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# Electron paramagnetic resonance of the $\mathrm{Eu}^{2+}$ ion in the diluted magnetic semiconductor $\mathrm{Pb}_{1-x}\mathrm{Eu}_x\mathrm{S}$

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X-band (9.56 GHz) electron-paramagnetic-resonance (EPR) measurements were performed on a $\mathrm{Pb}_{1-x}\mathrm{Eu}_x\mathrm{S}$ ($x\sim 0.016$) single crystal at room and liquid-helium temperatures. The values of the spin-Hamiltonian parameters were deduced to be $g=1.972$, $b_4=0.438$ GHz, and $b_6=-0.019$ GHz at 295 K, and $g=1.975$, $b_4=0.448$ GHz, and $b_6=-0.011$ GHz at 4.2 K. The EPR data show that the $\mathrm{Eu}^{2+}$ site symmetry is cubic, indicating a true substitution of $\mathrm{Pb}^{2+}$ ions by $\mathrm{Eu}^{2+}$ ions in the lattice of PbS. The resolved hyperfine structure in the EPR spectrum of $\mathrm{Eu}^{2+}$ was observed only at 2.2 K; the hyperfine constant was estimated to be $A=2.92$ mT. [S0163-1829(97)05545-8]

## I. INTRODUCTION

Many studies involving electron paramagnetic resonance (EPR) and magnetic properties on diluted magnetic semiconductors have been reported in the literature;[1–8] in particular, those on $\mathrm{Pb}_{1-x}\mathrm{Eu}_x\mathrm{Se}$,[4,5] on $\mathrm{Bi}_{2(1-x)}\mathrm{Gd}_{2x}\mathrm{Te}_3$ ($x=0.01$),[6–8] and on rare-earth ion ($\mathrm{Eu}^{2+}$,$\mathrm{Gd}^{3+}$)-doped IV-VI semiconductors PbSe and PbTe,[1,9,10] have been recently reported.

It is the purpose of the present paper to report EPR measurements on a $\mathrm{Pb}_{1-x}\mathrm{Eu}_x\mathrm{S}$ ($x=1.5\%$) single crystal at 295 and 4.2 K and in powder form at 2.2 K. EPR studies reporting spin-Hamiltonian parameters of the $\mathrm{Eu}^{2+}$ ion in $\mathrm{Pb}_{1-x}\mathrm{Eu}_x\mathrm{Se}$, with a structure similar to that of $\mathrm{Pb}_{1-x}\mathrm{Eu}_x\mathrm{S}$, have been published recently.[4,5]

## II. SAMPLE PREPARATION AND EXPERIMENTAL ARRANGEMENT

Single crystals of $\mathrm{Pb}_{1-x}\mathrm{Eu}_x\mathrm{S}$, with Eu concentration of $x=0.0158$, as estimated by a microprobe analysis, were grown by the well-known Bridgman technique. X-ray diffraction revealed the face-centered cubic structure of the crystals. A Bruker X-band (9.56 GHz) EPR spectrometer equipped with an Oxford Instrument helium gas-flow cryostat was used to measure single-crystal (1 mm×1 mm×1.5 mm size) EPR spectra down to about 4 K, while a Varian spectrometer (9.14 GHz) equipped with a commercial (Andonian) helium-immersion cryostat, wherein the temperature 2.2 K was obtained by pumping on liquid helium, was used to measure the powder sample spectrum.

## III. SPIN HAMILTONIAN

The $\mathrm{Eu}^{2+}$ ion is a $S$-state ($L=0$) rare-earth ion with seven electrons in the $4f$ shell (electron spin $S=\frac{7}{2}$ and nuclear spins $I=\frac{5}{2}$ for each of the two Eu isotopes, $^{151}\mathrm{Eu}$ and $^{153}\mathrm{Eu}$, with natural abundances 48% and 52%, respectively, with nonzero magnetic nuclear moments). The $\mathrm{Eu}^{2+}$ spin Hamiltonian (SH) at a site of cubic symmetry is given by[11]

$$\mathsf{H}=g\mu_B\mathbf{B}\cdot\mathbf{S}+\frac{b_4}{60}\,(O_4^0+5O_4^4)+\frac{b_6}{1260}\,(O_6^0-21O_6^4)+A\mathbf{I}\cdot\mathbf{S}. \tag{1}$$

