High frequency (208 GHz) determination of the cubic spin Zeeman term for the U^{3+} ion in the dilute magnetic semiconductor crystals of $Pb_{1-x}U_xTe$ and $Pb_{1-x}U_xSe$ at 5K by Electron Paramagnetic Resonance

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ABSTRACT

A high-frequency (208 GHz) Electron Paramagnetic Resonance (EPR) study on the U^{3+} ion ($5f^3$, $^4I_{9/2}$, $S = 3/2$) embedded with 3% concentration in the dilute magnetic semiconductor crystals of PbTe and PbSe, each characterized by cubic symmetry, has been performed at ~5 K, especially in view to determine the value of the Zeeman cubic spin term parameter u , and the site symmetry of the U^{3+} ion (radius 0.089 nm), substituting for the Pb^{2+} ion (radius 0.119 nm). The experimental spectra reveal the presence of only one set of EPR lines from U^{3+} ions in these host crystals, exhibiting cubic symmetry, whose magnetic axes are oriented along the crystal axes. The spin-Hamiltonian parameters are for both crystals: $g = 1.9811$, $u = -0.0257$.

Keywords: High-frequency EPR, Spin-Hamiltonian Parameters, $Pb_{1-x}U_xTe$ and $Pb_{1-x}U_xSe$ single crystals, U^{3+} ion, Zeeman cubic spin parameter, dilute magnetic semiconductor

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1. Introduction

Dilute magnetic semiconductors are interesting because they can be exploited as spintronic devices. To this end, electron paramagnetic resonance can be a useful tool to explore relevant properties. There have not been reported many EPR studies on the U^{3+} ion; a few of these are in the hosts UCl_3 [1], $LaCl_3$ [2], SrF_2 [3], $LiTmF_4$ [4], and a review on EPR of Uranium ions [5], covering the literature up to 2008. None of these is performed at frequencies higher than 35 GHz, or at temperatures below 20K, except for that reported in [4]. Thus, the EPR spectra for the lowest spin manifold are not clearly resolved, mainly due to the magnetic field not being sufficiently large and also because the spin-lattice relaxation is rather fast to broaden out the EPR lines not to be observed.

The U^{3+} ion possesses $5f^3(4I_{9/2}, S = 3/2)$ configuration. In cubic symmetry, as in $Pb_{1-x}U_xTe$ and $Pb_{1-x}U_xSe$ crystals, the free-ion state $4I_{9/2}$ decomposes in two quartets Γ_8 and a doublet Γ_6 [4]. The doublet Γ_6 is isotropic, unlike the two quartets Γ_8 . The lowest lying multiplet, a Γ_8 quartet, is characterized by the Koster-Statz term of the form uBS^3 [7, 8], which is a Zeeman term cubic in spin S . With the advent of high-field high-frequency EPR spectrometers, it is possible to significantly amplify the effect of the Zeeman terms in the spin-Hamiltonian (SH) on EPR spectra, which are field-dependent. In particular, it then becomes possible to estimate the coefficient, u , of the cubic-spin term. X-band EPR studies of the U^{3+} ion in PbTe were attempted by Isber [9] at room temperature, but no lines were observed due to the very high mobility of carriers in this compound at this temperature.

In this paper, a high-frequency (208 GHz) EPR study of the U^{3+} ion in single crystals of dilute magnetic semiconductors PbTe and PbSe at the liquid-helium temperature of 5 K is reported. The spin-Hamiltonian (SH) parameters are evaluated from a simultaneous fitting of all the observed EPR line positions using the least-squares fitting procedure [10]. The orientations of the magnetic axes with respect to the morphology of the crystal, as well as the symmetry at the site of the U^{3+} ion (radius 0.089 nm), substituting for the Pb^{2+} ion (radius 0.119 nm), which cannot be determined from X-ray diffraction due to the rather insufficient number of the U^{3+} ion in the two host lattices, have been deduced from the EPR line positions.

2. Experimental details

2.1 Crystal preparation and structure

$\text{Pb}_{1-x}\text{U}_x\text{Te}$ and $\text{Pb}_{1-x}\text{U}_x\text{Se}$ ($x \sim 0.03$) crystals were grown by Bridgman technique as reported by Isber *et al.* [11], wherein the trivalent U^{3+} ion (radius 0.089 nm) substitutes for the Pb^{2+} ion, (radius 0.119 nm), which results in charge compensation about the U^{3+} site. Their growth habits are such that some of the edges are parallel to the cubic symmetry axis, with the bright shiny face, depicted by parallel lines, being of the type [100]. Figure 1 shows the growth habit (morphology) of the crystal, in the form of a rectangular parallelepiped, with dimensions ~ 3.5 mm x 1 mm x 1 mm, along with the directions of the cubic x, y and z axes, denoted as first, second, and third orientations.

