_i^{k+1}} C_q^k(\Theta_i, \Phi_i) \quad (6)$$

$$C_q^k \equiv \sqrt{4\pi/(2k+1)} Y_{kq}$$

where R_i , Θ_i and Φ_i are the spherical coordinates of the i th ligand. The symbols q_i and Y_{kq} are the charge of the i th ligand and the spherical harmonic (Zhao and Yu 1988), respectively. The expectation value $\langle r^k \rangle$ for the d^n ion in a crystal is

$$\langle r^k \rangle = N^2 \langle r^k \rangle_0 \quad (7)$$

where $\langle r^k \rangle_0$ is the value of the free atom.

3.2. Superposition model

The superposition model has been shown to be quite successful in explaining the crystal-field splittings of the $4f^n$ ions (Newman 1970). More recently, this model has been employed to deal with some $3d^n$ ions (Newman *et al* 1978, Shen and Zhao 1984, Yeung and Newman 1986), and the results have been satisfactory.

As an empirical theory, the superposition model expresses the crystal field parameters as (Newman 1970, Yu and Zhao 1988)

$$B_{kq} = \sum \bar{A}_k(R_j) K_{kq}(\theta_j, \phi_j) \quad (8)$$

the summation being taken over all ligands. The coordination factors $K_{kq}(\theta_j, \phi_j)$ are the explicit functions of the angular position of the ligand given in table III of Yu and Zhao (1988). The intrinsic parameter $\bar{A}_k(R)$ is given by the power law (Newman 1970, Yu and Zhao 1988), i.e.

$$\bar{A}_k(R_j) = \bar{A}_k(R_0)(R_0/R_j)^{t_k} \quad (9)$$

where R_j is the distance between the d^n ion and the ligand ion, and $\bar{A}_k(R_0)$ is the intrinsic parameter of the reference crystal. The symbol t_k is the power-law exponent.

4. Analysis and discussion

The Bi^{3+} ion has an eightfold coordination, while the V^{5+} ion has a fourfold coordination bonded with O^{2-} . All bond lengths of $\text{Bi}^{3+}-\text{O}^{2-}$ and $\text{V}^{5+}-\text{O}^{2-}$ are less than approximately 3.5 Å (David 1983). The lengths of the next-nearest ligands around the Bi^{3+} ion are nearly 3.5 Å. Although the Bi^{3+} ion has an eightfold coordination (four nearest and four next-nearest oxygen ions), we considered only the four nearest oxygen ligands given in table III of David *et al* (1979). As can be seen in the following discussion, the crystal-field parameters B_{2q} and B_{4q} are proportional to R_i^{-3} and R_i^{-5} , respectively, according to the point-charge model, and to R_i^{-3} and R_i^{-7} , respectively, according to the superposition model. Furthermore, the formula for D given by equation (2) contains B_{kq}^2 terms. Therefore, the effect of the next-nearest ligand oxygen ions around a Bi^{3+} ion may be neglected. For V^{5+} all four nearest oxygen ligand ions are considered. The crystal structure parameters and bond lengths of Bi-O and V-O of BiVO_4 at 300 K summarized in tables II and III of David *et al* (1979) are used in our calculation.

The following theoretical values for the free Mn^{2+} ion, obtained from the two Slater-type d orbitals, are used (Zhao *et al* 1987):

$$B_0 = 911 \text{ cm}^{-1} \quad C_0 = 3273 \text{ cm}^{-1} \quad \zeta_d^0 = 336.6 \text{ cm}^{-1}. \quad (10)$$

Normalization parameters describing the covalent effect of Mn^{2+} ions which have covalent bonding in Mn-O are employed. The following values are used as the average covalency parameters of two manganese-oxygen bonds (Curie *et al* 1974):

$$\begin{aligned} N &= 0.942 && \text{for MnCO}_3 \\ N &= 0.956 && \text{for CaSiO}_3:\text{Mn}. \end{aligned} \quad (11)$$

4.1. Point-charge model

When the point-charge model with only the nearest neighbours is employed, the crystal-field parameters B_{kq} derived from equation (6) are as follows:

$$B_{20} = eq\langle r^2 \rangle [(3 \cos^2 \theta_1 - 1)/R_1^3 + (3 \cos^2 \theta'_1 - 1)/R_1'^3 + (3 \cos^2 \theta_2 - 1)/R_2^3 + (3 \cos^2 \theta'_2 - 1)/R_2'^3]/2 \quad (12)$$

$$B_{22} = \sqrt{\frac{3}{8}} eq\langle r^2 \rangle [(\sin^2 \theta_1)/R_1^3 + (\sin^2 \theta'_1)/R_1'^3 - (\sin^2 \theta_2)/R_2^3 - (\sin^2 \theta'_2)/R_2'^3] \quad (13)$$

