

Magnetic properties of Ce^{3+} in PbCeA (A= Te, Se, S)

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Abstract. The magnetic susceptibility of $\text{Pb}_{1-x}\text{Ce}_x\text{A}$ (A = S, Se and Te) crystals with $0.006 \leq x \leq 0.036$ were studied in the temperature range from 20 mK up to room temperature. X-band (~ 9.5 GHz) Electron Paramagnetic Resonance (EPR) showed small shifts in the effective Landé factors that were attributed to crystal-field admixture. The EPR measurements were correlated with the magnetic susceptibility data and resulted in estimating the crystal-field splitting $\Delta = E(\Gamma_8) - E(\Gamma_7)$ of the lowest $^2F_{5/2}$ manifold for Ce^{3+} ions in PbA (A = S, Se and Te) of about 340 K, 440 K and 540 K for $\text{Pb}_{1-x}\text{Ce}_x\text{Te}$, $\text{Pb}_{1-x}\text{Ce}_x\text{Se}$, and $\text{Pb}_{1-x}\text{Ce}_x\text{S}$, respectively. The values for the crystal-field splitting deduced from the magnetic data were found to be in agreement with the calculated ones based on the point charge model. Moreover, the de-Haas van-Alphen magnetic oscillations in the susceptibility measurements of $\text{Pb}_{1-x}\text{Ce}_x\text{Te}$ ($x \sim 0.05$ and 0.07) were observed at ultra-low temperature (20 mK); The oscillations were investigated and the values of the oscillatory period for $\text{Pb}_{1-x}\text{Ce}_x\text{Te}$ ($x = 0.0048$ and 0.007) are reported.

1 Introduction

Lead salts PbS , PbSe , and PbTe establish an significant group of Diluted magnetic semiconductors (DMS) consisting of a magnetic semiconducting host, in which fraction of cations is substituted by magnetic rare-earth or transition metal ions. In past few decades, various compound semiconductors from III-V, II-VI, IV-VI, etc. have been identified as potential candidates in thermoelectric materials with a high figure-of-merit, optoelectronic and spintronic applications [1-4]. The amount of knowledge, which has been accumulated, is less in IV-VI DMS than compared to the situation of II-VI DMS [5-13]. Magnetization, Magnetic Susceptibility and Electron Paramagnetic Resonance (EPR) measurements are powerful tools to study magnetic properties and electronic structures of DMS. Most of the investigated DMS systems in the literature are doped with transition metal and rare-earth ions having S ($L = 0$) states, such as Mn^{2+} , Gd^{3+} or Eu^{2+} [6-13]. However, the study of IV-VI DMS containing a fraction of non S-state rare-earth ions is much less explored [14-16]. For this class of DMS, the magnetic properties could be strongly affected by the presence of crystal-field splitting of the rare-earth states. For the rock salt structure of PbA (A = S, Se and Te), the crystal field at the cation site has cubic (O_h) symmetry and a crystal-field splitting of the $^2F_{5/2}$

manifold of Ce^{3+} ion is expected into a Γ_7 doublet and a Γ_8 quadruplet, the doublet being the ground state. Electron Paramagnetic Resonance (EPR) of Ce^{3+} ions located in cubic symmetry site was observed at 4.2 K in $\text{Pb}_{1-x}\text{Ce}_x\text{A}$ (A = S, Se and Te). The analysis of the EPR spectra lead to Landé $g = 1.331$, 1.361 and 1.400 for $\text{Pb}_{1-x}\text{Ce}_x\text{S}$, $\text{Pb}_{1-x}\text{Ce}_x\text{Se}$ and $\text{Pb}_{1-x}\text{Ce}_x\text{Te}$, respectively [17]. The theoretical value for Γ_7 is $g = 1.429$. The present work is focused on the magnetic susceptibility of $\text{Pb}_{1-x}\text{Ce}_x\text{A}$ (A = S, Se and Te). The present data were used to estimate the cubic crystal-field splitting of the $^2F_{5/2}$ manifold of Ce^{3+} in the three compounds.

