

Gd³⁺ EPR study of structural phase transition in NH₄La(SO)₂·4H₂O single crystal: a superposition-model calculation of zero-field splitting parameters

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1990 J. Phys.: Condens. Matter 2 9613

(<http://iopscience.iop.org/0953-8984/2/48/014>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 11/05/2010 at 07:01

Please note that [terms and conditions apply](#).

Gd³⁺ EPR study of structural phase transition in NH₄La(SO₄)₂ · 4H₂O single crystal: a superposition-model calculation of zero-field splitting parameters

Sushil K Misra and Xiaochuan Li

Physics Department, Concordia University, 1455 de Maisonneuve Boulevard West, Montreal, Quebec, Canada H3G 1M8

Received 19 June 1990

Abstract. An EPR study of a Gd³⁺-doped NH₄La(SO₄)₂ · 4H₂O (ALST) single crystal has been made between liquid-helium and room temperature. The behaviours of the overall splitting of EPR lines and EPR linewidth indicate the occurrence of a first-order phase transition at 201 ± 0.5 K; this is the first-ever report of the phase transition undergone by ALST. The spin-Hamiltonian parameters for Gd³⁺ at a room temperature have been estimated. The intrinsic parameter b_2 for Gd³⁺ in ALST crystal has been calculated, using the superposition model of Newman, to be -4.281 GHz, with the exponent $t_2 = 8.5$.

1. Introduction

The tetrahydrate rare-earth ammonium sulphate compounds NH₄R(SO₄)₂ · 4H₂O (R = rare-earth) are of analytical significance because of their use to separate light and heavy lanthanides (Callow 1967). They are interesting since they exhibit phase transitions below room temperature (RT). They form a series (R = La, Ce, Pr, Nd, Sm, Eu, Gd and Tb) of isostructural compounds (Eriksson *et al* 1974). EPR studies on Gd³⁺-doped NH₄Ce(SO₄)₂ · 4H₂O (hereafter ACST) and NH₄Sm(SO₄)₂ · 4H₂O (hereafter, ASST), between liquid-nitrogen temperature (LNT) and RT, were reported by Malhotra *et al* (1980) and Buckmaster *et al* (1981), respectively. They observed that each of ACST and ASST undergoes three phase transitions between LNT and RT. They evaluated the values of the RT spin-Hamiltonian parameters (SHP) of Gd³⁺ in these crystals, by assuming an orthorhombic site symmetry. No EPR studies have so far been reported on NH₄(La(SO₄)₂ · 4H₂O (hereafter ALST) single crystal. Further, no phase-transition study has been reported on ALST. It is the purpose of the present paper to report a detailed variable-temperature X-band EPR study on a Gd³⁺-doped ALST single crystal between liquid-helium temperature (LHT) and RT, with particular emphasis on the study of the phase transition undergone by ALST crystal below RT, as well as an explanation of the zero-field splitting parameters, b_2^0 and b_4^0 , of Gd³⁺.

2. Crystal structure, sample preparation and experimental arrangement

Single crystals of ALST are monoclinic (space group C_{2h}⁵; Eriksson *et al* 1974), containing four formula units in the unit cell, with the parameters $a = 6.719 \text{ \AA}$, $b = 19.073 \text{ \AA}$, $c =$

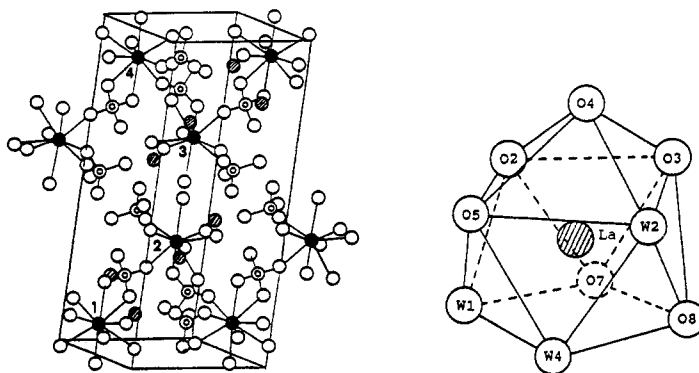


Figure 1. Crystal structure of ALST at room temperature. (a) A stereoscopic view of the unit cell; the La^{3+} ions in the unit cell are marked as 1, 2, 3 and 4. ●: $\text{La}(\text{Gd})$; ○: O or H_2O ; ⊗: NH_4 ; ⊙: S. (b) The coordination polyhedron about the La^{3+} ion; O_n and W_n represent oxygen ions and water molecules, respectively.

