ELECTRON PARAMAGNETIC RESONANCE AND SUPERPOSITION MODEL ANALYSIS OF ZERO FIELD SPLITTING FOR Mn^{2+} IN DOUBLE NITRATES

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Electron paramagnetic resonance of Mn^{2+} in $\text{La}_2\text{Zn}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ single crystals is studied at ≈ 9.45 GHz. Mn^{2+} substitutes for Zn^{2+} sites. The spin-Hamiltonian parameters are evaluated at ≈ 290 K. The superposition model has been applied to the zero-field splitting parameter D for Mn^{2+} in $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ and $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{D}_2\text{O}$ at both sites. It is shown that the calculated values of D are in agreement with the experimental values if local relaxation effects are taken into account.

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1. Introduction

Since the electron paramagnetic resonance (EPR) of Mn^{2+} is easily detectable even at room temperature, many EPR investigations result in the determination of zero-field splitting (ZFS) parameters. In most of these systems Mn^{2+} ions were coordinated by oxygens and the ZFS parameter D is quite sensitive with respect to small structure changes. The calculations of ZFS follow two lines [1]. In the first which is referred to as *ab initio* calculations, ZFS is generally reckoned using an electrostatic model of the crystal field, together with one or more of the splitting mechanisms. The second method of estimating ZFS is by the empirical superposition model (SPM) [2]. SPM has been applied to understand the ZFS of Mn^{2+} and to gain some useful information on the crystalline environment of these ions in a number of crystals [1]. This paper describes the EPR studies of Mn^{2+} in $\text{La}_2\text{Zn}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ (LZN) single crystals at 290 K and SPM analysis of the ZFS parameter D of Mn^{2+} has been described in isomorphous $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ (CMN) and $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{D}_2\text{O}$ (DLMN).

2. Crystal structure

The crystal structure of CMN [3], $\text{La}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$ (LMN) [4] and DLMN [5] isomorphous with LZN has been studied. The primitive cell containing one formula unit is rhombohedral. For CMN, lattice constant $a = 1.3165$ nm and $\alpha = 49.37^\circ$ [3]. The space group is $R\bar{3}$. The unit cell contains three divalent ions situated at two different lattice sites with the point symmetry C_{3i} (site I) and the other two divalent ions occupy lattice sites with the point symmetry C_3 (site II). The divalent ions are surrounded by six water molecules forming with the central ion a nearly octahedral complex. Each trivalent ion is coordinated with 12 oxygens belonging to six nitrate ions, located at the corners of a somewhat irregular icosahedron.

3. Experimental

Single crystals of LZN were grown at room temperature (≈ 290 K) by slow evaporation of an aqueous solution. Mn^{2+} was introduced into the host lattice by adding (0.2 wt%) manganese nitrate. The crystal grows in flat hexagonal plates, the plane of which is perpendicular to the trigonal axis. The EPR experiments were performed on a JEOL FE-3X homodyne spectrometer operating at ≈ 9.45 GHz equipped with a TE_{011} cylindrical cavity and 100 kHz field modulation. A speck of powdered DPPH used as a field marker (taking $g_{\text{DPPH}} = 2.0036$) was inserted simultaneously into the sample cavity. The crystals were mounted on quartz rods. The angular variation studies were done using a JES-UCR-2X sample angular rotating device.

4. Results and discussion

For an arbitrary orientation of the crystal the EPR spectrum consists of a number of lines corresponding to allowed and forbidden transitions. Angular variation studies of Mn^{2+} spectra reveal the presence of two inequivalent Mn^{2+} centres of unequal intensity. Mn^{2+} substitutes for Zn^{2+} and shows the spectrum of two Mn^{2+} complexes. The spectrum having greater intensity is due to Mn^{2+} substituting for Zn^{2+} at site II while the spectrum having lower intensity is due to Mn^{2+} at site I. The Mn^{2+} centre occupying the site II is more intense because there are twice as many II sites as I sites. It was found that the principal z axes of two Mn^{2+} complexes are along the trigonal axis (c axis) and x axes perpendicular to the c axis. The spectra of Mn^{2+} showing large ZFS (site I) were measured for various angles of the magnetic field relative to c axis. A $\pi/3$ rotational symmetry of the spectrum was observed when the crystal was rotated about the c axis.

