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Gd³⁺ EPR study of phase transitions in a NH₄Eu(SO₄)₂·4H₂O single crystal: a superposition-model calculation of zero-field splitting parameters

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Abstract. Detailed X-band EPR studies of the Gd³⁺ ion have been carried out in a europium ammonium sulphate single crystal between liquid-helium and room temperature. The behaviours of the overall splitting of EPR lines and the EPR linewidth indicate the occurrences of two first-order phase transitions at 273±0.5 and 166±0.5 K, respectively. The spin-Hamiltonian parameters for Gd³⁺ at room temperature have been evaluated. The intrinsic parameter \bar{b}_2 for Gd³⁺ in NH₄Eu(SO₄)₂·4H₂O crystal has been calculated by the use of the superposition model of Newman, and found to be -5.802 GHz, with the exponent $t_2 = 9.0$.

1. Introduction

The tetrahydrate rare-earth ammonium sulphate compounds, NH₄R(SO₄)₂·4H₂O (R = rare earth) exhibit phase transitions below room temperature (RT). They form a series of isostructural compounds (R = La, Ce, Pr, Nd, Sm, Eu, Gd and Tb). EPR studies on Gd³⁺-doped NH₄R(SO₄)₂·4H₂O (R = Ce, Sm, Nd, Pr and La; hereafter, ACST, ASST, ANST, APST and ALST, respectively) have been recently reported (ACST—Malhotra *et al* (1980), ASST—Buckmaster *et al* (1981), ANST—Misra *et al* (1990a), APST—Misra and Sun (1990b), and ALST—Misra and Li (1990)).

No phase-transition study by any technique has so far been reported on NH₄Eu(SO₄)₂·4H₂O (hereafter AEST). It is the purpose of the present paper to report a detailed variable-temperature X-band EPR study on a Gd³⁺-doped AEST single crystal between LHT (liquid helium temperature) and RT, with particular emphasis on the study of the phase transitions undergone by the AEST single crystal below RT. In addition, an explanation will be given of the zero-field splitting parameters, b_2^0 and b_4^0 , of Gd³⁺ based on the superposition model.

This paper is a sequel to the report published by Misra and Li (1990) on the Gd³⁺-doped ALST single crystal, which describes the motivation and other details of the present study. Thus, details of coordination of the Eu³⁺ ion with the surrounding oxygens, coordination polyhedra, crystal preparation, experimental arrangement, room temperature spectra, spin-Hamiltonian, evaluation of spin-Hamiltonian parameters and the superposition-model calculation of the intrinsic parameters are the same as those described by Misra and Li (1990).

Single crystals of AEST are monoclinic (space group C_{2h}^5) (Eriksson 1972), containing four formula units in the unit cell, with the parameters: $a = 0.6568$ nm, $b = 1.8833$ nm, $c = 0.8727$ nm, and $\beta = 96.98^\circ$. The positions of the four Eu^{3+} ions in the unit cell are at $(0.5, 0.1303, 0.0)$, $(0.5, 0.3651, 0.5)$, $(0.5, 0.6279, 0.5)$ and $(0.5, 0.8618, 0.0)$, which are hereafter referred to as ions 1, 2, 3 and 4, respectively.

2. RT EPR spectra and spin-Hamiltonian parameters

The RT EPR spectra revealed the presence of two magnetically inequivalent (referred to as I and II), but four physically equivalent, Gd^{3+} ions. The ZX planes for the two magnetically inequivalent ions I and II (see below) are coincident ($Z_1 \parallel X_2$ and $Z_2 \parallel X_1$, where the subscripts 1 and 2 refer to the ions I and II, respectively). The two Z axes are parallel to the respective $\text{Eu}^{3+}-\text{O}(4)$ bond axes, making angles of $(51^\circ, 45^\circ, 72^\circ)$ and $(51^\circ, 135^\circ, 72^\circ)$ relative to the (a, b, c) axes of the crystal; the Y axis, which is common to the two inequivalent ions, was determined to lie in the $ac, \{010\}$, plane, at 116° from the a -axis. The equality of the EPR line intensities for the two magnetically inequivalent Gd^{3+} ions indicates that the Gd^{3+} ions substitute with equal preference at the two magnetically inequivalent Eu^{3+} sites.