8.843 Å and $\beta = 97.45^\circ$. The lanthanum ion is coordinated to nine oxygen ions, of which six belong to sulphate ions and the rest to three waters of hydration. The coordination polyhedron formed by the oxygen ions can be described, either as a distorted-monocapped square anti-prism (C_{4v}), or as a distorted-tricapped trigonal prism (D_{3h}). The positions of the four La^{3+} ions in the unit cell are (0.5, 0.1312, 0.0), (0.5, 0.3677, 0.5), (0.5, 0.6323, 0.5) and (0.5, 0.8678, 0.0); they are labelled as 1, 2, 3 and 4, respectively in figure 1. The La^{3+} ions 1 and 2 form a pair, having the same orientations of the C_{4v} axes of their coordination polyhedra, being related, through the inversion (*ac*) plane, to the other pair of ions 3 and 4.

Single crystals of ALST, doped with Gd^{3+} , were grown at RT by slow evaporation of an aqueous solution of $\text{La}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{SO}_4$, mixed in the molar ratio of 1:4, to which 0.5 wt. % of $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$ was added, along with a few drops of dilute H_2SO_4 to avoid hydrolysis. Gd^{3+} ions substitute for La^{3+} ions in the ALST lattice. The crystals were stored in oil to avoid dehydration. They were white, possessing prismatic shapes; one of approximate size $1.5 \times 2.0 \times 2.5 \text{ mm}^3$ was chosen for the measurements reported here.

The experimental arrangement has been described elsewhere by Misra and Wang (1990).

3. RT, EPR spectra and spin-Hamiltonian parameters

The EPR spectra were recorded at RT for the orientations of the experimental Zeeman field (\mathbf{B}) in the magnetic *zx*, *xy* and *zy* planes, where the *z*, *x*, and *y* are the principal axes of the zero-field splitting tensor, b_2^m , for Gd^{3+} , such that the overall splitting of lines exhibit extrema for $\mathbf{B} \parallel z, x, y$ in decreasing order. In each plane, the orientation of \mathbf{B} was varied at 5° intervals. The spectra revealed the presence of two magnetically inequivalent, but four physically equivalent, Gd^{3+} ions. Each magnetically inequivalent Gd^{3+} ion exhibited seven allowed transitions lines ($\Delta M = \pm 1$, where M is the electronic magnetic quantum number), characteristic of the electron spin $S = \frac{7}{2}$ of Gd^{3+} .

The angular variation of the EPR line positions revealed that the zx planes for the two magnetically inequivalent ions I and II (see below) were coincident; the two z axes were found to be parallel to the respective $La^{3+}-O(4)$ 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 244° from the a axis. (Here the La^{3+} ions refer to those replaced by the Gd^{3+} ions.) Thus, consistent with the RT crystal structure, $z_1 \parallel x_2$ and $z_2 \parallel x_1$, where the subscripts 1 and 2 refer to the ions I and II, respectively. The splitting of EPR lines for $B \parallel y$ was found to be almost the same as that for $B \parallel x$ for any magnetically inequivalent Gd^{3+} ion.

The intensities of the lines belonging to the two magnetically inequivalent Gd^{3+} ions for the orientations of B along their respective z axes were found to be equal, implying that the Gd^{3+} ions substituted with equal preference at the two magnetically inequivalent La^{3+} sites.

Several spin Hamiltonians, appropriate to different sites symmetries (orthorhombic, monoclinic with the twofold axis $C_2 \parallel x_1$, monoclinic with $C_2 \parallel y_1$, and monoclinic with $C_2 \parallel z_1$) were tried to fit the Gd^{3+} RT line positions for ion I, as observed for the orientation of B in the z_1x_1 and x_1y_1 planes. It was found that the best fit, characterized by a much smaller χ^2 -value (defined in the caption of table 1, later) than that obtained for the other spin Hamiltonians, was obtained with the monoclinic spin Hamiltonian with $C_2 \parallel z_1$, described as follows (Misra and Rudowicz 1988):

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

In equation (1), μ_B is the Bohr magneton, g_{\parallel} , g_{\perp} are the spectroscopic splitting factors, b_l^m are the fine-structure spin-Hamiltonian parameters (SHP), and O_l^m are the spin operators as defined by Abragam and Bleaney (1970).

