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Magnetic properties of Ce^{3+} in $Pb_{1-x}Ce_xSe$: Kondo and crystal-field effect

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Electron paramagnetic resonance (EPR) experiments were performed on a $Pb_{1-x}Ce_xSe$ crystal at liquid-helium temperatures and show very clearly that the doublet Γ_7 is the ground state for cerium ions. The cubic symmetry is shown and the effective Landé factor for the Ce^{3+} is determined to be 1.354 ± 0.003. An orbital reduction factor is introduced to explain the g experimental value. High-field magnetization results are in good agreement with the EPR results. The nominal Ce composition in PbSe deduced from saturation of the magnetization, $x=0.0405\pm0.0003$, is very closed to the value determined by microprobe analysis ($x=0.04$). At 1.5 K, an antiferromagnetic interaction between the nearest-neighbor cerium atoms is found, $J_{\mathrm{ex}}/k_B=-0.715\ \mathrm{K}$. The low-field magnetic-susceptibility results show that the magnetic moment of cerium impurities is strongly temperature dependent, explained by the presence of the crystal-field effect and the Kondo effect. [S0163-1829(97)04434-2]

I. INTRODUCTION

In this paper, we present experimental results and analysis of EPR, low-field susceptibility vs temperature and high-field magnetization (0–100 kOe) performed on DMS $Pb_{1-x}Ce_xSe$. Recently, the magnetic properties of IV-VI chalcogenides with diluted S-state rare-earth magnetic ions have been studied.[1–4] Studies of IV-VI diluted magnetic semiconductors containing non-S-state ions are also investigated.[5,6] PbSe, PbTe, PbS are interesting host crystals because it is easier to dilute rare-earth ions in this class of semiconductors than in II-VI chalcogenides. In these semimagnetic semiconductors, characterized by a small gap, the nearest-neighbors (NN) exchange interaction is the dominant one. The magnetic susceptibility of $Pb_{1-x}Ce_xSe$ presents a strong temperature dependence affected by the conduction electron impurity spin-exchange interaction (Kondo effect).[7] The $Pb_{1-x}Ce_xSe$ magnetic properties are also affected by the cubic crystal field of the NaCl lattice structure.

II. ELECTRON SPIN RESONANCE RESULTS

A. Spin Hamiltonian

A single crystal of $Pb_{1-x}Ce_xSe$ is grown by the well-known Bridgman method. X-ray-diffraction analysis indicates a fcc structure for this sample. The nominal Ce composition, $x=0.04$, was determined by microprobe analysis. Only one phase was found in the crystal. In the cubic crystal field (including the possibility of a tetragonal distortion) of PbSe, the spin Hamiltonian which describes the energy levels within a manifold of angular momentum J, for the ground state ($L=3$, $S=1/2$, $J=5/2$) $^2F_{5/2}$ in the case of Ce^{3+} $4f^1$, is written as[8,9]

$$H=g\mu_B\mathbf{H}\cdot\mathbf{J}+B_4(O_4^0+5O_4^4)+B_2O_2^0. \tag{1}$$

In Eq. (1), the first term is the Zeeman term, $\mathbf{H}$ is the external magnetic field, g is the Landé factor of the Ce^{3+} ion, and μ_B is the Bohr magneton. b_4 and b_2 are the crystal-field coefficients: $b_4=60B_4$ and $b_2=2B_2$.

The crystal-field operators O_4^0,O_4^4,O_2^0 are considered simple operators with the same transformation as the spherical harmonic operators. Without tetragonal distortion and at zero field, the ground state $^2F_{5/2}$ splits into a doublet Γ_7 and a quadruplet Γ_8 with a splitting $\Delta=E(\Gamma_8)-E(\Gamma_7)=6b_4$. In an octahedral symmetry site (positive value of b_4), the ground state is the doublet Γ_7. The tetragonal distortion effect on the doublet cannot be seen with an EPR measurement, the distortion affects only the quadruplet Γ_8 which splits into two Kramers doublets and thus increases the zero-field splitting.

B. Landé factor value

Figure 1 shows the $Pb_{1-x}Ce_xSe$ ($x=0.0405$) EPR spectra ($\nu=9.54\ \mathrm{GHz}$) of a powder and a single crystal with an $H\|[001]$ crystal axis at 4.2 K. No anisotropy in the EPR line position was observed with an orientation of the external field. The Dysonian line shape of the $Pb_{1-x}Ce_xSe$ signal is due to the skin effect[10] manifested by the metal-like behavior of $Pb_{1-x}Ce_xSe$ ($Eg=0.29\ \mathrm{eV}$ for PbSe, $\rho[Pb_{1-x}Ce_xSe]=0.0058\Omega$ cm at 300 K). This isotropic line is attributed to

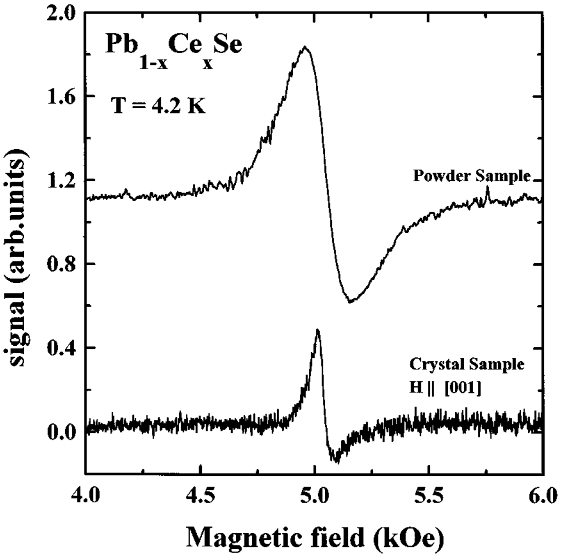

FIG. 1. Isotropic EPR spectra in the X band at 4.2 K for powder and crystal samples of Pb$_{1-x}$Ce$_x$Se.

the doublet Γ_7 which can be described using an effective spin 1/2 and an effective Landé factor $|g|=1.354\pm 0.003 = 5/3 g_J$. (Absolute value of the effective Landé factor means that the doublet Γ_7 case is an example of a negative effective Landé factor[8]). We deduced the experimental value of Landé factor g_J of the manifold J, $g_J = 0.812\pm 0.005$.

