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Abstract. A further study of the spin-Hamiltonian parameters for the trigonal defect which appears in $Bi_4Ge_3O_{12}$ doped with Mn^{2+} has been made. This allows us to estimate the rotation angle of the cubic field axes and to gain further insight into the neighbourhood of the Mn^{2+} ion.

1. Introduction

In a recent electron paramagnetic resonance (EPR) study of the Mn^{2+} ion in $Bi_4Ge_3O_{12}$ [1] (X band), it has been determined that the Mn^{2+} ion enters the Bi^{3+} trigonal site without local charge compensation. Also, information about the relaxation of the lattice in the neighbourhood of the impurity was obtained by means of Newman's [2, 3] superposition model, which deals with the fine-structure spin-Hamiltonian parameters.

As can be seen in figure 1, the six oxygen ions around the Bi^{3+} site are arranged in a distorted octahedron along the $\langle 111 \rangle$ directions, which are C_3 axes for the Bi^{3+} sites. Moreover, there are two sites, labelled 1 and 2, for the Bi^{3+} ions in $Bi_4Ge_3O_{12}$, which are related by a reflection in a $\{110\}$ plane, and their cubic field axes are rotated by an angle $\pm \alpha = \pm 17.2°$ around the same $\langle 111 \rangle$ threefold axis [4]. The spherical coordinates for site 1 are as follows: $R_a = 2.149$ Å, $\theta_a = 51.39°$ and $\varphi_a = 15.06° + n \times 120°$ ($n = 0, 1, 2$) for the three oxygen ions a; $R_b = 2.620$ Å, $\theta_b = 104.62°$ and $\varphi_b = 84.86° + n \times 120°$ ($n = 0, 1, 2$) for the three oxygen ions b. For site 2 the coordinates are the same except that $\varphi_a = 104.94° + n \times 120°$ and $\varphi_b = 35.14° + n \times 120°$ ($n = 0, 1, 2$).

Therefore, there are eight non-equivalent sets of axes for the Mn^{2+} impurity in the Bi^{3+} site (two for every one of the four $\langle 111 \rangle$ directions or Z axes). Thus, when the magnetic field is in an arbitrary direction, these eight sets of axes give rise to an EPR spectrum which consists of 40 sextets of lines corresponding to the allowed electronic transitions. However, the situation is simplified if the magnetic field lies in a principal plane such as (110), where the lines of the defects at sites 1 and 2 for the [111] direction coincide, as well as those for defects 1 and 2 for the [11$\bar{1}$] direction. Still further simplification results when the magnetic field is along a $\langle 100 \rangle$, $\langle 110 \rangle$ or $\langle 111 \rangle$ direction.
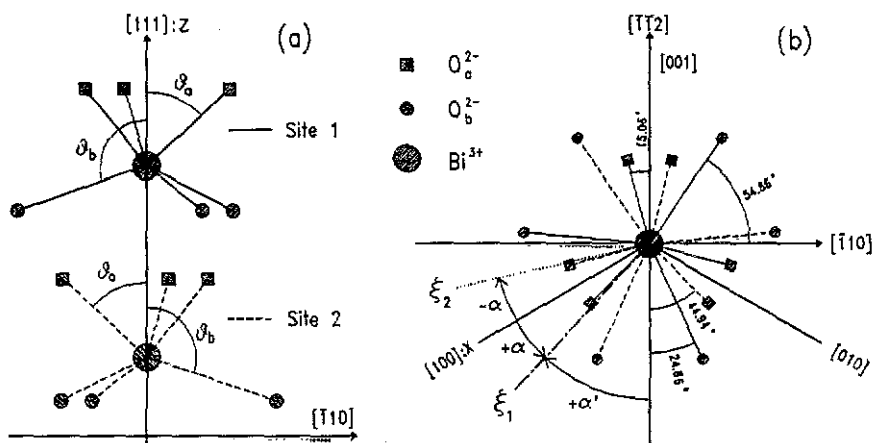
Figure 1. Projections of the coordination of oxygen ions O_a and O_b around two contiguous Bi^{3+} sites 1 (——) and 2 (– – –) along a $\langle 111 \rangle$ direction in $Bi_4Ge_3O_{12}$: (a) projection onto the $(11\bar{2})$ plane; (b) projection onto the (111) plane. In (b) the projections of the $\langle 100 \rangle$ crystallographic axes are also shown, together with the projections of the ξ_1 and ξ_2 cubic crystal field axes for sites 1 and 2, respectively. See text for explanation of the angles α and α', and for the spherical coordinates of the oxygen ions.