2.2 Spectrometer and EPR Data

2.2.1 Spectrometer. The 208-GHz EPR spectra were recorded on a home-built spectrometer at the EPR facility of NHMFL (National High Magnetic Field Laboratory, Tallahassee, Florida, USA). The instrument was a transmission-type set up in which microwaves are propagated in cylindrical light pipes. The microwaves were generated by a Virginia Diodes multiplier cascade pumped by a phase-locked source generating a frequency of 13 ± 1 GHz and producing harmonics of which the 4th, 8th, 16th, 24th and 32nd were available. A superconducting magnet (Oxford Instruments) capable of reaching a field of 17 T was employed. The field was calibrated using DPPH, with $g = 2.0037$. The differences between 'calibrated' and 'uncalibrated' fields are 5 – 9 mT. A non-resonant sample holder was used. The transmitted millimetre waves were detected using a liquid-helium-cooled InSb hot-electron bolometer (QMC Ltd., Cardiff, UK). Magnetic field modulation at 40 kHz and ca. 2 mT amplitude was employed. A Stanford SR830 lock-in amplifier was used to convert the modulated signal into a DC voltage.

2.2.2 EPR spectra.

(a) $\text{Pb}_{1-x}\text{U}_x\text{Te}$. Magnetic field sweeps were performed for the magnetic field (**B**) orientations along the three edges of the crystal in the form shown in Fig. 1. A careful examination of the spectra, shown in Fig. 2, revealed that the magnetic axes for the U^{3+} ion are coincident with these edges, for which the line positions are the same, within experimental error, indicating that the site

symmetry about the U^{3+} ion is cubic. (The magnetic axes for a paramagnetic ion are defined to be those directions of the magnetic field for which the spectra show extrema, with the overall splitting being the largest for $\mathbf{B}$ along the magnetic z-axis, and smallest for $\mathbf{B}$ along the magnetic y-axis. In the case of cubic symmetry the splittings are the same for all three directions). Furthermore, only two, rather than three, distinct lines are observed for each cubic orientation, as the allowed transitions $M=\pm 3/2 \leftrightarrow M=\pm 1/2$, where M is electronic magnetic quantum number, occur at the same magnetic field, distinct from where the $1/2 \leftrightarrow -1/2$ transition occurs. This is clearly seen from the eigenvalues versus magnetic field plot in Fig. 3, showing the three transitions. The line positions for the various transitions as observed for the three orientations for PbTe and one orientation for PbSe are listed in Table 1. It is noted that there occurred an error of about $6.0-9.0\text{ mT}$ in estimating the line positions due to a slight misorientation of the crystal. This was taken into account when calculating the errors of the spin-Hamiltonian parameters as evaluated from the various line positions. From Fig. 2 it is seen that the spectra for the three orientations are the same within the experimental error. This implies a four-fold symmetry about any of the X, Y, or Z-axes, which are coincident with the edges of the crystal, indicating that the site symmetry about the U^{3+} ion is cubic. The identified EPR line positions for the three orientations of the external magnetic field for the Mn^{3+} ion are listed in Table 1.

(b) $Pb_{1-x}U_xSe$. The details are the same for this crystal, except that a good spectrum could only be recorded for the magnetic field along only one edge the crystal, as shown in Fig. 2. The observed line positions are also listed in Table 1.

3. Analysis of U^{3+} EPR spectra

3.1 Spin-Hamiltonian (SH)

The SH for the U^{3+} ion (spin $S = 3/2$), without including the nuclear Zeeman and hyperfine terms, which are not resolved in the spectra, is

$$H = \mu_B \left[g\vec{B} \cdot \vec{S} + u(B_x S_x^3 + B_y S_y^3 + B_z S_z^3 - \frac{1}{5}(\vec{B} \cdot \vec{S})\{3S(S+1)-1\}) \right] \quad (1)$$

In Eq. (1), the first term represents the electronic Zeeman term, μ_B is the Bohr magneton, g is the isotropic g-factor for cubic symmetry, and $\mathbf{S}$ is the spin vector for the U^{3+} ion. The second term in u is the cubic-spin Zeeman term permitted for cubic symmetry as pointed out by Koster and Statz [5] and Bleaney [6], as described by Ham *et al.* [12] in context with the ion Co^{2+}

characterized by spin $S=3/2$ in ZnS, ZnSe, ZnTe, CdTe, and CaF_2 single crystals possessing cubic symmetry.

The SH given by Eq. (1) reduces to the following form for spin $S=3/2$, for the orientations of the magnetic field along any cubic axis:

$$H = \mu_B B_i S_i \left[g + u \left(S_i^2 - \frac{41}{20} \right) \right]; i = x, y, z \quad (2)$$

3.2 Eigenvalues and resonance condition

The eigenvalues of Eq. (2) for B along any cubic axis are the same for cubic symmetry, e.g. along the z -axis, they are found to be for $M = 3/2, 1/2, -1/2, -3/2$ for $S = 3/2$,

$$E_M = (\mu_B B_z M) \left(g + u \left\{ M^2 - \frac{41}{20} \right\} \right) \quad (3)$$