2 Experimental

Experiments were carried out on an n-type single crystal of Ce doped PbA (A = Te, Se, S) grown by the Bridgman method [18]. The crystals were not intentionally doped with any other element. The solubility limit of Ce in the PbA matrix is about 10%. X-ray diffraction analysis indicated a fcc structure for all samples. The EPR measurements in the X-band (~ 9.56 GHz) were performed on a parallelepiped sample with the longest axis along the [001] [17]. These $\text{Pb}_{1-x}\text{Ce}_x\text{A}$ crystals of few mm^3 were pulled out from the as grown ingots. The extracted samples were cut along the (001) planes in form

of small cubes. The Cerium content (x) in the samples was deduced from the saturation of the magnetization curves at high magnetic fields and by electron microprobe measurements. The magnetization was measured at 2 K in magnetic fields H up to 7 Tesla using a SQUID magnetometer. The magnetic susceptibility was measured at 0.1 Tesla over the temperature range from 2 to 300 K. The errors on the data were estimated to 2%. The samples of $Pb_{1-x}Ce_xA$ ($A = Te, Se$ and S) were all n -type with carrier concentrations ranging from 6×10^{18} to 10^{20} cm^{-3} . The magnetic susceptibility at 20 mK was measured in a system using a force magnetometer, a plastic dilution refrigerator, and a 9 Tesla superconducting magnet.

3 Experimental results and discussions

The fcc structure of the samples were checked by X-Ray diffraction and the cerium content were determined from the magnetization saturation at high external magnetic field; the calculation of the Ce concentration (x) in the sample were corrected for the lattice diamagnetism ($\chi_D = -3.77 \times 10^{-9} \text{ m}^3/\text{Kg}$ for PbS [19], $\chi_D = -4.52 \times 10^{-9} \text{ m}^3/\text{Kg}$ for PbSe [20], and $\chi_D = -3.77 \times 10^{-9} \text{ m}^3/\text{Kg}$ for PbTe [17]); The obtained average concentrations of cerium atoms were also checked by Microprobe measurements, as given in Table I; An excellent agreement between the Ce concentrations values by microprobe to those obtained from magnetic measurements indicated that cerium is present only in its trivalent (Ce^{3+}) state in our $Pb_{1-x}Ce_xA$ samples. The temperature variation of χ^{-1} for our $Pb_{1-x}Ce_xA$ ($A = S, Se$ and Te) samples were found to strongly deviates from the free Ce ion paramagnetic behavior; it was also noticed that the experimental magnetic susceptibility fits the predicted values of the susceptibility for the doublet (Γ_7) only at temperatures below 30 K indicating that the Kramer doublet (Γ_7) lies below the quadruplet (Γ_8).

Table I: Values of x , χ_D and Δ for $PbCeA$ ($A = Te, Se, S$). The concentration of Ce^{3+} ions (x) was obtained by three different techniques, ^(a)Modified Brillouin function, ^(b)Three-parameters fit of the magnetic susceptibility, ^(c)Microprobe measurements, ^(d)The agreement factor, defined as $S_e = [\phi/(N-L)]^{1/2}$, N is the number of data points, K is the number of parameters and $\phi = (R_{obs} - R_{calc})^2$ is the sum of the squares of the residuals.

A	$x^{(a)}/x^{(c)}/x^{(b)}$ (%)	Δ (K)	χ_D (m^3/Kg)	$S_e^{(d)}$
Se	1.2/--/1.1	407	-3.81×10^{-9}	7.2×10^{-3}
Se	2.0/1.9/1.8	442	-3.68×10^{-9}	3.2×10^{-3}
Se	3.4/3.1/3.6	420	-4.28×10^{-9}	7.3×10^{-3}
S	0.9/--/0.9	545	-3.67×10^{-9}	2.8×10^{-3}
S	1.9/--/1.8	542	-3.02×10^{-9}	3.5×10^{-3}
S	2.1/2.2/1.9	529	-3.3×10^{-9}	3.2×10^{-3}
Te	0.6/--/0.6	340	-3.64×10^{-9}	6.7×10^{-3}

This result was also confirmed by the values of the Landé factors obtained by EPR measurements [17]. In order to simulate our experimental magnetic susceptibility data, we accounted for the presence of the quadruplet (Γ_8)

laying at energy $\Delta = E(\Gamma_8) - E(\Gamma_7)$ above the doublet (Γ_7). In such a case, the magnetic susceptibility of $Pb_{1-x}Ce_xA$ can be described by the Van-Vleck expression given by:

$$\chi = N \frac{\mu_{eff}^2 \mu_B^2}{k_B T} x + \chi_D \quad (1)$$

Where μ_B and k_B are the Bohr magneton and Boltzmann constant, respectively, and N is the number of cation per gram. The effective magnetic moment μ_{eff} of Ce^{3+} is given by:

$$\mu_{eff}^2 = \mu_{eff}^2 (free) \left[\frac{5 + 26 \exp(-\Delta/k_B T) + \frac{32 k_B T}{\Delta} (1 - \exp(-\Delta/k_B T))}{21 (1 + 2 \exp(-\Delta/k_B T))} \right] \quad (2)$$

