Electron paramagnetic resonance of Eu^{2+} in the dilute magnetic semiconductor $Pb_{1-x}Eu_xSe$ (x=0.013) with a cubic structure

1995 J. Phys.: Condens. Matter 7 9897

(http://iopscience.iop.org/0953-8984/7/50/022)

J. Phys.: Condens. Matter 7 (1995) 9897–9904. Printed in the UK

Electron paramagnetic resonance of Eu^{2+} in the dilute magnetic semiconductor $Pb_{1-x}Eu_xSe$ ($x = 0.013$) with a cubic structure

Sushil K Misra†, Yongmao Chang†, Vesselin Petkov†, Samih Isber‡, Salam Charar‡, Claude Fau‡, Michel Averous‡ and Zbigniew Golacki§

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

‡ Group d'Etudes des Semiconducteurs, Unité de Recherche associée au CNRS 357, Université-Montpellier II, Place E Bataillon, 34095 Montpellier Cédex, France

§ Institute of Physics, Polish Academy of Sciences, Pl. 02-668, Warsaw, Poland

Received 14 July 1995

Abstract. Detailed X-band (about 9.5 GHz) electron paramagnetic resonance (EPR) measurements were carried out at 295, 77 and 4.2 K on the Eu^{2+} ion in a $Pb_{1-x}Eu_xSe$ single crystal. The values of the spin-Hamiltonian parameters have been determined by a simultaneous fitting of all the EPR line positions recorded for various orientations of the external magnetic field in the [010] plane using a rigorous least-squares fitting procedure. The absolute sign of the zero-field splitting parameter b_4 was determined to be positive from the relative intensities of lines at liquid-helium temperature (4.2 K). The excellent fit of the line positions to a cubic spin Hamiltonian confirms that the site symmetry for Eu^{2+} ions is, indeed, cubic in the $Pb_{1-x}Eu_xSe$ single crystal over the temperature range 4.2–295 K. The Dynosian shape of the EPR lines indicates the metallic nature of the $Pb_{1-x}Eu_xSe$ sample. The nearest-neighbour Eu^{2+}–Eu^{2+} exchange interaction has been estimated to be 20.4 GHz (antiferromagnetic) from the exchange-pair EPR spectrum at 4.2 K. The hyperfine interaction constants for the isotopes ^{151}Eu and ^{153}Eu have been estimated.

1. Introduction

$Pb_{1-x}Eu_xSe$ is a dilute magnetic semiconductor consisting of IV–VI materials. Eu^{2+} ions easily enter the lattice of PbSe with the cubic rock-salt structure, replacing Pb^{2+} ions without charge compensation. Thus, $Pb_{1-x}Eu_xSe$ also possesses the cubic rock-salt structure. This provides an excellent opportunity to study the electron paramagnetic resonance (EPR) of the Eu^{2+} ion in an undistorted environment as the surroundings of Eu^{2+} are often distorted due to charge compensation when it replaces a trivalent rare-earth ion, e.g. La^{3+} in LaF_3 [1]. A magnetization study on Eu^{2+} in $Pb_{1-x}Eu_xSe$ has been reported by Isber *et al* [2]. The purpose of this paper is to present a more detailed EPR study of the Eu^{2+} ion in $Pb_{1-x}Eu_xSe$ over the temperature range 4.2–295 K. It is interesting to study the zero-field splitting of the S-state Eu^{2+} ion and to compare it with that of the Gd^{3+} ion which has not been fully understood as yet [3]. To this end, knowledge of the spin-Hamiltonian parameters determining the zero-field splittings of the two S-state ions Eu^{2+} and Gd^{3+} might provide further insight. To date, not many papers have been published on the EPR of the Eu^{2+} ion, unlike the situation for the Gd^{3+} ion.

0953-8984/95/509897+08$19.50

2. Sample preparation and experimental arrangement

Single crystals of n-type $Pb_{1-x}Eu_xSe$ with a nominal Eu concentration $x = 0.013$ were grown by the use of the well known Bridgman technique, taking into account the fact that the solubility limit of Eu in the PbSe lattice is only about 10%. X-ray diffraction patterns confirmed that the samples, indeed, possessed the face-centred cubic structure. For EPR studies, a parallelepiped-shaped sample with the approximate dimensions 3 mm × 3 mm × 2 mm was chosen, with the longer axis along the (001) direction.