A spin-Hamiltonian appropriate to the monoclinic symmetry with its twofold axis $C_2 \parallel Z_1$, was found to fit best the Gd^{3+} RT line positions for ion I. It is described as follows using the standard notation (Misra and Wang 1989, Misra and Rudowicz 1988):

$$H = \mu_B [g_{\parallel} B_z S_z + g_{\perp} (B_x S_x + B_y S_y)] + \left(\frac{1}{3} \sum_{m=0, \pm 2} b_2^m O_2^m + \frac{1}{60} \sum_{m=0, \pm 2, \pm 4} b_4^m O_4^m + \frac{1}{1260} \sum_{m=0, \pm 2, \pm 4, \pm 6} b_6^m O_6^m \right).$$

The resulting values of the spin-Hamiltonian parameters for Gd^{3+} ion I at RT are listed in table 1. The value of the parameter α at RT, which determines the admixture of the excited state ${}^6P_{7/2}$ into the ground state ${}^8S_{7/2}$, is also included in table 1.

3. Superposition-model calculation of the intrinsic parameters \bar{b}_2 and \bar{b}_4

The particular results as calculated for AEST, following Newman and Urban (1975) and Misra *et al* (1981), are as follows:

(i) The required crystal data for AEST were estimated from the reported data for the isostructural ASST (Eriksson *et al* 1972) by the use of Vegard's law (Vegard 1921).

(ii) The intrinsic parameter \bar{b}_2 and the corresponding value of t_2 for AEST were calculated to be $\bar{b}_2 = -5.802 \pm 0.011$ GHz and $t_2 = 9.0 \pm 1.0$, where the reference bond distance R_0 was chosen to be 2.353 Å, equal to the $\text{Eu}^{3+}-\text{O}(2)$ length. It is noted that the currently estimated value of b_2^0 for Gd^{3+} in AEST is much smaller than those in some other host crystals (Misra *et al* 1981, Misiak and Misra 1988). This small value can be explained as being due to partial mutual cancellations of the contributions of the various nearest-neighbour ligands of the Eu^{3+} ion to b_2^0 in the superposition-model calculation (Misra and Li 1990).

Table 1. Spin-Hamiltonian parameters for Gd^{3+} in an AEST host crystal as calculated by the use of a least-squares fitting procedure (Misra 1976, Misra and Subramanian 1982) at room temperature. The units of b_l^n are GHz, while the g values are dimensionless. The fit was characterized by the χ^2 value of 0.54 GHz^2 ; the details have been described by Misra and Li (1990). A total of 152 resonant line positions was used simultaneously in the fitting. α is the coefficient that represents the admixture of ${}^6P_{7/2}$ state in the ${}^8S_{7/2}$ state, as determined from $(g_{\parallel} + g_{\perp})/2 = (1 - \alpha^2)g_s + \alpha^2 g_p$, where $g_s (= 2.0023)$ and $g_p (= 1.716)$ are, respectively, Landé factors for Gd^{3+} in the ground and first excited states (Lacroix 1957).

Parameters	values	Parameters	Values
g_{\parallel}	1.9960 ± 0.0003	b_4^{-4}	-0.0101 ± 0.0004
g_{\perp}	1.9967 ± 0.0004	b_6^0	0.0028 ± 0.0001
b_6^0	0.3306 ± 0.0003	b_6^2	0.0055 ± 0.0002
b_2^2	-0.0034 ± 0.0005	b_6^4	0.0182 ± 0.0002
b_2^{-2}	-0.0103 ± 0.0004	b_6^6	0.0252 ± 0.0003
b_4^0	0.0198 ± 0.0003	b_6^{-2}	-0.0478 ± 0.0004
b_4^2	-0.0420 ± 0.0004	b_6^{-4}	-0.0118 ± 0.0001
b_4^4	-0.0112 ± 0.0002	b_6^{-6}	-0.0219 ± 0.0004
b_4^{-2}	0.1290 ± 0.0005	α	0.1427 ± 0.0003