According to the above considerations, the appropriate spin Hamiltonian to analyse this trigonal defect is ($S = \frac{5}{2}, I = \frac{5}{2}$)

$$\hat{\mathcal{H}} = g_\parallel \beta H_Z \hat{S}_Z + g_\perp \beta (H_X \hat{S}_X + H_Y \hat{S}_Y) + \tfrac{1}{6}a\{\hat{S}_\xi^4 + \hat{S}_\eta^4 + \hat{S}_\zeta^4 - \tfrac{1}{5}S(S+1)[3S(S+1)-1]\}$$
$$+ D[\hat{S}_Z^2 - \tfrac{1}{3}S(S+1)] + \tfrac{1}{180}F[35\hat{S}_Z^4 - 30S(S+1)\hat{S}_Z^2 + 25\hat{S}_Z^2$$
$$- 6S(S+1) + 3S^2(S+1)^2] + A_\parallel S_Z \hat{I}_Z + A_\perp (S_X \hat{I}_X + S_Y \hat{I}_Y) - g_n \beta_n \boldsymbol{H} \cdot \hat{\boldsymbol{I}}$$

$$(1)$$

where X, Y, Z is the defect axes system ($Z \| \langle 111 \rangle$) and $\xi \eta \zeta$ are the axes for the fourth-order cubic crystal-field term, which are different for the two sites 1 and 2 along the same $\langle 111 \rangle$ direction. This situation produces a splitting of the lines corresponding to these two sites in the EPR spectrum for an arbitrary orientation of the magnetic field. Other common expressions for the spin Hamiltonian use the parameters B_n^m or b_n^m ($D = 3B_2^0 = b_2^0, a = (9/\sqrt{2})B_4^3, F - a = 180B_4^0, b_4^m = 60B_4^m$).

In the previous work [1], it was determined that the oxygen ligands strongly relax around the Mn^{2+} ion. In fact, there are small ranges in which the possible values of their spherical coordinates R and θ must lie: $R_a = 2.1 \pm 0.05$ Å, $R_b = 2.2 \pm 0.1$ Å, $\theta_a = 55 \pm 5°$ and $\theta_b = 125 \pm 9°$. Therefore, it was concluded that the neighbourhood tends to form an almost regular octahedron of MnO_6^{10-}. These coordinates for the six oxygen ions were obtained from the experimental values of the isotropic contribution (A_{iso}) to the hyperfine interaction of Mn^{2+} and those of the fine-structure parameters b_2^0 and b_4^0 which were analysed by means of Newman's superposition model in [1].

The EPR spectra studied in [1] show a strong overlapping of the lines (which have a peak-to-peak width of about 20 G). This makes it impossible to follow the whole angular variation of the EPR spectrum. Thus, the rotation angle $\pm \alpha$ of the cubic field axes could not be determined experimentally, such as has been done for the Gd^{3+} ion in $Bi_4Ge_3O_{12}$

[4, 5] according to the method first used by Geschwind [6]†. Therefore, the value obtained for B_4^3 in the previous study [1] must be regarded as an 'effective value' B_4^3 ($\alpha = 0°$), because it was determined by considering that the axes of the crystal-field term $B_4^3 O_4^3$ are not rotated around the $\langle 111 \rangle$ threefold axis, i.e. the cubic field axes were assumed to be coincident with the $\langle 100 \rangle$ crystallographic axes ($\alpha = 0°$).

In this work a further study has been made which allows us to obtain an estimation of the angle α and thus the true value of B_4^3. This also gives further insight into the neighbourhood of the Mn^{2+} ion in Bi$_4$Ge$_3$O$_{12}$.

2. Estimation of the angle α and the true value of B_4^3

First of all, we shall describe the method for obtaining the value of B_4^3 as a function of the angle α considered and of the measured B_4^3 ($\alpha = 0°$). For this purpose, we use the perturbative expressions for the resonant fields of a 3d^5 ion in an axially distorted cubic field, given by Bleaney and Trenam [7]. In these expressions we consider only the first-order contribution to the position of the resonance lines, because in our case the second-order corrections due to the $B_4^m O_4^m$ terms are negligible.

The first-order contribution to the $|\pm \frac{5}{2}\rangle \rightarrow |\pm \frac{3}{2}\rangle$ resonance lines is given by $2D(3\cos^2\theta - 1) + 2pa + (q/6)F$, where $D = 3B_2^0 = b_2^0$, $a = (9/\sqrt{2})B_4^3$ and $F - a = 180B_4^0$ ($b_4^m = 60B_4^m$) are the fine-structure parameters and θ is the angle between the magnetic field and the $\langle 111 \rangle$ trigonal axis. The angular factors are $q = 35\cos^4\theta - 30\cos^2\theta + 3$, $p = 1 - 5\varphi$ ($\varphi = l^2m^2 + m^2n^2 + n^2l^2$) and (l, m, n) are the director cosines of the magnetic field in the $\xi\eta\zeta$ cubic axes of the crystalline field.