EPR measurements were carried out at 295, 110 and 4.2 K on X-band Bruker spectrometers (model 200D-SRC) with liquid nitrogen (B-VT-2000) and Oxford liquid-helium accessories to produce liquid-nitrogen and liquid-helium temperatures at the sample inside the cavity.

3. Electron paramagnetic resonance spectra

The EPR spectra were recorded for a large number of orientations of the external magnetic field in one of the cubic faces of the crystal, say the [010] plane. Seven 'allowed' fine-structure transitions $M \leftrightarrow M-1 (M = 7/2, 5/2, 3/2, 1/2, -1/2, -3/2, -5/2$, where M is the electronic magnetic quantum number) were clearly observed at 295, 110 and 4.2 K. The spectra did not change appreciably over the range of temperatures investigated, except that the resolution improved considerably at 4.2 K, clearly exhibiting exchange-pair lines and some weak hyperfine lines. The first-derivative EPR spectrum at 4.2 K, for the $\mathbf{B}||(001)$ direction is exhibited in figure 1, the inset of which includes an enlarged version of the central transition $1/2 \leftrightarrow -1/2$ at 3 K, which indicates the presence of weak hyperfine lines.

The angular variation in EPR line positions as observed at 110 K is exhibited in figure 2. The lines appear symmetrically situated about the central allowed fine-structure transition ($1/2 \leftrightarrow -1/2$). A slight deviation of the rotation axis of the crystal from the (010) direction was indicated by a small departure from the symmetry of the observed angular pattern about the angle 45° in figure 2, as verified by comparison with the room-temperature angular variation in EPR line positions when the crystal was rotated around two mutually perpendicular axes.

3.1. Lineshapes

Except for the outermost lines ($\pm 7/2 \leftrightarrow \pm 5/2$) the shapes of all the lines were observed to be Dynosian [4], reflecting the metal-like character (high conductivity) of the sample. Since the outermost lines are most sensitive to the distribution of the parameters b_4 and b_6 over the volume of the sample [5] as compared with the other lines, their Dynosian shapes are smeared out due to the overlap of the lines slightly displaced from each other for these transitions for the various Eu^{2+} ions in the lattice.

4. Spin Hamiltonian and parameters

Eu^{2+} is an S-state (orbital angular momentum $L = 0$) rare-earth ion possessing a $4f^7$ structure, with the electron spin $S = 7/2$ and nuclear spins $I = 5/2$ for each of the two isotopes (^{151}Eu and ^{153}Eu, with natural abundances 48% and 52%, respectively) with non-zero nuclear magnetic moments. The spin Hamiltonian at a site of cubic symmetry for the

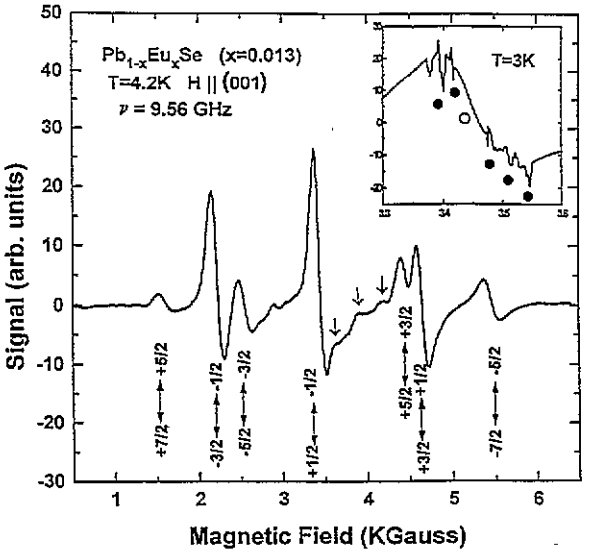

Figure 1. First-derivative EPR spectrum for Eu^{2+} at 4.2 K for the orientation of the external magnetic along the (001) direction. The vertical arrows indicate some of the transition lines between the energy levels of the Eu^{2+}–Eu^{2+} exchange pairs. The inset exhibits amplified spectrum for the central transition at 3 K, exhibiting hyperfine splitting for the two isotopes ^{151}Eu and ^{153}Eu with non-zero nuclear magnetic moments. The full circles below the lines indicate five of ^{151}Eu HF lines (the third expected HF line indicated by an open circle is not resolved). The magnetic field is expressed in units of kilogauss (= 1000 G ≡ 10^{-1} T).

