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An X- and Q-band Gd^{3+} EPR study of a single crystal of $EuAlO_3$: EPR linewidth variation with temperature and low-symmetry effects

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ABSTRACT

Detailed electron paramagnetic resonance (EPR) studies on a single crystal of Gd^{3+} -doped Van-Vleck compound $EuAlO_3$, potentially a phosphorescent/luminescent/laser material, with the Gd^{3+} ion substituting for the Eu^{3+} ion, were carried out at X-band (9.2 GHz) over the 77–400 K temperature range. They provide new physical results on magnetic properties of the Eu^{3+} ion in a low symmetry environment. The asymmetry exhibited by the variation of the Gd^{3+} EPR line positions for the orientations of the external magnetic field about the Z and X magnetic axes in the ZX plane was ascribed to the existence of low, monoclinic, site symmetry, as revealed by the significant values of the spin-Hamiltonian (SH) parameters b_4^1 and b_4^2 , estimated by fitting all the observed EPR line positions at room temperature for the orientation of the magnetic field in the magnetic ZX plane using a least-square fitting procedure. The temperature dependence of the Gd^{3+} EPR linewidth is interpreted to be due to the “life-time” broadening, caused by dynamical exchange and dipolar interactions between the impurity Gd^{3+} ions and the host Eu^{3+} ions.

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1. Introduction

$RAIO_3$ (R=rare earth) single crystals, characterized by the perovskite structure at and below room temperature, are interesting due to their phosphorescence and luminescence properties [1,2] as well as for their use as laser materials [1]. There exists further interest in perovskite-like compounds because of possessing a structure similar to that of manganites, which exhibit giant magnetostriction. Their peculiarities can be investigated in mixed compounds, where Al ions are partly replaced by Mn [3,4] ions. A detailed electron paramagnetic resonance (EPR) investigation of the Gd^{3+} ion in the isostructural crystal $LaGaO_3$ was recently reported by Vazhenin et al. [5]. Low symmetry effects in Gd^{3+} and Fe^{3+} spectra in $YAlO_3$ were also analyzed with the use of maximum invariant components (MIC) in Ref. [6]. Physical properties of $EuAlO_3$ have not yet been investigated extensively. A preliminary investigation of Gd^{3+} EPR spectra in an $EuAlO_3$ single crystal was carried out by Andronenko et al. [7]. In addition, EPR studies on the Cr^{3+} ion in $EuAlO_3$ have been reported [8], as well as those on Gd^{3+} in the isostructural $LaAlO_3$

and $YAlO_3$ crystals [9,10]. A relevant detailed EPR study of the Gd^{3+} ion in monoclinic $La_2Si_2O_7$ and $LaNbO_4$ crystals, which are also characterized by a low (C_s , and C_2 , correspondingly) point symmetry of the Gd^{3+} ion and exhibit low-symmetry effects, was reported by Misra and Andronenko [11] and Misra et al. [12].

Europium aluminate ($EuAlO_3$) is an insulating Van-Vleck paramagnet, whose paramagnetism is due to the admixture of the levels of the 7F_1 term, split by the orthorhombic crystal field into three singlets (281, 359, and 479 cm^{-1}), in the singlet ground state 7F_0 [13], which by itself is non-magnetic. This admixture makes it paramagnetic, known as Van-Vleck paramagnetism. For a review of the peculiarities of magnetic resonance in Van-Vleck paramagnets, see Aminov et al. [14].

This paper reports a detailed EPR investigation on the Gd^{3+} ion in $EuAlO_3$ single crystal at X-band (9.22 GHz). The EPR spectra are recorded for various orientations of the external magnetic field (\mathbf{B}) in the magnetic ZX plane in the 77–400 K range. [The magnetic Z, X, and Y axes are defined to be those orientations of \mathbf{B} for which the extrema of the allowed line positions ($\Delta M = \pm 1$; M is the electronic magnetic quantum number) occur; of these the maximum splitting of the EPR lines occurs for \mathbf{B} along the magnetic Z-axis, while the minimum splitting of EPR lines occurs for \mathbf{B} along the magnetic Y axis.] Some additional measurements were made at Q-band (36 GHz) and 140 K.