In Eq. (1), $\mathbf{B}$ is the external magnetic-field vector, and $\mu_B$ is the Bohr magneton. The spin operators $O_l^m$ are those described by Abragam and Bleaney.[11] $g$, $b_4$, and $b_6$ are the usual spin-Hamiltonian parameters. The $^8\mathrm{S}_{7/2}$ state of the $\mathrm{Eu}^{2+}$ ion is split by the cubic crystal field into two doublets, $\Gamma_7$ and $\Gamma_6$, and a quadruplet $\Gamma_8$, with an overall splitting $\Delta=32b_4-8b_6$. The $g$ and $A$ tensors have here been assumed to be isotropic due to the cubic site symmetry. The hyperfine (hf) structure of the EPR spectrum is represented by the last term in Eq. (1). All the observed fine-structure line positions as recorded for different orientations of the external magnetic field in the [100] plane were simultaneously fitted to the spin Hamiltonian, given by Eq. (1), by matrix diagonalization as described in Ref. 12. The SH parameters are listed in Table I, which reveals that the $g$ value does not change between 4.2 and 295 K, within experimental error, while the values of the parameters $b_4$ and $b_6$ increase by about 2.4% and 45% from those at 295 K. It is found, in particular, that the value of the parameter $b_4$ for the $\mathrm{Eu}^{2+}$ ion in PbS is larger than that for the $\mathrm{Eu}^{2+}$ ion in PbSe (Refs. 4 and 5) due to the lattice parameter $a$ in PbS being smaller than that in PbSe.

The intensity of the highest-field line increased from 1.1 to 1.8 compared to that of the lowest-field line when the temperature decreased from 295 to 4.2 K, implying that at low temperatures the levels with negative $M$, where $M$ is the electronic magnetic quantum number, are more populated

TABLE I. The spin-Hamiltonian parameters for the $Eu^{2+}$ ion in a $Pb_{1-x}Eu_xS$ ($x=0.015$) crystal at 295 and 4.2 K. Here $\alpha$ is the admixture of the first-excited state $^6P_{7/2}$ in the ground state $^8S_{7/2}$ of $Eu^{2+}$, $n$ is the number of resonant line positions simultaneously fitted to estimate the values of the parameters, and RMSL is the average % deviation of calculated energy difference of the pair of levels participating in resonance from the klystron frequency (the experimental difference). The misorientation angle, $\varphi$, fitted along with the SH parameters, represents the deviation of the plane of rotation of the external magnetic field from the crystallographic plane [100].

| Parameters | 295 K | 4.2 K |
|---|---|---|
| $g$ | $1.972\pm0.002$ | $1.975\pm0.002$ |
| $b_4$ (GHz) | $0.438\pm0.002$ | $0.448\pm0.002$ |
| $b_6$ (GHz) | $-0.019\pm0.001$ | $-0.011\pm0.001$ |
| $\alpha$ | 0.28 | 0.28 |
| $\varphi$ (deg) | $5.8\pm0.1$ | $6.3\pm0.1$ |
| $n$ | 125 | 127 |
| RMSL (%) | 2.0 | 2.3 |

than those with positive $M$, identifying the highest-field EPR line to be the $-7/2\leftrightarrow-5/2$ transition, and the absolute sign of $b_4$ to be positive. This sign is consistent with that deduced from magnetization-step measurements as described in Ref. 1.