Where $\mu_{eff}^2 (free) = \frac{1}{3} g_J^2 J(J+1)$ is the effective magnetic moment of the Ce^{3+} free ion which was obtained from the experimental g -value of the Γ_7 doublet and $g_J = 3/5 g$. The values for $\mu_{eff}^2 (free)$ were found to be 2.33, 2.38 and 2.45 for $Pb_{1-x}Ce_xS$, $Pb_{1-x}Ce_xSe$ and $Pb_{1-x}Ce_xTe$, respectively. In Eq. (2), Δ represents the cubic Crystal-Field Splitting (CFS), (i.e. the energy difference between Γ_8 and Γ_7). In our simulation of the magnetic susceptibility data, the effect of the exchange integral between Ce^{3+} ions was ignored as its magnitude is very small ($|J/k_B| \leq 1 \text{ K}$) when compared to the CFS [15, 20]. In order to obtain the CFS value Δ , the effective magnetic moment for each of the three compounds was fitted to Eq. (1) in the temperature range from 2 to 300 K with three fitting parameters x , Δ and χ_D . The obtained values of x , Δ and χ_D are given in Table I. Figure 1 shows the

temperature variation of $R = \frac{\mu_{eff}^2}{\mu_{eff}^2 (free)}$ for the three

compounds. The obtained values of the fitting parameters x and χ_D are given in Table I. The values of CFS (Δ) were found to be 536 K, 443 K and 340 K for $Pb_{1-x}Ce_xS$, $Pb_{1-x}Ce_xSe$ and $Pb_{1-x}Ce_xTe$, respectively. We interpreted the results of our measurements on magnetic susceptibilities and electron paramagnetic resonance of Ce doped lead chalcogenides by fitting the crystal field and diamagnetic susceptibility parameters. The temperature dependence of the single ion susceptibilities was computed according to Eq. (2). Furthermore, the obtained values of the CFS were compared to the ones calculated from the point charge model [21, 22]. In our calculations, we accounted for the six doubly negative charges of the nearest neighbor anions located at $a/2$ from the Ce^{3+} ions, where $a = 0.6454 \text{ nm}$, 0.6124 nm and 0.5936 nm for PbTe, PbSe and PbS, respectively. We used the Hartree-Fock method with a $\langle r^{-4} \rangle$ value of 3.5 a.u. for the fourth power of the 4f electron radius [23].

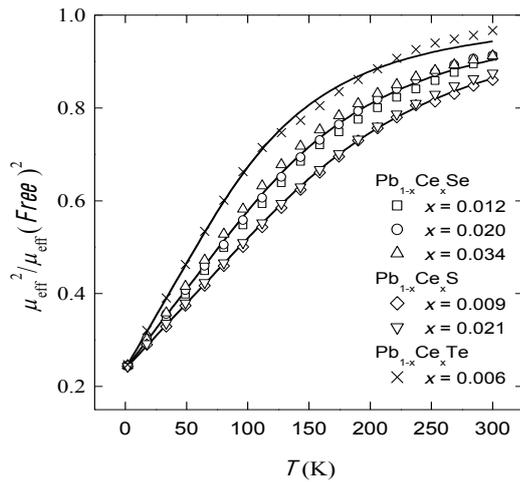


Fig. 1: Experimental data (symbols) and theoretical (continuous lines) reduction of the effective magnetic moment of Ce^{3+} in $\text{Pb}_{1-x}\text{Ce}_x\text{S}$, $\text{Pb}_{1-x}\text{Ce}_x\text{Se}$ and $\text{Pb}_{1-x}\text{Ce}_x\text{Te}$ samples. The effective magnetic moment was normalized to its value for the free Ce^{3+} ion. Fewer points of the data were displayed for a better view. The lines are the fit between 2 K and 300 K using the expressions in Eqs. (1) and (2).

The values of the CFS obtained from the point charge model were $\Delta = 400$ K, 340 K and 262 K for $\text{Pb}_{1-x}\text{Ce}_x\text{S}$, $\text{Pb}_{1-x}\text{Ce}_x\text{Se}$, and $\text{Pb}_{1-x}\text{Ce}_x\text{Te}$, respectively which are about 100 K below the values obtained from the magnetic susceptibility results. In our calculation, the