The SHP were evaluated by use of a least-squares fitting (LSF) procedure, employing numerical diagonalization of the 8×8 Gd^{3+} spin-Hamiltonian matrix on a digital computer (Misra 1976, Misra and Subramanian 1982), fitting a total of 131 EPR line positions simultaneously. The resulting SHP values are listed in table 1. The absolute signs of the parameters could not be determined from the present data, since no relative-intensity data are available at LHT; the crystal being in a different phase (see section 5) at LHT. The sign of b_2^0 was, then, assumed to be positive, in accordance with that determined for Gd^{3+} in the RF_3 hosts (Misra *et al* 1981a). The sign of the other fine-structure parameters, b_l^m , relative to that of b_2^0 as determined by the LSF procedure, are correct. The SHPs for ion II are expected to be about the same as those for ion I, since the total spectrum for $B \parallel z_1(x_2)$ is about, but not exactly, the same for $B \parallel z_2(x_1)$.

4. Application of the superposition model

In this section only the b_2^0 and b_4^0 parameters have been considered, since, in order to consider the parameters b_2^m and b_4^m ($m \neq 0$) one needs the exact values of the azimuthal angles (φ_i) for the various ions, which have not been determined experimentally, while the parameters b_6^m are too small to warrant consideration. The details of the superposition-model calculation (Newman and Urban 1975) have been described by Misra *et*

Table 1. Spin-Hamiltonian parameters for Gd^{3+} in the ALST host as calculated using the least-squares fitting (LSF) procedure (Misra 1976) at room temperature. The g values are dimensionless while the units of b_l^m are GHz. The parameter errors are estimated by the use of a statistical method (Misra and Subramanian 1982). The sign of b_2^0 has been assumed to be positive; the relative signs of all b_l^m , as yielded by the LSF procedure, are correct. This fit was characterized by the χ^2 -value of 0.5 GHz^2 ;

$$\chi^2(\text{GHz}^2) = \sum_i (\Delta E_i - h\nu_i)^2$$

where ΔE_i and $h\nu_i$ are, respectively, the calculated and experimental energy differences between the energy levels participating in resonance, the index i covers all the resonant line positions (a total of 131) used simultaneously in the fitting, h is Planck's constant and ν_i is the klystron frequency for the i th line.

Parameters	Values	Parameters	Values
g_{\parallel}	1.9774 ± 0.0004	b_4^{-4}	-0.0032 ± 0.0002
g_{\perp}	1.9772 ± 0.0007	b_6^0	0.0002 ± 0.0002
b_2^0	0.3871 ± 0.0002	b_6^2	0.0340 ± 0.0001
b_2^2	-0.0053 ± 0.0004	b_6^4	-0.0167 ± 0.0003
b_2^{-2}	0.1015 ± 0.0004	b_6^6	-0.0224 ± 0.0002
b_4^0	-0.0087 ± 0.0002	b_6^{-2}	0.0067 ± 0.0002
b_4^2	-0.0066 ± 0.0002	b_6^{-4}	0.0860 ± 0.0002
b_4^4	-0.0321 ± 0.0001	b_6^{-6}	-0.0511 ± 0.0002
b_4^{-2}	-0.0111 ± 0.0004		

al (1981b), to estimate the intrinsic parameters \bar{b}_l and the corresponding exponents t_l defined by the following equations:

$$b_l^m = \sum_i \bar{b}_l(R_i) K_l^m(\theta_i, \varphi_i) \quad (2)$$

where

$$\bar{b}_l(R_i) = \bar{b}_l(R_0)(R_0/R_i)^{t_l}. \quad (3)$$

In equations (2) and (3), $(R_i, \theta_i, \varphi_i)$ are the coordinates for the ligand i , and R_0 is a particular bond length, used as a reference. The K_l^m in equation (2) are angular functions, listed by Misra *et al* (1981b).