## IV. EXPERIMENTAL RESULTS

### A. EPR spectra

The spectra were recorded for numerous orientations of the external magnetic field in the [100] plane. All seven allowed fine-structure transitions ($M\leftrightarrow M-1$) were observed at 295 and 4.2 K. Electrical transport measurements at room temperature show that the sample is highly conducting, being of $p$ type with carrier concentration $p=2.5\times10^{18}\ \mathrm{cm}^{-3}$ and carrier mobility $\mu=233\ \mathrm{cm}^2/\mathrm{V\,s}$ responsible for Dysonian lineshapes. Figure 1 shows the first-derivative EPR spectrum at 4.2 K for $\mathbf{B}\|(001)$ direction. A small misorientation of the rotation plane of $\mathbf{B}$ from the [100] plane is responsible for the small asymmetry observed in the angular variation of the EPR line positions for $\mathbf{B}$ in the [100] plane. The rather large EPR linewidth $\Delta B_{pp}\geqslant300$ G is probably due to: (i) The high value of the concentration ($x$) of $Eu^{2+}$ ions ($x\geqslant1.5\%$), which influences $\Delta B_{pp}$ due to $Eu^{2+}$-$Eu^{2+}$ dipolar and exchange interactions,[15,16] and (ii) distribution of the values of the parameter $b_4^0$ for the $Eu^{2+}$ ion over the sample, due to local strains, leading to an inhomogeneous broadening due to variations in the line positions of the $Eu^{2+}$ ions distributed in the crystal. Figure 2 exhibits the calculated angular variation of the allowed fine-structure line positions at 4.2 K taking into account the Dysonian line shape.[13]

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

The admixture coefficient $\alpha$ of the first excited state $^6P_{7/2}$ in the ground state $^8S_{7/2}$ of the $Eu^{2+}$ ion was estimated using the $g$ value determined presently:[17]

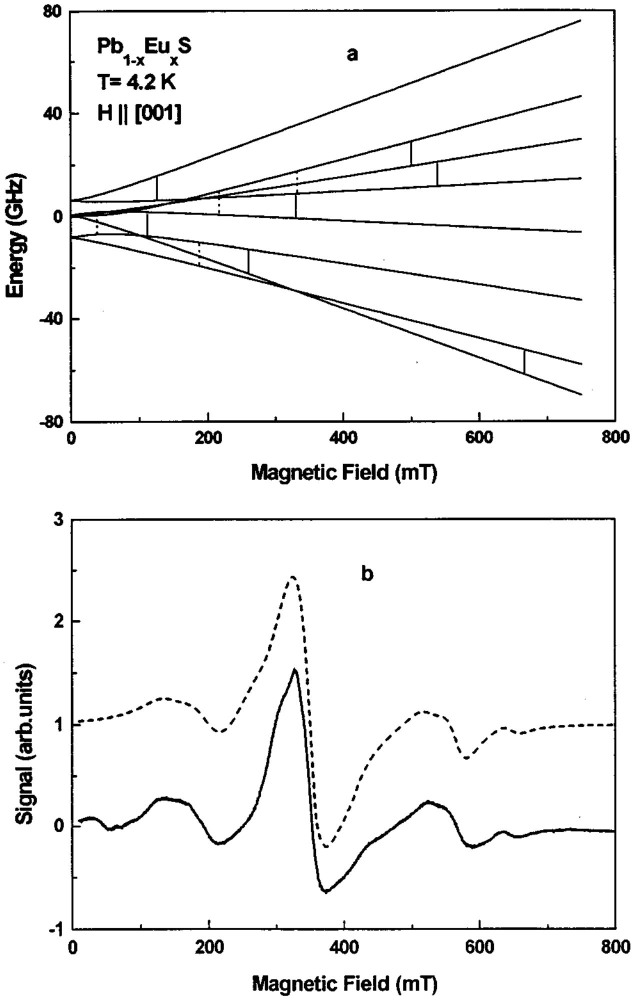

FIG. 1. (a) A plot of the energy levels of $Eu^{2+}$ ions in $Pb_{1-x}Eu_xS$ ($x\sim0.016$) as functions of the external magnetic field intensity $\mathbf{B}$ along the (001) direction within about 5°, calculated using the spin Hamiltonian, Eq. (1), with the parameters evaluated at 4.2 K. The vertical lines indicate the positions of the EPR lines, while the continuous and dashed lines represent the allowed and forbidden transitions, respectively. (b) First-derivative EPR spectrum for $Eu^{2+}$ in $Pb_{1-x}Eu_xS$ at 4.2 K. The dotted line represents the theoretically simulated spectrum, taking into account the Dysonian line shape (Refs. 13 and 14) due to the sample's high conductivity. By a comparison of Figs. 1(a) and 1(b), identification of the transitions corresponding to the various peaks in the experimental spectrum can be made.

$$g=(1-\alpha^2)g_s+\alpha^2 g_p \tag{2}$$

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 value of the admixture coefficient both at 295 and at 4.2 K is 0.28.