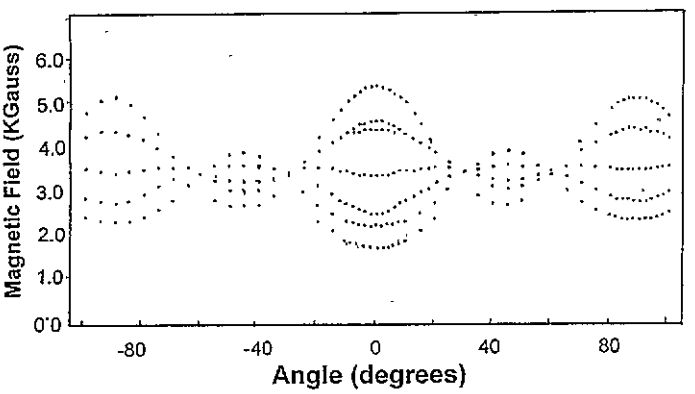

Figure 2. Angular variation at the X band of the EPR line positions for the rotation of the external magnetic field in the [010] plane. A slight misorientation of the rotation plane of B from the [010] plane is responsible for the observed small asymmetry of the rotation pattern about the (101) direction. The magnetic field is expressed in units of kilogauss (= 1000 G ≡ 10^{-1} T).

Eu^{2+} ion is expressed as [5]

$$\mathbf{H} = \mathbf{g}\mu_B \boldsymbol{B}\cdot\boldsymbol{S} + \frac{b_4}{60}(O_4^0 + 5O_4^4) + \frac{b_6}{1260}(O_6^0 + 21O_6^4) + \mathbf{A}\boldsymbol{I}\cdot\boldsymbol{S}. \qquad (4.1)$$

In equation (4.1), $\boldsymbol{B}$ is the external magnetic field, the $\mathbf{g}$ and $\mathbf{A}$ tensors have been assumed to be isotropic, μ_B is the Bohr magneton and O_4^0, O_4^4, O_6^0 and O_6^4 are spin operators as defined by Abragam and Bleaney [5]. The hyperfine structure of the EPR spectrum is

determined by the term $\mathbf{A}\boldsymbol{I} \cdot \boldsymbol{S}$.

All the observed fine-structure line positions for the various orientations of $\boldsymbol{B}$ in the [010] plane were simultaneously fitted to the spin Hamiltonian given by equation (4.1) using a rigorous least-squares fitting (LSF) procedure developed by Misra [6], wherein the required eigenvalues and their derivatives with respect to the spin-Hamiltonian parameters were evaluated on a digital computer using an appropriate subroutine and numerical techniques, respectively.

4.1. Absolute sign of the parameter b_4

As measured at present, the intensity of the highest-field EPR line ($-7/2 \leftrightarrow -5/2$) relative to that of the lowest-field line ($5/2 \leftrightarrow 7/2$) increased from 1.21 to 2.52 as the temperature was lowered from 295 to 4.2 K. This indicates a positive absolute sign for the parameter b_4 [5] as seen from the plot of eigenvalues versus $\boldsymbol{B}$ in figure 3. The absolute positive sign of the parameter b_4 has also been confirmed by the magnetization measurements of Shapira [7] at 30 mK which indicate an abrupt increase in magnetization as the magnetic field is increased. This corresponds to the crossing at about 2000 G of the $M = -7/2$ energy level to lie below the $M = -5/2$ level which was lying the lowest for lower values of B as the external field intensity is increased, increasing abruptly the contribution of the $M = -7/2$ level to the magnetization, which is expected to be almost 100% populated at 30 mK having the lowest energy. Since the LSF procedure enables determination of the correct relative signs of the spin-Hamiltonian parameters, and the absolute sign of the parameter b_4 has been determined to be positive, the signs of all the fine-structure parameters as listed in table 1 should be considered to be absolute. An examination of table 1 reveals that the values of the spin-Hamiltonian parameters g and b_4 do not change significantly between 4.2 and 295 K, within experimental error. In order to account for the slight disorientation of the plane of rotation of the external magnetic field with the [010] plane, a misorientation angle (ϕ), representing the angular deviation of the two planes with respect to each other, was introduced in the fitting. Excellent fits to the spin Hamiltonian given by equation (4.1) were then obtained with the best-fit values of ϕ, confirming the cubic symmetry at the site of the Eu^{2+} ions.