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The EPR data enable one to (i) determine the local symmetry at the site of the Gd^{3+} ion, (ii) estimate accurately the values of all the Gd^{3+} spin-Hamiltonian (SH) parameters in the $EuAlO_3$ single crystal at 77 and 295 K, and (iii) analyze the EPR line broadening due to the dynamical magnetic interactions of the Eu^{3+} host ions with the Gd^{3+} impurity ions.

2. Crystal structure and sample preparation

Single crystals of $EuAlO_3$ were grown by crystallization from a molten solution; they were parallelepipeds of $\sim 2 \times 2 \times 3$ mm³ dimensions. At room temperature, single crystals of $EuAlO_3$ are characterized by the orthorhombic space-group symmetry D_{4h}^{16} . There exists C_5 point symmetry at the Eu^{3+} sites, substituted for by the Gd^{3+} ions. The reflection plane is normal to the c crystallographic axis, which can be considered as a pseudo-two-fold axis. The lattice parameters of $EuAlO_3$ are $a=5.271$ Å, $b=5.292$ Å, and $c=7.458$ Å, the distance between two adjacent Eu^{3+} ions being 3.732 Å, as determined by Geller and Bala [15]. Further refinement of the orthorhombic aluminate structure was carried out by Marezio et al. [16]. The unit cell of $EuAlO_3$ crystal contains four Eu^{3+} ions, located at two sets of magnetically inequivalent sites [17]. Thus, two distinct sets of Gd^{3+} EPR spectra are expected. These sets are reflections of each other in the planes perpendicular to the a and b axes. As a consequence, the Y -axes of these magnetically inequivalent Gd^{3+} ions are coincident, oriented along the c -axis, whereas the Z - and X -axes lie in the ab -plane. A single crystal of $EuAlO_3$ possesses the shape of a thin rectangular plate, with the c -axis being oriented along the larger dimension of the plate. The (0 0 1), (0 1 0), and (1 0 0) faces of the crystal are pseudocubic.

2.1. Synthesis

The $EuAlO_3$ compound was first synthesized in powder form following the standard solid-phase reaction by mixing high-purity (99.9%) Eu_2O_3 and Al_2O_3 compounds in stoichiometric proportions and maintaining the mixture at 1600 °C, which contain trace amounts of Gd^{3+} as impurities. The completion of the reaction was verified by X-ray diffraction and chemical analysis. The crystals were then grown from the melt of this powder in Ar atmosphere. The single crystals may exhibit twinning with the following twinning pattern: the c axes are coincident, whereas the a and b axes are transposed. However, no twinning was found in the investigated crystals.

3. Experimental results

The spectra were recorded at 77 K, as well as in the range 120–400 K at X-band frequencies 9.05 and 9.22 GHz, respectively; some additional measurements were made also at Q-band (36 GHz) at 140 K. The X-band EPR spectra of Gd^{3+} : $EuAlO_3$ were recorded on a RE1306 spectrometer, equipped with a liquid-nitrogen gas-flow temperature controller (120–400 K). Two sets of EPR lines from Gd^{3+} ions at magnetically inequivalent sites were observed. The room-temperature (RT, 295 K) and liquid-nitrogen temperature (77 K) Gd^{3+} EPR spectra are shown in Fig. 1(a) and (b), respectively, for the orientation of the magnetic field (\mathbf{B}) along the magnetic Z -axis of one of the magnetically inequivalent Gd^{3+} ions; the allowed transitions $M \leftrightarrow M+1$ for the second magnetically inequivalent Gd^{3+} ion are indicated by Z . Fig. 1(c) shows Gd^{3+} EPR spectrum for $\mathbf{B} \parallel Y$ -, Y' -axes, which are both parallel to the crystallographic c -axis. The Q-band (36 GHz) EPR spectrum is shown in Fig. 1(d) at 140 K for $\mathbf{B} \parallel Z$ -axis. From

Fig. 1(a)–(d), it is seen that additional EPR lines are observed, whose magnetic axes are not coincident with any crystallographic plane of the crystal. They are most likely due to Eu^{2+} ion present as impurity. No further analysis is made here of these lines due to their large linewidth and complexity.