### C. Hyperfine interaction

At liquid-helium temperature the fine-structure $+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transition splits into six allowed hf transitions ($\Delta M=\pm1$, $\Delta m=0$; $m$ is the nuclear magnetic quantum number) for each of the two Eu isotopes. The value of the hyperfine structure parameter $A$ was estimated to be $2.92\pm0.05$ mT from the hf splitting of the central fine-structure transition

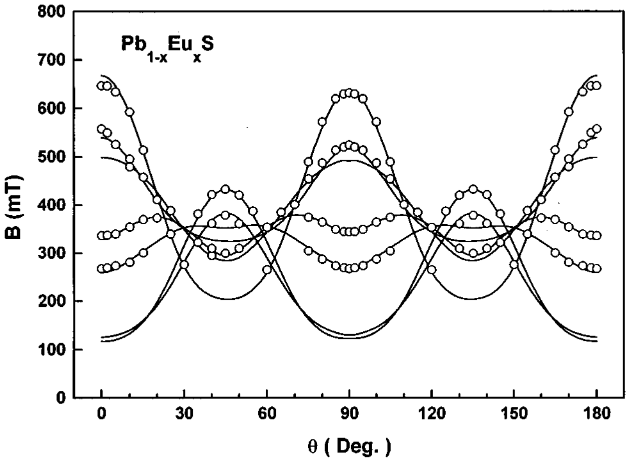

FIG. 2. Angular variation of the positions of the allowed transitions as calculated by diagonalizations of the spin-Hamiltonian matrix for rotation of the magnetic field in the [100] plane. The circles represent experimental line positions (data).

$+\frac{1}{2}\leftrightarrow-\frac{1}{2}$ in a powder sample as displayed in Fig. 3, showing the X-band (9.2 GHz) spectrum at 2.2 K. (No hyperfine splitting was observed in $Pb_{1-x}Eu_xS$ single crystals, due to the skin effect, which is much more prominent in the dense crystalline state than in the more porous powder state.) This value represents the average of the hf constants for the isotopes $^{151}$Eu and $^{153}$Eu, due to considerable overlapping of the corresponding lines.

## V. CONCLUDING REMARKS

The $Eu^{2+}$ site symmetry is confirmed to be cubic, indicating a true substitution of $Pb^{2+}$ ions by $Eu^{2+}$ ions in the lattice of PbS the $Eu^{2+}$ site symmetry in $Pb_{1-x}Eu_xS$ is cubic (octahedral), characterized by a positive sign of the SH parameter $b_4$. The values of the SH parameters were estimated. The admixture $\alpha$, of the $^6P_{7/2}$ state in the ground state $^8S_{7/2}$ is 28%. The hf parameter $A$, representing the average value for the two isotopes $^{151}$Eu and $^{153}$Eu, was estimated to be 2.92 mT at 2.2 K.

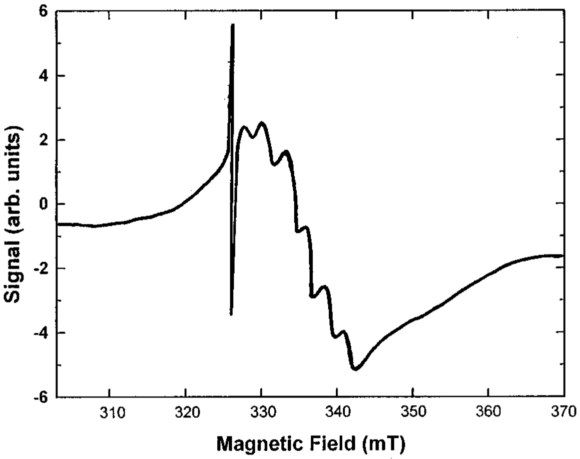

FIG. 3. X-band (9.2 GHz) $Eu^{2+}$ EPR spectrum in $Pb_{1-x}Eu_xS$ powder at 2.2 K. The central transition $(\frac{1}{2}\leftrightarrow-\frac{1}{2})$ splits clearly into six hyperfine transitions corresponding to the $^{151}Eu^{2+}$ and $^{153}Eu^{2+}$ isotopes. The hf lines due to the two isotopes strongly overlap each other so as not to appear resolved.

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