Table 1. The spin-Hamiltonian parameters (SHP) for the Eu^{2+} ion in $Pb_{1-x}Eu_xSe$ crystal at 295, 110 and 4.2 K. n represents the number of lines simultaneously fitted to evaluate the parameters and SMDL is the mean percentage deviation per line of the calculated energy difference of Eu^{2+} energy levels participating in resonance from the klystron frequency. The parameter errors are estimated by the use of a statistical method [11].

	Value at the following temperatures		
SHP	295 K	110 K	4.2 K
g	1.981 ± 0.001	1.975 ± 0.001	1.976 ± 0.001
b_4 (GHz)	0.275 ± 0.005	0.280 ± 0.005	0.278 ± 0.005
b_6 (GHz)	0.003 ± 0.002	0.001 ± 0.002	-0.003 ± 0.002
n	109	118	59
SMDL	0.8	1.0	1.1
α	0.27	0.31	0.30

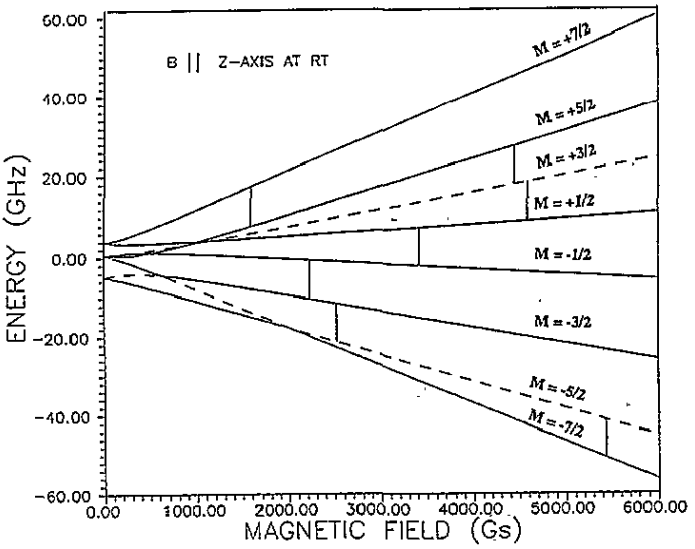

Figure 3. Variation in the eigenvalues calculated for the spin Hamiltonian (4.1) with the parameters evaluated at 295 K (table 1) as functions of the external magnetic field intensity for orientation of the external magnetic field along the (001) direction. The magnetic field is expressed in units of gauss ($\equiv 10^{-4}$ T). The magnetic quantum numbers corresponding to the various eigenvalues at high magnetic fields are indicated.

4.2. Admixture of the excited state ($^6P_{7/2}$) in the ground state ($^8S_{7/2}$) of Eu^{2+}

The g-values as determined at present for Eu^{2+} can be used to estimate the admixture coefficient α of the first excited state $^6P_{7/2}$ in the ground state $^8S_{7/2}$ of the Eu^{2+} ion, as given by Lacroix [8]:

$$g = (1-\alpha^2)g_S + \alpha^2 g_P$$

where $g_S = 2.0023$ and $g_P = 1.716$ are the g-values for the $^8S_{7/2}$ and $^6P_{7/2}$ states, respectively. The estimated values of the admixture coefficients at 295, 110 and 4.2 K which are about 30%, are listed in table 1.

4.3. Hyperfine interaction

The hyperfine-(HF) structure parameter A was estimated from the HF splitting of the lines in the central fine-structure transition $1/2 \leftrightarrow -1/2 (m = 5/2, 3/2, 1/2, -1/2, -3/2, -5/2$, where m is the nuclear magnetic quantum number corresponding to the nuclear spin $I = 5/2$ for each of the isotopes ^{151}Eu and ^{153}Eu), expected to be equal to A between successive HF lines as a first-order approximation. The inset of figure 1 shows the HF structure which is not too well resolved. Taking into account the fact that the magnetic moment of ^{151}Eu is about 2.5 times that for ^{153}Eu with about the same natural abundance, one could identify the sextet of HF lines corresponding to ^{151}Eu. (That for ^{153}Eu is hardly resolved.) From the overall spacing of 145 G, equal to five successive separations of six adjacent HF lines, the HF interaction constant for ^{151}Eu is estimated to be $^{151}A \approx 0.08$ GHz. This would imply the magnitude of the HF interaction constant for ^{153}Eu isotope to be $^{153}A \approx 0.03$ GHz, assuming that $^{153}A/^{151}A = 2.5$, the same ratio as that of the respective nuclear magnetic moments. (It was not possible to determine the absolute sign of A since the HF lines were not well resolved.)