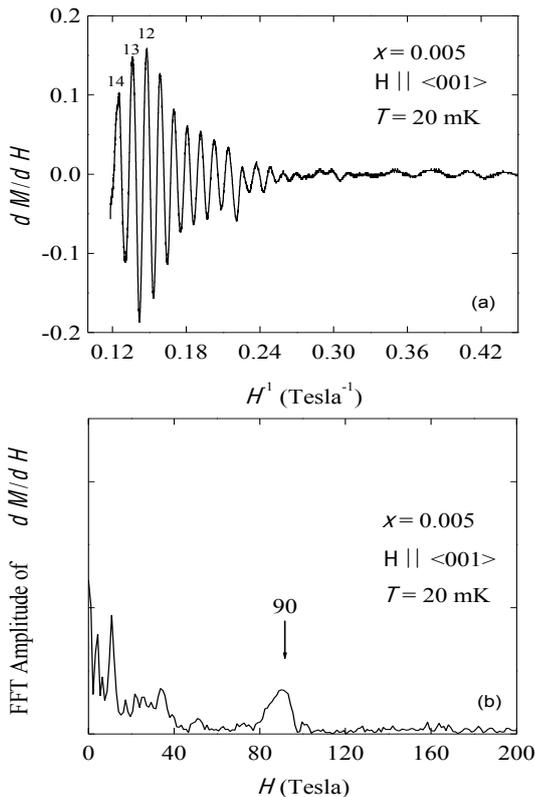


Fig. 2: Field dependence of the oscillatory part of the magnetic susceptibility at 20 mK for $H \parallel [001]$ (upper figure); Fourier transform of the oscillatory part of the susceptibility at 20 mK between 0 and 200 Tesla, revealing a single frequency $f \sim 90$ Tesla (lower figure).

spin-orbit constant was taken from the literature (1600 K) while the Landé factors were deduced from low temperatures EPR measurements. The existence of four types of sites was attributed to the presence of Pb vacancies acting as charge compensators near the Ce^{3+} ions. The results were explained by the formation of two lead vacancies per five Ce^{3+} ions. The presence of these vacancies could explain the existence of two types of antiferromagnetic nearest neighbor (NN) Ce^{3+} pairs previously reported by magnetization steps measurements [15]. We propose that cerium pairs with isotropic exchange interaction are due to two NN Ce^{3+} ions located into cubic sites with no lead vacancy in the near vicinity. The other group of NN pairs is ascribed to pairs with a nearby lead vacancy affecting both strength of the exchange interaction and its anisotropy. Figure 2 represents the Field dependence of the oscillatory part of the magnetic susceptibility at 20 mK for $H \parallel [001]$; in this figure the de Haas-van Alphen (dHvA) oscillatory part of the magnetic susceptibility were clearly observed (upper figure); These oscillations are periodic in $1/H$, and the Fourier transform of the oscillatory part revealed one frequency $f \sim 90$ Tesla as shown in the lower part of figure 2. The analysis of the oscillatory component in the direction $H \parallel \langle 001 \rangle$ show periods of 1.12×10^{-2} and $1.23 \times 10^{-2} \text{ Tesla}^{-1}$ for $\text{Pb}_{1-x}\text{Ce}_x\text{Te}$ samples with $x = 0.0048$ and 0.007, respectively.

4 Conclusion

On the basis of the simplified Van Vleck paramagnetic susceptibility model of the Ce^{3+} ion in a octahedral site symmetry, the temperature dependence of the magnetic susceptibilities of three Ce^{3+} chalcogenide compounds PbA ($A = \text{Te}, \text{Se}, \text{and S}$), within the temperature range 4.2-300 K have been investigated and interpreted. In our study, the CFS parameter Δ were found to be 536 ± 50 K, 440 ± 50 K and 340 ± 50 K for $\text{Pb}_{1-x}\text{Ce}_x\text{S}$, $\text{Pb}_{1-x}\text{Ce}_x\text{Se}$ and $\text{Pb}_{1-x}\text{Ce}_x\text{Te}$, respectively. It was also shown that the doublet Γ_7 lies below the quadruplet Γ_8 . A good explanation of our observed magnetic data shows that the experimental magnetic susceptibilities including the comparison of the Crystal-Field Splitting Δ to: (i) the spin-orbit splitting (~ 1600 K) between the $^2F_{5/2}$ and $^2F_{7/2}$ manifolds and (ii) to the point charge model. This simple model can be further used along with other physical measurements such as EPR, optical spectroscopy or low temperature magnetization, as basis for reconstruction the magnetic functions of the compound. The comparison of the obtained CFS values to those calculated from the point charge model was satisfactory; we expect that this agreement can be further improved by accounting for the magnetic dipole interactions, the exchange interactions and the presence of distorted Ce^{3+} sites. Further analysis on the dHvA results will follow in future communications.

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