The EPR spectrum of Mn^{2+} for both sites can be described by a spin Hamiltonian of the form [6]

$$\mathcal{H} = \beta_e g_{\parallel} S_z B_z + \beta_e g_{\perp} (S_x B_x + S_y B_y) + D(S_z^2 - 35/12)$$

$$-(7/36)(a - F)[S_z^4 - (95/14)S_z^2 + 81/16]$$

$$+a(\sqrt{2}/36)\{S_z[S_+^3 \exp(-3i\phi) + S_-^3 \exp(3i\phi)] + [S_+^3 \exp(-3i\phi) + S_-^3 \exp(3i\phi)]S_z\} + A_{\parallel}S_zI_z + A_{\perp}(S_xI_x + S_yI_y),$$

where the z axis is parallel to the c axis of the crystal. The symbols have their usual meaning and $S = I = 5/2$ for Mn^{2+} . Using the above spin Hamiltonian, the Mn^{2+} EPR spectra are analysed and the best fit parameters (all ZFS and hyperfine splitting parameters are in units of 10^{-4} cm^{-1}) thus obtained at 290 K, for site I, are: $D = -184(1)$, $a - F = -6(1)$, $A_{\parallel} = -89(1)$, $A_{\perp} = -89(1)$, $g_{\parallel} = 2.003(1)$, $g_{\perp} = 2.005(2)$ and for site II are: $D = 13(2)$, $a - F = 7(1)$, $A_{\parallel} = -89(2)$, $A_{\perp} = -90(2)$, $g_{\parallel} = 2.002(2)$, $g_{\perp} = 2.003(2)$. The signs of the parameters are relative assuming $A_{\parallel}$ to be negative [1]. It is clear that the ZFS parameter D is very different for the two sites indicating that the two sites differ greatly in the crystal field seen by the ions.

Assuming ZFS to be solely due to the distortion of the first coordinate sphere of oxygens of water molecules, the experimental ZFS can be compared with those calculated from the crystal structure data for the pure host compound. SPM allows one such a comparison [1, 2]. SPM is based on two assumptions: (i) ZFS is due to the close neighbour ions and (ii) ZFS is given by a sum of axially symmetric contributions of the i ligands of MX_i unit. The contribution of more distant neighbours as well as interaction between ligands, are ignored. The ZFS parameter D is written as [1, 2]:

$$D = \sum K_2^0(\theta_i, \phi_i) \bar{b}_2(R_i), \quad (1)$$

where $K_2^0 = (3 \cos^2 \theta_i - 1)/2$, the summation runs over all ligands; R_i , θ_i and ϕ_i are the spherical coordinates of the i -th ligand (the paramagnetic ion is placed at the origin). The dependence of $\bar{b}_2(R)$ on metal-ligand distance R can be approximated by

$$\bar{b}_2(R) = \bar{b}_2(R_0)(R_0/R_i)^{t_2}, \quad (2)$$

the exponent $t_2 = 7 \pm 1$ for Mn^{2+} . $R_0 = 0.22 \text{ nm}$ is the reference distance for Mn^{2+} surrounded by six oxygens and $\bar{b}_2 = -0.05 \text{ cm}^{-1}$ [1].