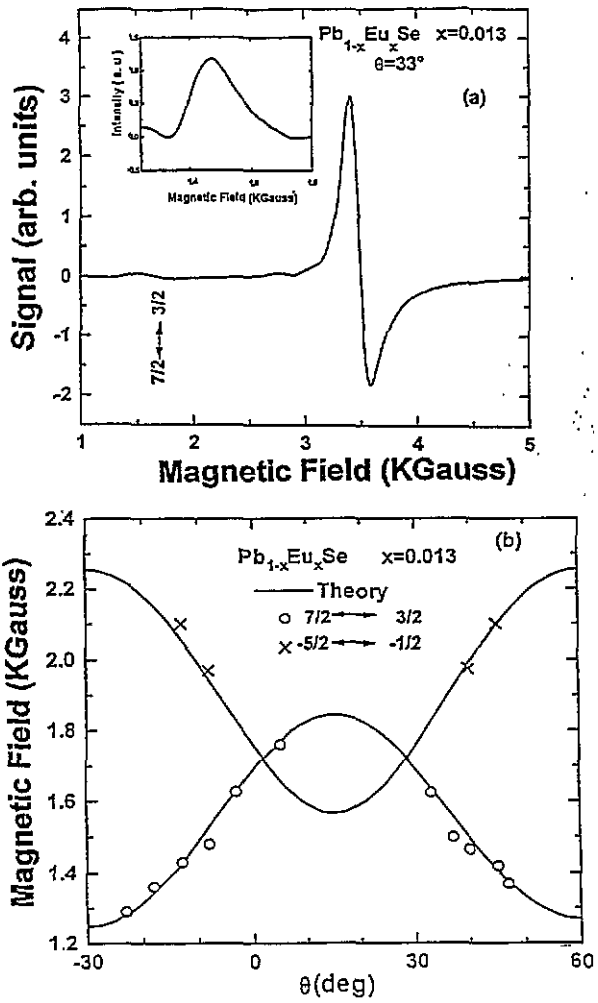

Figure 4. Eu^{2+} forbidden fine-structure transitions: (a) the EPR spectrum for the orientation of B at 33° from the (001) direction in the [010] plane at 4.2 K. The inset amplifies the region around the forbidden transition $7/2 \leftrightarrow 3/2$. (b) Calculated and observed line positions of the forbidden transitions $7/2 \leftrightarrow 3/2$ and $-1/2 \leftrightarrow -5/2$ for different orientations of B in the [010] plane. The magnetic field is expressed in units of kilogauss ($= 1000\ G = 10^{-1}$ T).

5. Electron paramagnetic resonance lines due to Eu^{2+}–Eu^{2+} exchange pairs

It was possible to observe the EPR spectra corresponding to the nearest Eu^{2+}–Eu^{2+} exchange pairs, with the interaction energy $J_p S_1 \cdot S_2$ where S_1 and S_2 refer to the electronic spins of the two Eu^{2+} ions, at liquid-helium temperature (4.2 K). These pairs are expected to have the total spin S_T as obtained from the vector addition of two Eu^{2+} spins (7/2 each), i.e. $S_T = 0, 1, 2, 3, 4, 5, 6, 7$, possessing the energy in an external magnetic field B [9]:

$$E_{ex}(S_T, m_T) = m_T g \mu_B B + J_P[S_T(S_T+1)/2 - S_0(S_0+1)]. \tag{5.1}$$

In equation (5.1), m_T is the magnetic quantum number corresponding to $S_T (-S_T \leqslant m_T \leqslant S_T$ in steps of unity) and $S_0 = 7/2$. Thus, the resonant transition between the pair states