Fig. 2 shows the RT angular variation of Gd^{3+} EPR line positions in $EuAlO_3$ for the orientations of \mathbf{B} in the magnetic ZX -plane. The angle between the b -axis and the magnetic Z -axis for the two magnetically inequivalent Gd^{3+} sites in the ab -plane is $\alpha = \pm(13 \pm 1)^\circ$ in $EuAlO_3$ as seen from Fig. 2; this does not change with temperature. The value of α for Gd^{3+} is very close to 16° for Gd^{3+} : $LaGaO_3$ [5], and it differs considerably from those for Er^{3+} ($\alpha=38^\circ$) and Yb^{3+} ($\alpha=30^\circ$) in $EuAlO_3$ [18,19].

The angular variation of the line positions for the orientations of \mathbf{B} in the ZY magnetic plane was found to be symmetrical about the Z - and Y -axes, unlike that in the ZX -plane, which is not symmetrical about the Z and X axes. It is seen from Fig. 2 showing the angular variation of line positions for the orientation of \mathbf{B} in the ZX -plane that the extrema of the line positions for \mathbf{B} about the X -axis for the various EPR transitions are non-coincident and non-symmetrical about the magnetic Z - and X -axes. This indicates monoclinic symmetry at the Gd^{3+} sites.

4. Spin-Hamiltonian parameters

The asymmetry of line positions about the Z - and X -axes in the angular variation of Gd^{3+} EPR line positions in the ZX -plane reveals the existence of a monoclinic symmetry at the Gd^{3+} sites. The low-symmetry effects for C_5 point symmetry were discussed in Refs. [20,21], pointing out the similarity of C_2 (real two-fold axis) and C_5 (pseudo-two-fold axis). Therefore, the observed EPR spectra are described by the following SH, as discussed by Misra and Rudowicz [22] and by Misra [21] for $C_5 \parallel Y$ -axis:

$$\begin{aligned} \mathcal{H} = & \mu_B [g_z S_z B_z + g_x S_x B_x + g_y S_y B_y + g_{xz} (S_x B_z + S_z B_x)] \\ & + \sum_{m=0,1,2} (1/3) b_2^m O_2^m + \sum_{m=0,1,2,3,4} (1/60) b_4^m O_4^m \\ & + \sum_{m=0,1,2,3,4,5,6} (1/1260) b_6^m O_6^m \end{aligned} \quad (1)$$

In Eq. (1), μ_B is the Bohr magneton; g_z , g_x , and g_y are the diagonal elements of the g -matrix, g_{xz} is the only nonzero off-diagonal element of the g -matrix, and S ($S=7/2$) is the electron spin operator for the Gd^{3+} ion; b_n^m are the ZFS parameters; and the O_n^m are the operator equivalents as defined by Abragam and Bleaney [23], whose matrix elements are listed by Misra [21], including those with negative m , which were not included in Abragam and Bleaney [23]. The notion of extended Stevens operators, i.e. full set of operator equivalents O_n^m , was first introduced in Ref. [24]; for a review of other operators used in EMR, see Refs. [21,25,26].

Three different orientations of the axes, with their symmetry axes (C_5 , C_2) being parallel to the X , Y , and Z magnetic axes lead to three different spin Hamiltonians. The corresponding non-zero SH parameters were discussed in Refs. [22,29], and later used for the interpretation of low-symmetry effects in Ref. [30]. In the present case of $EuAlO_3$, the Y -axis has been chosen to be that direction of the magnetic field for which the extrema of the line positions occur for the same direction of the magnetic field. The Z -, X -axes are then in the plane perpendicular to it, which is the a - b plane. Further, the Z -axis has been chosen to be such that $b_2^m/b_2^0 \leq 1$. Thus, the other two extrema of the line positions, which are slightly non-coincident, lie very close to the principal Z - and X -axes of the D -tensor, as discussed in [30]. The C_5 -axis in $EuAlO_3$ has here been chosen to be parallel to the Y -axis, so that only those b_n^m , where $m (\leq n)$ are odd and positive and n are 2, 4, and 6,

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