The contribution to first order from the fourth-order terms is $2pa + (q/6)F$ and both terms depends on α. This can be expressed as

$$2pa + (q/6)F = (2p + q/6)a + (q/6)(F - a) = (9/\sqrt{2})(2p + q/6)B_4^3 + 180(q/6)B_4^0$$

(2)

where the term with B_4^0 does *not* depend on α. Therefore, for a given value of θ (q fixed), different values of the angle α (which imply different sets of cubic axes) provide different values of B_4^3 since the value of p changes. In the previous work [1] the value of the parameter a was determined to be $a = (11.5 \pm 1.3) \times 10^{-4}$ cm^{-1}, i.e. $B_4^3 = (1.8 \pm 0.2) \times 10^{-4}$ cm^{-1}, *by assuming that* $\alpha = 0°$. Then, what has actually been obtained is the quantity $(9/\sqrt{2})[2p(\alpha = 0°) + q/6]B_4^3(\alpha = 0°)$, where $p(\alpha = 0°)$ is the value of p for $\alpha = 0°$. Therefore, for different values of α the following relation is obtained:

$$\frac{[2p(\alpha = 0°) + q(\theta)/6]}{[2p(\alpha) + q(\theta)/6]} = \frac{B_4^3(\alpha)}{B_4^3(\alpha = 0°)}$$

(3)

which can be used to calculate the true value of B_4^3 if one knows the correct value of α. Moreover, when the magnetic field lies in a {110} plane the 'effective' value of B_4^3 does not depend on the angle θ, but only on the value of α through equation (3). We have taken into account only the expressions for the $|\pm \frac{5}{2}\rangle \rightarrow |\pm \frac{3}{2}\rangle$ resonance lines, although

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† It is to be noted that the X, Y, Z set of axes used by Fisher and Waldner [4] is different from that used in this work. Here we have taken the same convention as used by Geschwind [6], i.e. the X axis is the projection of the [100] crystallographic axis in the (111) plane (see figure 1). Moreover, the angle used in [4], that we label α' in figure 1, is related to our angle α by $\alpha' = 60° - \alpha$. Thus, the case $\alpha = 0°$ corresponding to a set of cubic axes coincident with the crystallographic axes, is the same as $\alpha' = 60°$ for the set used in [4].

the same results can be obtained by using the first-order perturbative expressions for the $|\pm\frac{3}{2}\rangle \rightarrow |\pm\frac{1}{2}\rangle$ resonance lines.

The next step deals with the value of the angle α. This angle of rotation of the cubic field axes can be evaluated from the positions of the six oxygen ions by using a point-charge model (PCM) [4]. The angle α(PCM) = 17.2° for the Bi^{3+} site (see figure 1) has been obtained from the positions of nuclei known from neutron diffraction data [4]. However, for the case of the Gd^{3+} ion in the Bi^{3+} site [4, 5] the angle α(EPR) = 22.4° directly measured by EPR is somewhat different. This change has been interpreted by Fisher and Waldner [4] as due to deformations of the surroundings of the impurity. Therefore, in the case of Mn^{2+}, a change in the value of α is also expected, because the surroundings of this ion have been proved to relax considerably [1].

In order to estimate the value of α and the true value of B_4^3, the calculation procedure is as follows. First, we obtain the value of B_4^3 by means of the superposition model [1] from a set of values of R_a, R_b, θ_a, θ_b (included in the intervals given above) and one value of φ_a close to that of the perfect lattice†. Second, the value of α(PCM) is calculated for the same set of spherical coordinates by the PCM method [4] and the value of B_4^3 is obtained again with (3). Next, φ_a is varied until the values of B_4^3 calculated by both methods coincide. This provides a consistent solution for φ_a, α and B_4^3. The process is repeated, by scanning the intervals for R_a, R_b, θ_a, θ_b given above, to obtain the valid intervals for φ_a, α and B_4^3. The results are $\varphi_a = 10.1 \pm 2.0°$, $\alpha = 14.4 \pm 1.3°$ and $B_4^3 = (2.5 \pm 0.3) \times 10^{-4}$ cm^{-1}.

This value of B_4^3 must be more correct than $B_4^3 = 1.8 \times 10^{-4}$ cm^{-1} given in [1], because the new value is consistent with that provided by the superposition model. Moreover, the value obtained for α ($=14.4°$) is very reasonable; it is even less different from the value α(PCM) = 17.2° for the perfect lattice, than the value $\alpha(Gd^{3+})$ = 22.4° measured by EPR for Gd^{3+} [4].

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† We consider that the difference $\varphi_a - \varphi_b$ between the azimuthal angles for the oxygen ions a and b remains constant when Mn^{2+} substitutes for Bi^{3+}.