$S_T = 1$, $m_T = -1$ and $S_T = 0$, $m_T = 0$ will occur at the magnetic field

$$B_{pair}(1, 1 \leftrightarrow 0, 0) = (J_P - h\nu)/g\mu_B \tag{5.2}$$

which yields the value of the pair exchange interaction constant J_p to be

$$J_p = h\nu + g\mu_B B_{pair}(1, 1 \leftrightarrow 0, 0). \tag{5.3}$$

In equation (5.3), h is Planck's constant, ν is the klystron frequency and g is the Eu^{2+} g-factor. Noting now that $B_{pair} \approx 3900$ G (figure 1) (at 4.2 K) and $\nu = 9.56$ GHz, one obtains $J_p \approx 20.4$ GHz ($\equiv 0.98$ K) which is close to the value of 21.65 GHz ($\equiv 1.04$ K) as determined from magnetization measurements [2].

It is further noted from equation (5.2) that, if the **g**-tensor is isotropic, there will be no anisotropy in the EPR line positions due to the exchange-pair interaction. Further, these transitions are seen only at 4.2 K; thus it was not possible to observe the temperature dependence characteristic of antiferromagnetically coupled pairs.

6. Forbidden transitions

An attempt was made to observe 'forbidden' fine-structure transitions at 4.2 K. These transitions grow in intensity as the orientation of the external magnetic field deviates from the symmetry axis [10]. As shown in figure 4(a) at an orientation of $\boldsymbol{B}$ at $\theta = 33°$ from the (100) direction the $7/2 \leftrightarrow 3/2$ transition is clearly observed, further supported by theoretical calculations as indicated in figure 4(b), which also contains experimentally observed positions for the forbidden transitions $7/2 \leftrightarrow 3/2$ and $-5/2 \leftrightarrow -1/2$ at various orientations of $\boldsymbol{B}$ in the [010] plane.

7. Concluding remarks

The salient features of the present Eu^{2+} EPR study in $Pb_{1-x}Eu_xSe$ ($x = 0.013$) study are as follows.

(i) The Eu^{2+} site symmetry is cubic.

(ii) The parameters b_4 and b_6 are almost independent of temperature in the range 4.2–295 K.

(iii) The absolute sign of the parameter b_4 is positive.

(iv) The lineshapes are generally Dynosian, confirming the metallic nature of the samples.

(v) The admixture of the $^6P_{7/2}$ state in the ground state $^8S_{7/2}$ is about 30%.

(vi) From the transition line corresponding to the Eu^{2+}–Eu^{2+} pair exchange interaction the value of the nearest-neighbour interaction constant has been estimated to be $J_p = 20.4$ GHz (antiferromagnetic).

(vii) Some $\Delta M = 2$ forbidden transitions have been observed at 4.2 K.

(viii) The magnitudes of the values of HF interaction of the electronic moment of the Eu^{2+} ion with the nuclear magnetic moments of isotopes ^{151}Eu and ^{153}Eu have been estimated.

Acknowledgments

This work was partially supported by the Natural Sciences and Engineering Research Council of Canada (SKM, YC and VP), CNRS, France (SI, SC, CF and MA) and the Polish Committee for Scientific Research (ZG).

References

[1] Misra S K, Fabre F, Frandon J and Mikolajczak P 1984 *Solid State Commun.* **50** 541
[2] Isber S, Charar S, Fau C, Mathet V, Averous M and Golacki Z 1995 *Phys. Rev.* B **52** 1678
[3] Misra S K and Lewis N R 1985 *Phys. Rev.* B **31** 8335
[4] Poole C P Jr 1967 *Electron Spin Resonance: A Comprehensive Treatise on Experimental Techniques* (New York: Wiley–Interscience)
[5] Abragam A and Bleaney B 1970 *Electron Paramagnetic Resonance of Transition Metal Ions* (Oxford: Oxford University Press)
[6] Misra S K 1976 *J. Magn. Reson.* **23** 403
[7] Shapira Y 1994 Private communication
[8] Lacroix R 1957 *Helv. Phys. Acta* **30** 374
[9] Vu T Q, Bindilatti V, Shapira Y, McNiff E J, Agosta C C, Papp J, Kershaw R, Dwight K and Wold A 1992 *Phys. Rev.* B **46** 11 617
[10] Misra S K and Upreti G C 1987 *Magn. Reson. Rev.* **12** 1
[11] Misra S K and Subramanian S 1982 *J. Phys. C: Solid State Phys.* **15** 7199