$$B_{40} = eq(r^4)[(35 \cos^4 \theta_1 - 30 \cos^2 \theta_1 + 3)/R_1^5 + (35 \cos^4 \theta'_1 - 30 \cos^2 \theta'_1 + 3)/R_1'^5 + (35 \cos^4 \theta_2 - 30 \cos^2 \theta_2 + 3)/R_2^5 + (35 \cos^4 \theta'_2 - 30 \cos^2 \theta'_2 + 3)/R_2'^5]/8 \quad (14)$$

$$B_{42} = \sqrt{\frac{5}{32}}eq(r^4)[\sin^2 \theta_1(7 \cos^2 \theta_1 - 1)/R_1^5 + \sin^2 \theta'_1(7 \cos^2 \theta'_1 - 1)/R_1'^5 - \sin^2 \theta_2(7 \cos^2 \theta_2 - 1)/R_2^5 - \sin^2 \theta'_2(7 \cos^2 \theta'_2 - 1)/R_2'^5] \quad (15)$$

$$B_{44} = \sqrt{\frac{35}{128}}eq(r^4)[(\sin^4 \theta_1)/R_1^5 + (\sin^4 \theta'_1)/R_1'^5 + (\sin^4 \theta_2)/R_2^5 + (\sin^4 \theta'_2)/R_2'^5]. \quad (16)$$

The following theoretical values for the free Mn^{2+} ion, obtained with the two Slater-type d orbitals (Sharma 1968), are used for calculation:

$$\langle r^2 \rangle_0 = 2.7755 \text{ au} \quad \langle r^4 \rangle_0 = 23.2594 \text{ au}. \quad (17)$$

4.2. Superposition model

The crystal-field parameters B_{kq} can be obtained using the superposition model given by equation (8) and are as follows:

$$B_{20} = \bar{A}_2(R_0)[(R_0/R_1)^{t_2}(3 \cos^2 \theta_1 - 1) + (R_0/R_1')^{t_2}(3 \cos^2 \theta'_1 - 1) + (R_0/R_2)^{t_2}(3 \cos^2 \theta_2 - 1) + (R_0/R_2')^{t_2}(3 \cos^2 \theta'_2 - 1)] \quad (18)$$

$$B_{22} = \sqrt{6}\bar{A}_2(R_0)[(R_0/R_1)^{t_2} \sin^2 \theta_1 + (R_0/R_1')^{t_2} \sin^2 \theta'_1 - (R_0/R_2)^{t_2} \sin^2 \theta_2 - (R_0/R_2')^{t_2} \sin^2 \theta'_2]/2 \quad (19)$$

$$B_{40} = \bar{A}_4(R_0)[(R_0/R_1)^{t_4}(35 \cos^4 \theta_1 - 30 \cos^2 \theta_1 + 3) + (R_0/R_1')^{t_4} \times (35 \cos^4 \theta'_1 - 30 \cos^2 \theta'_1 + 3) + (R_0/R_2)^{t_4}(35 \cos^4 \theta_2 - 30 \cos^2 \theta_2 + 3) + (R_0/R_2')^{t_4}(35 \cos^4 \theta'_2 - 30 \cos^2 \theta'_2 + 3)] \quad (20)$$

$$B_{42} = \sqrt{10}\bar{A}_4(R_0)[(R_0/R_1)^{t_4} \sin^2 \theta_1(7 \cos^2 \theta_1 - 1) + (R_0/R_1')^{t_4} \sin^2 \theta'_1(7 \cos^2 \theta'_1 - 1) - (R_0/R_2)^{t_4} \sin^2 \theta_2(7 \cos^2 \theta_2 - 1) - (R_0/R_2')^{t_4} \sin^2 \theta'_2(7 \cos^2 \theta'_2 - 1)] \quad (21)$$

$$B_{44} = \sqrt{70}\bar{A}_4(R_0)[(R_0/R_1)^{t_4} \sin^4 \theta_1 + (R_0/R_1')^{t_4} \sin^4 \theta'_1 + (R_0/R_2)^{t_4} \sin^4 \theta_2 + (R_0/R_2')^{t_4} \sin^4 \theta'_2]/2. \quad (22)$$