In CMN, Mg^{2+} at site I is surrounded by six water molecules at a distance $R = 0.2058 \text{ nm}$ and at site II is surrounded by two sets of three oxygens of water ligands at distance 0.2056 and 0.2058 nm [3]. The angle θ which Mg-O makes with c axis at site I is 54.10° and for site II are 54.83° and 123.69° . The ZFS parameter D calculated by using (1) and (2) are $-76 \times 10^{-4} \text{ cm}^{-1}$ and $104 \times 10^{-4} \text{ cm}^{-1}$ for site I and II, respectively. The experimentally determined D values for Mn^{2+} doped CMN at site I and II are -188.7 and $19.4 \times 10^{-4} \text{ cm}^{-1}$, respectively [7]. SPM predicts the correct sign for both sites. The calculated value of D for site I is smaller than the experimental value and larger for site II.

In these calculations, the assumption has been made that the crystalline structure in the vicinity of the magnetic ion is unchanged from those of the host lattice. The difference in calculated and experimental values of D may be principal results from the local relaxation. It has been shown that if R (metal-ligand bond distance) is larger than normal Mn-ligand bond distance, the introduction of substitutional Mn^{2+} gives rise to an inward relaxation while the opposite occurs for R smaller than Mn-ligand bond distance [8]. The ionic radii of Mn^{2+} and

Mg²⁺ are 0.080 and 0.066 nm, respectively [9]. Therefore, Mn²⁺ substitution for Mg²⁺ would allow one some expansion of O²⁻ octahedron around Mn²⁺. A movement of oxygen along the *c* axis is assumed such that Mn-oxygen bond length increases from that of the Mg-oxygen. This causes a change in the value of θ . It is found that an increase of about 1.45% in bond length (from 0.2058 to 0.2088 nm) causes the angle θ to change to 53° for site I. An increase of about 0.9% in bond length of Mg(2)-O(2) (from 0.2055 to 0.2073 nm) and Mg(2)-O(3) (from 0.2058 to 0.2076 nm) causes θ to change to 54.24° and 124.39°, respectively. These values of *R* and θ lead to *D* values -187 and $20 \times 10^{-4} \text{ cm}^{-1}$ for site I and II, respectively. Similar SPM analysis has been performed for Mn²⁺ in DLMN. It is shown that deuteration of LMN has no effect on Mn²⁺ parameters [10]. Therefore the *D* values are taken from Mn²⁺ doped LMN [11]. The *D* values of Mn²⁺ at sites I and II are -188.6 and $21 \times 10^{-4} \text{ cm}^{-1}$, respectively. The values of *D* obtained from SPM using structural data [3, 5] are -64 and $108 \times 10^{-4} \text{ cm}^{-1}$ for site I and II, respectively. An increase in bond length, of about 1.63% for Mg(1)-O(1) and about 1.1% for Mg(2)-O(2) and Mg(2)-O(3) gives values of *D* in agreement with the experimental values. Agreement between calculated and experimental values is also obtained for LMN:Mn²⁺ if Mg(1)-O(1) bond length is increased by 1.8% and that of Mg(2)-O(2) and Mg(2)-O(3) by 0.4%. A change of bond lengths of about 3-4 % is observed from EXAFS measurements in KZnF₃, KCdF₃ and CaF₂ doped with Mn²⁺ [8, 12]. SPM analysis for the ZFS parameter *D* of Mn²⁺ in LZN could not be performed because crystal structure has not been determined. However, it is expected that Mn-O bond length in LZN would be larger than Zn-O bond length as the ionic radii of Mn²⁺ is larger than of Zn²⁺ [9]. Therefore, an outward relaxation takes place when Mn²⁺ substitutes for Zn²⁺ in LZN. A comparison of the ZFS parameter *D* in double nitrates indicates nearly the same value for site I [1]. The value of *D* for site II is very different from that of site I but has nearly the same value in various double nitrates [1].

Therefore, it may be concluded that whatever the difference between the structure of double nitrates as regards to lattice parameters and coordinates of ions, the substitution of Mn²⁺ in place of divalent cation forms [Mn(H₂O)₆]²⁺ complexes which have nearly the same configuration irrespective of the double nitrate. This indicates that $(3 \cos^2 \theta_i - 1)/R_i^7$ has nearly the same value for Mn complexes in various double nitrates.

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