

# EPR study of the hyperfine structure of $\text{Yb}^{3+}$ ion in $\text{Pb}_{1-x}\text{Yb}_x\text{S}$ , $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$ , and $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$ single crystals

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$X$ -band (9.56 GHz) electron paramagnetic resonance (EPR) measurements were performed on  $\text{Pb}_{1-x}\text{Yb}_x\text{S}$ ,  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$ , and  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$  samples ( $x \sim 0.5-2\%$ ) at liquid-helium temperatures to study hyperfine transitions, and to estimate the value of the effective Landé factor  $g$  and the hyperfine-interaction constants of the two isotopes  $^{171}\text{Yb}$  and  $^{173}\text{Yb}$  possessing nonzero nuclear magnetic moments. The data indicated that the site symmetry at the  $\text{Yb}^{3+}$  ion in all the host crystals,  $\text{Pb}_{1-x}\text{Yb}_x\text{S}$ ,  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$ , and  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$ , is octahedral. The EPR line positions were found not to vary with the orientation of the external magnetic field, indicating that the  $g$  tensors and the hyperfine-interaction tensors are isotropic. The  $\text{Yb}^{3+}$  Landé factors ( $g$ ) were deduced to have the values  $2.545 \pm 0.005$ ,  $2.585 \pm 0.005$ , and  $2.525 \pm 0.005$ , respectively, in  $\text{Pb}_{1-x}\text{Yb}_x\text{S}$ ,  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$ , and  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$ . The calculated Landé factors are slightly different from these; the degree of covalent bonding was estimated from the differences in the experimental and calculated Landé factors. The values of the hyperfine-interaction constants for  $^{171}\text{Yb}^{3+}$  and  $^{173}\text{Yb}^{3+}$  isotopes were estimated to have the values  $^{171}A = 138 \pm 2$  mT,  $^{173}A = 39 \pm 1$  mT in  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$ ,  $^{171}A = 59 \pm 2$  mT,  $^{173}A = 19 \pm 1$  mT in  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$ , and  $^{171}A = 60 \pm 2$  mT in  $\text{Pb}_{1-x}\text{Yb}_x\text{S}$ . [S0163-1829(96)07835-6]

## I. INTRODUCTION

Electron paramagnetic resonance (EPR) is a sensitive tool to study the magnetic properties and electronic structure of the rare-earth ions in diluted magnetic semiconductors. The IV-VI chalcogenides are suitable host crystals, because they are easily doped by rare-earth ions, unlike the II-VI chalcogenides. In the present paper, an EPR study at liquid-helium temperatures on three diluted magnetic semiconductor samples,  $\text{Yb}^{3+}$ -doped  $\text{PbTe}$ ,  $\text{PbSe}$ , and  $\text{PbS}$ , is reported.

## II. SAMPLE PREPARATION AND EXPERIMENTAL ARRANGEMENT

Single crystals of  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$ ,  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$ , and  $\text{Pb}_{1-x}\text{Yb}_x\text{S}$  were grown by the use of the well-known Bridgman method. The sample dimensions were about ( $3 \times 2 \times 1.5$  mm<sup>3</sup>), the longest axis being along the [001] direction. The nominal Yb composition was  $x = 0.027$ , 0.04, and 0.01 in  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$ ,  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$ , and  $\text{Pb}_{1-x}\text{Yb}_x\text{S}$ , respectively, as determined by a microprobe analysis. The EPR measurements were performed at the  $X$  band (9.56 GHz) using a Bruker spectrometer equipped with an Oxford liquid-helium accessory; the temperature was regulated with a gas-flow system, and measured with a thermocouple.