The parameters t_2 , t_4 , $\bar{A}_2(R_0)$ and $\bar{A}_4(R_0)$ based on the superposition model in a $BiVO_4$ single crystal have not been determined yet. However, these may be obtained from other crystals having similar $Mn^{2+}-O^{2-}$ bonds (Yu and Zhao 1987a, Yu 1990). Usually $\bar{A}_2(R_0)$ is in the range 4000–5000 cm^{-1} (Yu and Zhao 1988). For example, the value of $\bar{A}_2(R_0)$ ($= 4703 \text{ cm}^{-1}$) for the $Mn^{2+}-O^{2-}$ bond is in the above range (Siu 1988). Here, we take $\bar{A}_2(R_0)$ to be 4500 cm^{-1} ($R_0 = 2.1 \text{ \AA}$) as in

the work of Yu (1990), which is the average value of the above range. The value of $\bar{A}_4(R_0)$ is taken from the work of Yu and Zhao (1988) on MgO:Mn^{2+} . The values of t_2 and t_4 are taken from the work of Yu (1990). The adopted parameters are

$$\begin{aligned} t_2 &= 3 & t_4 &= 7 & R_0 &= 2.1 \text{ \AA} \\ \bar{A}_2(R_0) &= 4500 \text{ cm}^{-1} & \bar{A}_4(R_0) &= 1005 \text{ cm}^{-1}. \end{aligned} \quad (23)$$

The above parameters for the Mn–O bond are close to the true values and are reasonable for an estimation of the ZFS parameters for $\text{Mn}^{2+}:\text{BiVO}_4$.

The calculated ZFS parameters for the Mn^{2+} centre at the Bi site and the V site, respectively, in the BiVO_4 crystal using the point-charge model are summarized in table 1. The experimental values are also shown in table 1 for comparison. The calculated values of the second-order axial and rhombic terms at the Bi^{3+} site turn out to be very similar to the values obtained from our experiment (Yeom *et al* 1992). On the other hand, the calculated values at the V^{5+} site are about six times the experimental values. The fourth-order term F at the V^{5+} site appears to be more similar to the experimental value than that at the Bi^{3+} site, but the experimental value (Yeom *et al* 1992) was determined without the other fourth-order term a of equation (1). Therefore, the experimental ZFS parameter F may contain substantial uncertainty.

Table 1. Comparison of the ZFS parameters calculated by the point-charge model for the Mn^{2+} centre at the Bi and V sites in a BiVO_4 single crystal with the experimental values.

	Values of ZFS parameter (cm^{-1})				
	Bi site (calculation)		V site (calculation)		Experimental (Yeom <i>et al</i>)
	$N = 0.942$	$N = 0.956$	$N = 0.942$	$N = 0.956$	
D	0.0626	0.0588	0.5517	0.5190	0.0814
E	0.0229	0.0216	0.0984	0.0925	0.0164
F	0.00005	0.00004	0.00200	0.00176	0.00313

The experimentally determined ZFS parameters for an Mn^{2+} centre in BiVO_4 can also be analysed using the superposition model. The calculated ZFS parameters for the Mn^{2+} centre at each site are summarized in table 2. The experimental D - and E -values are more similar to those at the Bi^{3+} site than to those at the V^{5+} site.

Although we considered only the nearest ligand oxygen ions, the calculated ZFS parameters using the point-charge model and the superposition model may be used to identify the site of the Mn^{2+} centre. From the above comparison of the ZFS parameters at each site, we may confirm that the Mn^{2+} ion substitutes for Bi^{3+} . Baran *et al* (1985a) suggested that Mn_1^{2+} replaces the Bi^{3+} ion. Our calculation based on the nearest-point-charge model and the superposition model supports the reported experimental results.

5. Conclusion

The EPR ZFS parameters have been investigated using the nearest-point-charge electrostatic model and the superposition model. These two models give the same

Table 2. Comparison of the ZFS parameters calculated by the superposition model for the Mn^{2+} centre at the Bi and V sites in a $BiVO_4$ single crystal with the experimental values.

	Values of ZFS parameter (cm^{-1})				Experimental (Yeom <i>et al</i>)
	Bi site (calculation)		V site (calculation)		
	$N = 0.942$	$N = 0.956$	$N = 0.942$	$N = 0.956$	
<i>D</i>	0.0348	0.0311	0.9192	0.8137	0.0814
<i>E</i>	0.0075	0.0067	0.1836	0.1625	0.0164
<i>F</i>	0.00004	0.00003	0.00373	0.00306	0.00313

results, namely that the experimental ZFS parameters for the Mn^{2+} ion obtained for a $BiVO_4$ single crystal are more similar to the calculated ZFS parameters at the Bi^{3+} site than to those at the V^{5+} site. A short $Mn^{2+}-O^{2-}$ bond length for the V^{5+} site gives values of the ZFS parameters that are larger than the experimental values. We suggest that the Mn^{2+} ion substitutes for Bi^{3+} in $BiVO_4$. Our result supports the reported proposals derived from experimental data.

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