For ALST, the summation in (2) is over the nine ligand oxygen ions, which are the nearest neighbours to a Gd^{3+} ion, substituting for a La^{3+} ion, as shown in figure 1(b). The required values of $(R_i, \theta_i, \varphi_i)$ for ALST, whose experimental values have not been reported so far, were estimated from the reported data for the isostructural ASST (Eriksson *et al* 1974) by the use of Vegard's law (Vegard 1921). The intrinsic parameter \bar{b}_2 and the value of t_2 for ALST were calculated from the value of b_2^0 to be $\bar{b}_2 = -4.281 \pm 0.013 \text{ GHz}$ and $t_2 = 8.5 \pm 1.0$, where the reference bond distance R_0 has been chosen to be 2.755 \AA , equal to the length of the $\text{La}^{3+}\text{-O}(4)$ bond. This value of \bar{b}_2 is very close to those calculated for Gd^{3+} in RF_3 ($\text{R} = \text{La, Ce, Pr and Nd}$) ($\bar{b}_2 = -4.457 - (-5.472) \text{ GHz}$) by Misra *et al* (1981b), in the isostructural $\text{NH}_4\text{Nd}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (hereafter ANST) ($\bar{b}_2 = -5.263 \text{ GHz}$) (Misra *et al* 1990a), and in the isostructural $\text{NH}_4\text{Pr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (hereafter APST) ($\bar{b}_2 = -4.85 \text{ GHz}$) (Misra and Sun 1990b) crystals. The t_2 -value for ALST is close to that for ANST ($t_2 = 8.5$) (Misra *et al* 1990a) and

APST ($t_2 = 9.5$) (Misra and Sun 1990b), and RF_3 ($t_2 = 9$) (Misra *et al* 1981b). It is noted that the value of b_2^0 for Gd^{3+} in ALST estimated here is much smaller as compared with those in some other host crystals, e.g. $b_2^0 = 0.7 - 0.8$ GHz for RF_3 (Misra *et al* 1981b) and $|b_2^0| = 2.4 - 2.6$ GHz for $LiYb_xY_{1-x}F_4$ ($x = 0.1 - 1.0$) (Misiak *et al* 1988). The small value for ALST can be explained to be due to partial mutual cancellations of the contributions of the various nearest-neighbour ligands of the La^{3+} ion to b_2^0 in equation (2) in the superposition-model calculation.

The estimation of \bar{b}_4 , whose value is expected to be close to those determined for RF_3 (Misra *et al* 1981b) and for the isostructural ANST (Misra *et al* 1990a) and APST (Misra and Sun 1990b) crystals, i.e., 0.020 GHz, requires that t_4 be equal to 34. This is much larger than was determined for Gd^{3+} in RF_3 , for which $t_4 = 14$ (Misra *et al* 1981a). 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 La^{3+} ion, due to their difference in their ionic radii, the resulting t_4 -value may be quite different. These distortions are not known, so some simple distortions were considered. For example, increases by the same values $\Delta\theta = 1^\circ, 3^\circ$ and 5° of all the nine vertical angles θ_i for the oxygen ions, as depicted in figure 1(b), yield the value of t_4 to be 23, 10 and 3, respectively. This implies that an increase in the values of all θ_i by $\Delta\theta = 2.1^\circ$ yields $t_4 = 14$, which is consistent with those for RF_3 (Misra *et al* 1981b), ANST (Misra *et al* 1990a) and APST (Misra 1990b) hosts.

5. Low-temperature EPR spectra and the phase transition

The EPR spectra for $B \parallel z_1$ (RT phase) in the 3.8–249 K range are shown in figure 2. The crystal was cooled slowly to avoid shattering, and to measure the phase-transition temperature accurately.

It is seen from figure 2 that as the crystal was cooled from RT, 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 202 ± 0.5 K only seven very broad lines were observed. The spectrum underwent a drastic change at $T_c = 201 \pm 0.5$ K. Below T_c , a spectrum with considerably narrower and more intense lines was observed, indicating the presence of eight magnetically inequivalent Gd^{3+} ions in the unit cell. This implies that a first-order phase transition occurred at T_c . The two phases above and below T_c coexist over a narrow temperature range of about 2 K. Below T_c , the overall splitting of the spectrum increased monotonically with lowering temperature; however, no significant changes appeared in the spectrum down to 3.8 K.