## III. EPR SPECTRA

Figure 1 shows the EPR spectra for  $\mathbf{B} \parallel [001]$  in the single crystals of  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$ ,  $\text{Pb}_{1-x}\text{Yb}_x\text{S}$ , and  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$  at 4.2 K. No anisotropy in the EPR line positions was observed in any sample with respect to the orientation of the external magnetic field relative to the [001] axis. The EPR lines corresponding to the three Yb isotopes could be clearly identified in all the  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$ ,  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$ , and  $\text{Pb}_{1-x}\text{Yb}_x\text{S}$  samples. In  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$ , all  $\text{Yb}^{3+}$  EPR lines were found to be Dysonian as indicated by their asymmetric shapes. On the other hand, for  $\text{Yb}^{3+}$  in  $\text{Pb}_{1-x}\text{Yb}_x\text{S}$  and  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$  the shape was symmetrical indicating absence of Dysonian behavior. The Dysonian shape of the  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$  signal is caused by the skin effect manifested due to metal-like behavior, characterized by low resistivity.<sup>1-3</sup> The resistivity was measured to be, indeed, small:  $\rho = 0.009$   $\Omega$  cm at 4.2 K for  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$ , unlike that for  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$  for which the resistivity was rather large at 4.2 K, being  $\rho = 0.85$   $\Omega$  cm. The satellite hyperfine transitions were not symmetric with respect to the central line; this is due to the shift of Landé factor  $g$  when the hyperfine structure is absent.<sup>4</sup> This effect is most pronounced in  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$ .

## IV. SPIN HAMILTONIAN

The magnetic properties of the  $\text{Yb}^{3+}$  ion arise from its partially filled  $4f$  shell, possessing 13 electrons. The ground

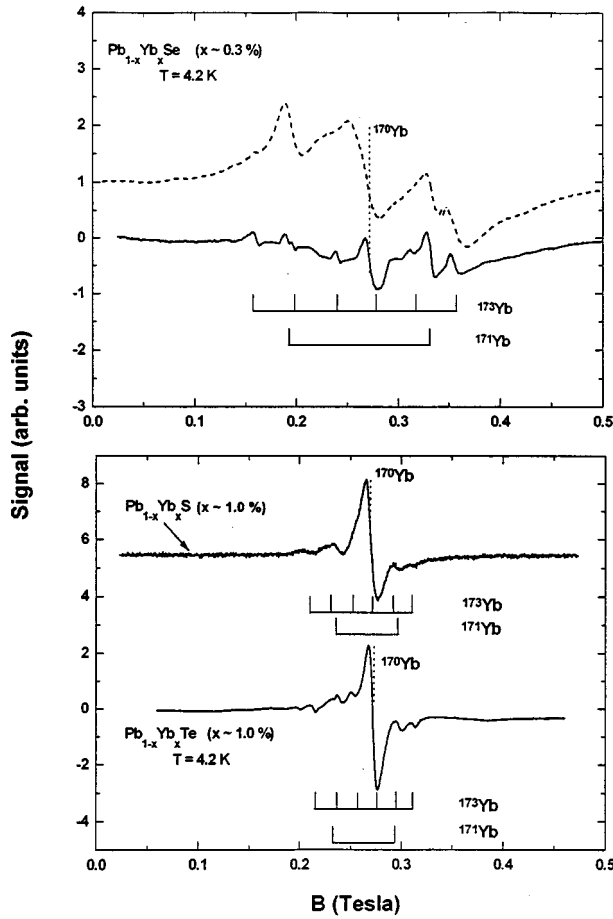


FIG. 1. X-band (9.56 GHz) first-derivative absorption EPR spectra of the  $\text{Yb}^{3+}$  ion in  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$ ,  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$ , and  $\text{Pb}_{1-x}\text{Yb}_x\text{S}$  single crystals for  $\mathbf{B}||[001]$  at 4.2 K. The spectrum represented by broken lines is that due to the powder sample and the full lines represent spectra in single crystals. The hyperfine multiplets corresponding to the two isotopes  $^{171}\text{Yb}$  and  $^{173}\text{Yb}$  have been indicated. The positions of the fine-structure line ( $+\frac{1}{2} \leftrightarrow -\frac{1}{2}$ ) for the nonmagnetic isotope ( $^{170}\text{Yb}$ ) has been indicated by the vertical dashed lines.