(iii) The value of the exponent t_4 has been estimated to be 19, assuming $\bar{b}_4 = 0.021 \text{ GHz}$ in accordance with ALST (Misra and Li 1990). This value of t_4 is much larger than determined for RF_3 , for which $t_4 = 14$ (Misra *et al* 1981). However, if one considers distortions of the positions of the ligand oxygen ions, which are caused by the substitution of a Gd^{3+} ion for a Eu^{3+} ion, due to the difference in their ionic radii, the resulting t_4 value may be quite different. For example, increases by the same values $\Delta\theta = 0.5^\circ, 1^\circ$ and 3° of all the nine vertical angles θ_i for the oxygen ions, yield the value of t_4 to be 17, 15 and 7, respectively. This implies that an increase in the values of all θ_i by $\Delta\theta = 1.1^\circ$ yields the value $t_4 = 14$.

4. Low-temperature EPR spectra and the phase transitions

The temperature variation of EPR spectrum for $B \parallel Z_1$ (where Z_1 is the magnetic Z -axis in the RT phase for one of the magnetically inequivalent ions), as recorded by lowering the temperature from 295 to 4.2 K, is shown in figure 1. The crystal was cooled slowly to avoid shattering, and to measure accurately the phase-transition temperatures.

It is seen from figure 1, that as the crystal was cooled from 295 K, the overall splitting of the 14-line spectrum due to the two magnetically inequivalent Gd^{3+} ions for $B \parallel Z_1$ increased, the lines broadened, and the intensities of the lines decreased. At $274 \pm 0.5 \text{ K}$ only seven very broad lines were observed. A new spectrum consisting of 14 transitions, associated with a larger overall splitting, appeared below $T_{c1} = 237 \pm 0.5 \text{ K}$, indicating that a first-order phase transition had occurred at T_{c1} . This phase transition at T_{c1} is spread over a temperature range of about 5 K. As the temperature was further decreased, the EPR lines became much better resolved than they were above 274 K. Below 272 K, the overall splitting of the spectrum increased monotonically with lowering temperature, experiencing an abrupt increase in an interval of 4 K above 166 K, the spectrum undergoing a dramatic change at $T_{c2} = 166 \pm 0.5 \text{ K}$. A well-resolved

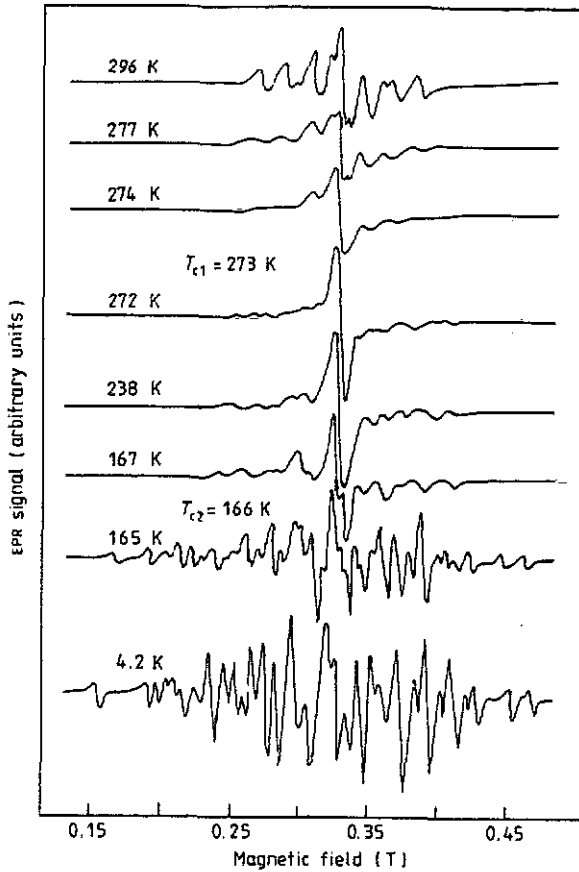


Figure 1. EPR spectra for Gd^{3+} -doped AEST crystal in 4.2–295 K range at different temperatures for $B \parallel Z_1$ (RT phase) with decreasing temperature. Occurrences of two first-order phase transitions at $T_{c1} = 273 \pm 0.5$ K and $T_{c2} = 166 \pm 0.5$ K are clearly seen.