In the range of about 4 K below T_c ($= 201$ K), the observed increase in the EPR linewidths, exhibited in figure 3, can be attributed to the fluctuations of the three water molecules, which are coordinated to the Gd^{3+} ion in ALST (Owens 1977). Below T_c , the observed sudden increase in the intensity of the EPR lines is probably due to a decrease in the dielectric constant of ALST at T_c (Owens *et al* 1979), the intensities of EPR lines being inversely proportional to the dielectric constant of the sample. This conforms to the observations of Malhotra *et al* (1980) and Buckmaster *et al* (1981) for the ACST and ASST hosts, respectively.

The overall splitting of the EPR spectrum of Gd^{3+} ion in ALST, for $B \parallel z_1$ (RT), is plotted as a function of temperature (T) in the 3.8–295 K range, in figure 3, which also includes a plot of the linewidths of the transitions designated as A ($T < T_c$) and B ($T > T_c$) in figure 2. The abrupt changes in both the overall splitting of lines and the linewidth confirm the occurrence of a first-order phase transition at $T_c = 201 \pm 0.5$ K.

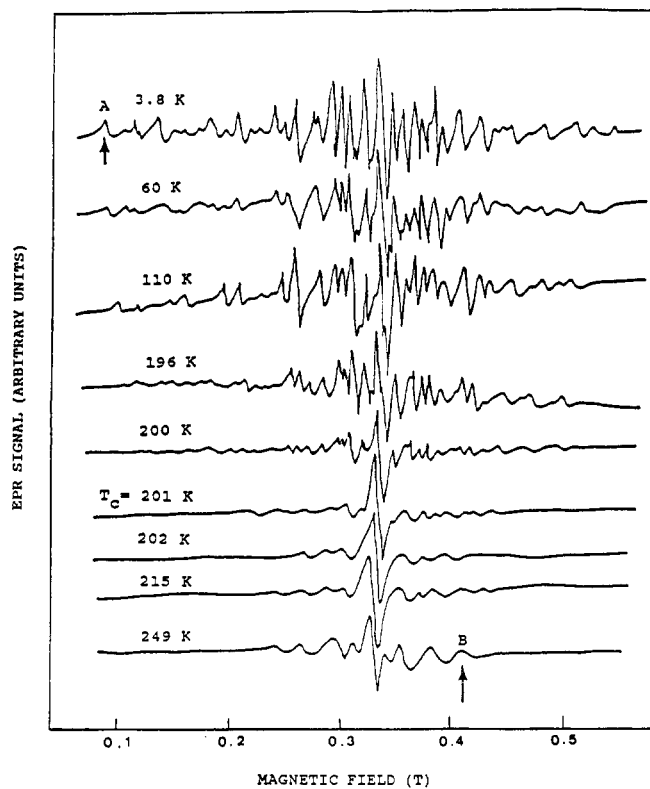


Figure 2. Changes with lowering temperature in the spectrum for $B \parallel z_1$ of Gd^{3+} -doped ALST crystal in 3.8–249 K range. It is clearly seen that above and below $T_c = 201 \pm 0.5$ K the spectra are drastically different, implying the occurrence of a first-order phase transition in ALST at T_c . (The lines A and B are used in figure 3.)

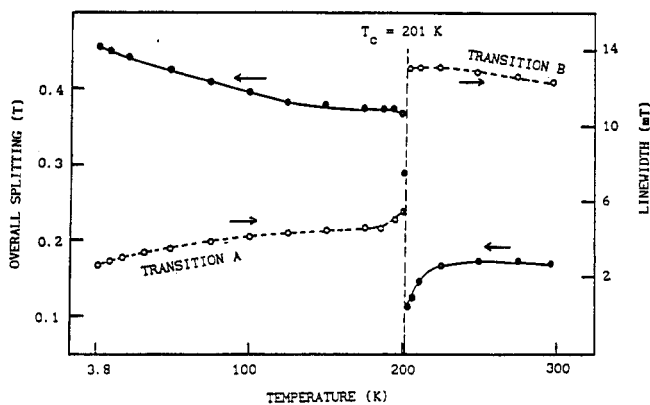


Figure 3. Temperature dependence of the overall splitting (full curves) and linewidth (broken curves) of transition lines A and B, as indicated in figure 2.