state  $^2F_{7/2}$  of the  $\text{Yb}^{3+}$  ion, with  $J = \frac{1}{2}$ , in the crystal field is situated at about  $10\,000\text{ cm}^{-1}$  below the next excited state with  $J = \frac{5}{2}$ .<sup>5</sup> In the cubic crystal fields of  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$ ,  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$ , and  $\text{Pb}_{1-x}\text{Yb}_x\text{S}$ , the ground manifold further splits into two doublets (spin =  $\frac{1}{2}$ ),  $\Gamma_6$  and  $\Gamma_7$ , and a quadruplet (spin =  $\frac{3}{2}$ )  $\Gamma_8$ .<sup>6</sup> The present EPR data are thus interpreted in terms of a spin Hamiltonian describing the energy levels of the ground state of a manifold of effective spin  $S = \frac{1}{2}$ , since as discussed below the  $\Gamma_6$  doublet lies lowest. In the presence of an external magnetic field, the spin Hamiltonian for the cubic site symmetry, as in the present case, is given by

$$\mathcal{H} = g\mu_B \mathbf{B} \cdot \mathbf{S} + {}^{171}\text{A}_1 \cdot \mathbf{S} + {}^{173}\text{A}_2 \cdot \mathbf{S}. \quad (1)$$

In Eq. (1), the first term is the Zeeman term;  $g$  is the effective Landé factor of the  $\text{Yb}^{3+}$  ion and  $\mu_B$  is the Bohr magneton. The second and third terms describe the hyperfine interactions of the nuclear magnetic moments of the two isotopes  $^{171}\text{Yb}$  and  $^{173}\text{Yb}$  with the electron magnetic moment of the  $\text{Yb}^{3+}$  ion;  ${}^{171}\text{A}$  and  ${}^{173}\text{A}$  are the hyperfine-interaction tensors for interaction of the  $^{171}\text{Yb}$  and  $^{173}\text{Yb}$  nuclei with the

$\text{Yb}^{3+}$  ionic electronic moment, both of which are found to be isotropic, consistent with the cubic site symmetry.

### A. Landé factors

The values of the effective Landé factors ( $g$ ) for  $\text{Yb}^{3+}$  as deduced from the center of the main line belonging to the nonmagnetic isotope  $^{170}\text{Yb}$ , as indicated in Fig. 1, which lies in the middle, but not necessarily at the center, of the hyperfine lines belonging to the magnetic isotopes, are  $g = 2.545 \pm 0.005$  in  $\text{Pb}_{1-x}\text{Yb}_x\text{S}$ ,  $g = 2.585 \pm 0.005$  in  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$ , and  $g = 2.525 \pm 0.005$  in  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$ . These  $g$  values confirm that the  $\text{Yb}^{3+}$  Kramers doublet  $\Gamma_6$  represents the ground state in each of  $\text{Pb}_{1-x}\text{Yb}_x\text{S}$ ,  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$ , or  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$ , as deduced by comparison with the expected theoretical value of the  $g$  factor for the  $\Gamma_6$  state, which is 2.667.<sup>5-7</sup> The small differences between the theoretical and experimental  $g$  factors (about 3–5%) are due to the existence of covalent bonding in rare-earth ions, as described below.

### B. Orbital reduction factors

One can account for the different theoretically calculated value of the  $g$  factor to the experimental one by introducing a factor  $k$  representing the reduction of the value of the orbital momentum  $L$ . In the present case of cubic symmetry, the calculations are relatively easy because the excited crystal field states for the  $\text{Yb}^{3+}$  ion corresponding to  $J = \frac{5}{2}$  do not contain an admixture of the  $\Gamma_6$  states.<sup>7</sup> The theoretical  $g$  factor of the doublet  $\Gamma_6$  is given by  $\frac{7}{3}g_{J'}$ , where  $g_{J'}$  is the reduced Landé factor,<sup>6</sup> expressed as

$$g_J = g_{J'} - (1-k) \left[ \frac{J(J+1) - S(S+1) + L(L+1)}{2J(J+1)} \right]. \quad (2)$$

In Eq. (2)  $S = \frac{1}{2}$ ,  $L = 3$ , and  $J = \frac{7}{2}$ .