spectrum with considerably narrower and more intense lines was observed below T_{c2} , there being a total of 56 lines corresponding to eight magnetically inequivalent Gd^{3+} ions, indicating that another first-order phase transition had occurred at T_{c2} . It is seen from figure 1, that the two phases above and below T_{c2} coexist over a narrow temperature range of about 2 K. Below 166 K, the overall splitting continued to increase monotonically as the temperature was lowered further; no abrupt changes appeared in the features of the spectrum down to 4.2 K.

The overall splitting of the EPR spectrum of Gd^{3+} ion in AEST, i.e. the separation of the lowest- and highest-field EPR lines, for $B \parallel Z_1$ is plotted in figure 2 as a function of temperature in the 4.2–295 K range. This plot clearly indicates the occurrences of two first-order phase transitions in AEST at $T_{c1} = 273 \pm 0.5$ K and at $T_{c2} = 166 \pm 0.5$ K.

In order to understand the physical mechanisms of the phase transitions, the angular variations of the EPR spectra were recorded for B in the Z_1X_1 -plane (RT phase) at 4.2 and 210 K. On the basis of these, along with the previously reported EPR studies (Misra and Li 1990), the following conclusions can be drawn regarding the

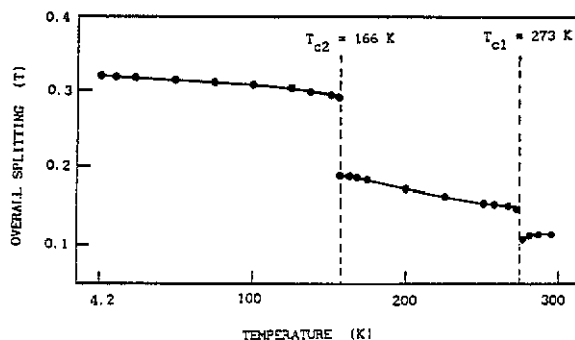


Figure 2. Temperature dependence of the overall splitting of the EPR spectrum of Gd^{3+} ion in AEST, i.e. the separation of the lowest- and highest-field EPR lines, for $B \parallel Z_1$ (RT phase).

phase-transition mechanisms:

(i) Between 166 and 273 K, the angular variation of EPR line positions for B in the ZX plane (RT phase) indicates that there are two extrema of line positions, which occur at those orientations of B which are not separated by 90° , unlike that at RT, corresponding to the two magnetically inequivalent Gd^{3+} ions. This implies that the Eu^{3+} ions still exist in pairs; however, they are no longer symmetrically situated about the RT inversion (ac) plane in this temperature range.

(ii) Between 4.2 and 166 K, the angular variation of EPR line positions for B in the ZX plane (RT phase) exhibits eight maxima, implying the existence of eight magnetically inequivalent sites for the Gd^{3+} ion. This is only possible if the pair equivalence of Eu^{3+} ions is destroyed, and one of the unit-cell size parameters (a, b, c) is doubled, so that there are now eight molecules in the unit cell of the new superstructure.

5. Concluding remarks

The main points of the present study are as follows:

(i) Two first-order phase transitions have been deduced to occur, at 273 ± 0.5 and 166 ± 0.5 K, in the $NH_4Eu(SO_4)_2 \cdot 4H_2O$ crystal between 4.2 K and 295 K. These are the first-ever observations of the phase transitions undergone by an AEST crystal.

(ii) A monoclinic (with the twofold C_2 axis parallel to the magnetic Z axis for Gd^{3+}) spin-Hamiltonian fits best the observed RT Gd^{3+} EPR line positions in AEST at RT. The RT spin-Hamiltonian parameters have been estimated.

(iii) The values of the intrinsic parameters, \bar{b}_2 and \bar{b}_4 , and those of the corresponding exponents, t_2 and t_4 , have been calculated within the framework of the superposition model of Newman.

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