It is noted that for each of the isostructural ASST and ACST crystals, three phase transitions were observed in 77–295 K range by Malhotra *et al* (1980) and Buckmaster *et al* (1981). For ANST and APST hosts, three and two phase transitions were observed to

occur, respectively, in the 3.8–295 K range, by Misra *et al* (1990a) and Misra and Sun (1990b). In contrast, only one phase transition has been presently observed for ALST crystal in the 3.8–295 K range.

The angular variation of the EPR spectra, as observed for **B** in the z_1x_1 plane at 3.8 K, indicated the presence of eight sets of Gd^{3+} lines, in turn implying the existence of eight magnetically inequivalent sites at this temperature. This is only possible if the pair equivalence of La^{3+} ions is destroyed below T_c and one of the unit-cell parameters (a , b , c) is doubled, so that there are now eight molecules in the unit cell of the new super structure.

6. Concluding remarks

The main points of the present study are as follows.

(i) Only one, first-order, phase transition has been deduced to occur, at 201 ± 0.5 K, in the $NH_4La(SO_4)_2 \cdot 4H_2O$ crystal between 3.8–295 K. This is the first ever observation of the phase transition undergone by an ALST crystal.

(ii) The spin Hamiltonian that best fits the observed RT Gd^{3+} EPR line positions in ALST, indicate the local site symmetry to be monoclinic, with the twofold C_2 axis parallel to the magnetic z axis for Gd^{3+} .

(iii) The value of the intrinsic parameter \bar{b}_2 , and that of the exponent t_2 , have been calculated within the framework of the superposition model of Newman. The value of the exponent t_4 has been estimated to be 14, assuming $\bar{b}_4 = 0.20$ which is the value for RF_4 , ANST and APST host crystals. This value of t_4 is obtained when one considers a (hypothetical) distortion of $\Delta\theta_i = 2.1^\circ$ for each of the nine ligand oxygens, caused by the introduction of Gd^{3+} in place of La^{3+} in the lattice of ALST.

Acknowledgments

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support (Grant No. OGP0004485), and to the Concordia University Computer Centre for providing their facilities to analyse the data.

References

- Abraham A and Bleaney B 1970 *Electron Paramagnetic Resonance of Transition Ions* (Oxford: Clarendon)
- Buckmaster H A, Malhotra V M and Bist H D 1981 *Can. J. Phys.* **59** 596
- Callow R J 1967 *The Industrial Chemistry of the Lanthanides: Yttrium, Thorium and Uranium* (Oxford: Pergamon)
- Eriksson E, Larsson L O, Niinisto L and Skoglund U 1972 *Inorg. Chem.* **13** 290
- Malhotra V M, Buckmaster H D and Bist H D 1980 *Can. J. Phys.* **58** 1667
- Misiak L E and Misra S K 1988 *Phys. Rev. B* **38** 8673
- Misra S K 1976 *J. Mag. Reson.* **23** 403
- Misra S K, Li X, Misiak L E and Wang C 1990a *Physica B* to be published
- Misra S K, Mikolajczak P and Korczak S 1981a *J. Chem. Phys.* **74** 922
- Misra S K, Mikolajczak P and Lewis N R 1981b *Phys. Rev. B* **24** 3729
- Misra S K and Rudowicz C 1988 *Phys. Status Solidi b* **147** 677
- Misra S K and Subramanian S 1982 *J. Phys. C: Solid State Phys.* **15** 7199

Misra S K and Sun J 1990b *Phys. Status Solidi b* to be published

Misra S K and Wang C 1990 *Phys. Rev. B* **41** 1

Newman J and Urban W 1975 *Adv. Phys.* **24** 793

Owens F J 1977 *Phys. Status Solidi b* **79** 623

Owens F J, Poole C P and Farach H A (ed) 1979 *Magnetic Resonance of Phase Transitions* (New York: Academic) p 303

Vegard L 1921 *Z. Phys.* **5** 17