If  $\Delta g$  is defined to be the difference between the theoretically calculated and experimentally determined  $g$  values: ( $\Delta g \equiv g_{\text{theo}} - g_{\text{exp}}$ ), then

$$\Delta g = \frac{7}{3}(g_{J'} - g_J) = 2(1-k). \quad (3)$$

Using Eq. (3), one obtains  $(1-k) = 0.061 \pm 0.003$  for  $\text{Pb}_{1-x}\text{Yb}_x\text{S}$ ,  $(1-k) = 0.041 \pm 0.003$  for  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$ , and  $(1-k) = 0.073 \pm 0.003$  for  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$ .

### C. Hyperfine-interaction constants

From the hyperfine structure of the satellite transitions due to the magnetic isotopes  $^{171}\text{Yb}$  ( $I = \frac{1}{2}$ , natural abundance 14.3%) and  $^{173}\text{Yb}$  ( $I = \frac{5}{2}$ , natural abundance 14.3%) around the central line due to the nonmagnetic isotope of  $\text{Yb}^{3+}$  (natural abundance 69.6%), the values of the hyperfine coupling constants were estimated, using Eq. (1). They are listed in Table I. The reason for the significant increase in the values of the hyperfine constants for the two isotopes of Yb in  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$  as compared to those in  $\text{Pb}_{1-x}\text{Yb}_x\text{S}$  or  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$  is not clear. However, it may be noted that the electrical properties in the two materials  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$  or  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$  are very different from each other.<sup>8</sup> It is likely that the conduction-electron hybridization strongly influences the hyperfine field in the  $\text{Yb}^{3+}$  ion, and is therefore respon-

TABLE I. Values of the Landé factor ( $g$ ) and hyperfine-interaction constant for  $\text{Yb}^{3+}$  in PbSe, PbTe, and PbS. The value of  $^{173}\text{A}$  in PbS is characterized by large errors, since the corresponding hyperfine multiplet is not too well resolved.

Sample	Landé factor	$^{171}\text{A}$ (mT)	$^{173}\text{A}$ (mT)
$\text{Pb}_{1-x}\text{Yb}_x\text{Se}$	$2.585 \pm 0.005$	$138 \pm 2$	$39 \pm 1$
$\text{Pb}_{1-x}\text{Yb}_x\text{Te}$	$2.520 \pm 0.005$	$59 \pm 2$	$18.5 \pm 1$
$\text{Pb}_{1-x}\text{Yb}_x\text{S}$	$2.545 \pm 0.005$	$60 \pm 2$	$19 \pm 2$

sible for the observed increase in the hyperfine constants in  $\text{Pb}_{1-x}\text{Yb}_x\text{Se}$  as compared to those in  $\text{Pb}_{1-x}\text{Yb}_x\text{S}$  and  $\text{Pb}_{1-x}\text{Yb}_x\text{Te}$ .

### V. CONCLUDING REMARKS

It has been concluded from the present EPR measurements that the  $\text{Yb}^{3+}$  ion substitutes for the  $\text{Pb}^{2+}$  ions in PbS,

PbSe, and PbTe, because the isotropic nature of the EPR line positions is consistent with the cubic site symmetry as at the Pb site. The values of the hyperfine constants and the effective Landé factor have been estimated in these samples. The  $g$  values confirm that the ground state of the  $\text{Yb}^{3+}$  ion is the  $\Gamma_6$  doublet in all the samples. The orbital reduction factor ( $1-k$ ) is determined to be of the order of a few percent (4–7 %) for the  $\text{Yb}^{3+}$  ion in PbS, PbSe, and PbTe samples.

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