The resonance conditions, $h\nu = |E_M - E_{M-1}|$, for the allowed EPR transitions for B along any cubic axis are then:

$$\text{For } M = 1/2 \leftrightarrow M = -1/2: \quad h\nu = \mu_B B_z \left\{ g + \frac{6}{5} u \right\}, \quad (4)$$

$$\text{For } M = \pm 3/2 \leftrightarrow M = \pm 1/2: \quad h\nu = \mu_B B_z \left\{ g - \frac{9}{5} u \right\}. \quad (5)$$

Using Eqs. (4) and (5), it is seen that the transitions $M = \pm 3/2 \leftrightarrow M = \pm 1/2$ occur at the same magnetic field. This is shown in Fig. 3, which is a plot of the eigenvalues versus magnetic field for $M = 3/2, 1/2, -1/2, -3/2$.

3.3 Evaluation of SH parameters

In the present analysis, least-squares fitting (LSF) method was employed, using the eigenvalues and eigenvectors of the spin-Hamiltonian (SH) matrix to calculate the required derivatives in the LSF method [10]. The SH parameters (SHP) for the U^{3+} ion were thereby determined by simultaneously fitting the 6 allowed EPR line positions for $\text{Pb}_{1-x}\text{U}_x\text{Te}$ observed at 5 K at 208 GHz, for the three orientations of the magnetic field ($\mathbf{B}$) along the cubic axes. For $\text{Pb}_{1-x}\text{U}_x\text{Se}$, this was done only for the two line positions obtained for $\mathbf{B} \parallel$ cubic z -axis. The resulting SH parameters for the U^{3+} ion are as follows. For $\text{Pb}_{1-x}\text{U}_x\text{Te}$: $g = 1.981 \pm 0.002$; $u = -0.0257 \pm 0.0002$; for $\text{Pb}_{1-x}\text{U}_x\text{Se}$: $g = 2.10 \pm 0.15$; $u = -0.025 \pm 0.003$. Thus, within experimental error, the

parameters are the same for the two host crystals. In particular, it is noted that the percentage deviation of the calculated energy level separation of the levels participating in resonance from the klystron frequency for PbTe, listed in table 1, are all less than 0.02%, which is quite reasonable, confirming a convincing evaluation of parameters

3. Discussion and concluding remarks

The salient features of the high-frequency (208 GHz) EPR study presented here on the U^{3+} ion in $Pb_{1-x}U_xTe$ and $Pb_{1-x}U_xSe$ single crystals at 5 K are as follows.

- (i) The U^{3+} ion is situated at a site characterized by cubic symmetry in the lattices of PbTe and PbSe single crystals. The three magnetic axes are oriented along the three edges of the crystal, which is in the form of a rectangular parallelepiped.
- (ii) The U^{3+} SH parameters have been evaluated from the observed line positions as precisely as possible using the least-squares fitting method.
- (iii) The Zeeman splitting parameter, u , representing the term cubic in spin S , has been estimated to be -0.027 in the two host crystals.

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Table 1. Experimental (exp.) line positions in Tesla for the 208-GHz EPR spectrum at 5 K for the magnetic orientation $\mathbf{B}$ along z-, x-, and y-axis for $\text{Pb}_{1-x}\text{U}_x\text{Te}$ ($x \sim 0.03$), along with SD, the square of the deviation (in frequency units) of the energy separations of the levels participating in resonance from the klystron frequency.

	$(\mathbf{B} \parallel z - \text{axis})$		$(\mathbf{B} \parallel x - \text{axis})$		$(\mathbf{B} \parallel y - \text{axis})$	
Exp.	7.3199	7.6185	7.3314	7.6153	7.3446	7.6327
SD (GHz^2)*	0.015	0.014	0.016	0.088	0.062	0.032

* Here $SD = \left(\text{klystron frequency-calculated energy level separation in GHz} \right)^2$

Table 2. Same caption as for Table 1 for data and results for $\text{Pb}_{1-x}\text{U}_x\text{Se}$ ($x \sim 0.03$).

	$(\mathbf{B} \parallel z - \text{axis})$	
Exp.	7.3314	7.6236
SD (GHz^2)	0.16	0.15

Figure captions

Figure 1. A schematic drawing of the $\text{Pb}_{1-x}\text{U}_x\text{Te}$ ($x \sim 0.03$) single-crystal growth habit, indicating the three cubic axes. The first, second, and third orientations mentioned in the text are also indicated. The face marked with parallel lines is the shiny $[100]$ face.

Figure 2. 208-GHz first-derivative observed EPR spectra for the U^{3+} ion at 5 K for $\text{Pb}_{1-x}\text{U}_x\text{Te}$ and $\text{Pb}_{1-x}\text{U}_x\text{Se}$ single crystals. The fields at the centers of the two EPR line positions have been indicated.

Figure 3. A plot showing the eigenvalues as functions of the magnetic field. The allowed transitions are shown. It is seen that the transitions $M = \pm 3/2 \leftrightarrow M = \pm 1/2$ occur at the same magnetic field.

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