The 5% reduction of the g_J experimental value, compared to the theoretical value of the free ion $(6/7)$, is due to the existence of covalent bonding in the rare-earth ions (neglecting the effect of admixtures from excited states).[11] The experimental value can be explained if the orbital reduction factor is taken into account as follows:

$$g_j^{\mathrm{expt}} = g_j^{\mathrm{theor}} - (1-k)\left[\frac{J(J+1)-S(S+1)+L(L+1)}{2J(J+1)}\right] = \frac{6}{7} - \frac{8}{7}(1-k) \tag{2}$$

with $L=3$, $S=1/2$, and $J=5/2$.

Since Δg_j is the difference between the theoretical and experimental value of g_J, then

$$1-k = (7/8)\Delta g_J .$$

Using this expression, we obtain $1-k=0.039\pm 0.005$ for Pb$_{1-x}$Ce$_x$Se. This value is very similar to the case of Pb$_{1-x}$Yb$_x$Se $(1-k=0.041\pm 0.003)$.[5,6] At 4.2 K, the g value confirms that the Ce^{3+} Kramers doublet, Γ_7 is the ground state, and Ce^{3+} is in an octahedral symmetry site, i.e., the substitution of Pb ions by Ce ions.

III. MAGNETIZATION AND MAGNETIC SUSCEPTIBILITY

A. Magnetization results

Magnetization measurements were performed on a same crystal at different temperatures with a superconducting quantum interference device (SQUID) system at Louis Néel Laboratory (Grenoble). Figures 2(a) and 2(b) show magnetization at 1.5 and 4.2 K. The symbols represent the experimental data, the full lines are the best fit obtained using the modified cluster model[12,13] which take into account the contributions of the differents clusters. In this way, the total magnetization can be written as follows:

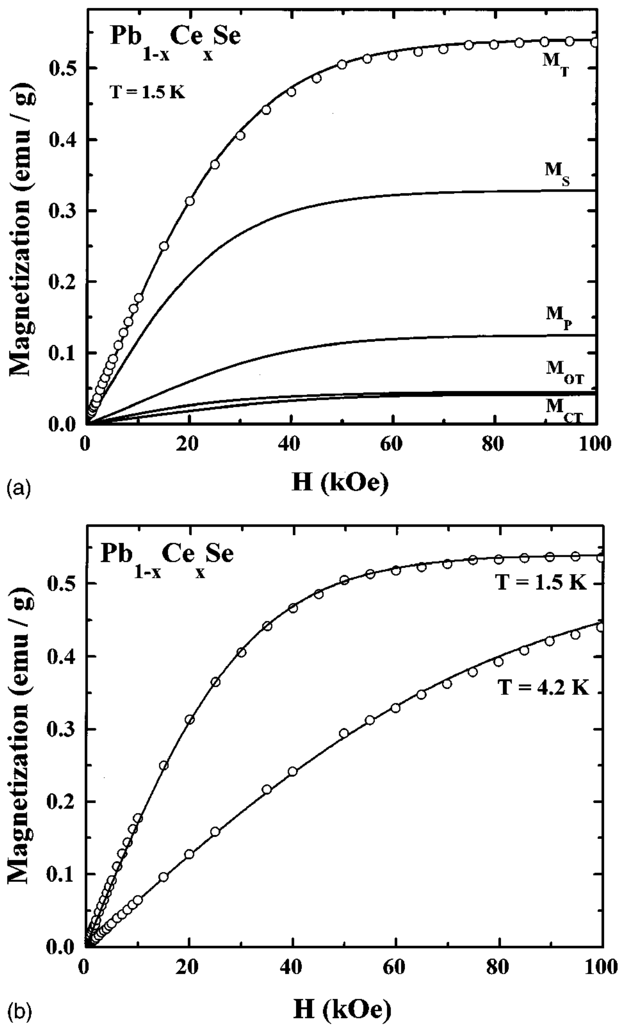

FIG. 2. Magnetization vs magnetic field. (a) Open circles, experiment; solid lines, calculated with different cluster contributions. (b) Open circles, experiment; solid lines, calculated total magnetization from a modified cluster model at 4.2 and 1.5 K.

$$M_T = M_{\mathrm{Ce}^{3+}} + M\chi_d \quad \text{with} \quad M_{\mathrm{Ce}^{3+}} = M_S + M_P + M_{\mathrm{OT}} + M_{\mathrm{CT}}, \tag{3}$$

where M_S, M_p, M_{OT}, and M_{CT} are, respectively, the contributions to the magnetization of the singles, the pairs, the open triplets, the closed triplets, and $M\chi_d$ is the PbSe lattice diamagnetic contribution with $\chi_d = -3.6\times 10^{-7}$ emu/g Oe.[14,15]

The single contribution is given by[16]

$$M_S = M_0 \tilde{S} x_{\mathrm{SAT}} B_{\tilde{S}}(\xi),$$

where

$$M_0 = g\mu_B \frac{Na}{m(x_{\mathrm{SAT}})}. \tag{4}$$

$m(x_{\mathrm{SAT}})$ is the molar mass of the compound: $m(x_{\mathrm{SAT}})=(1-x_{\mathrm{SAT}})m_{\mathrm{Pb}}+x_{\mathrm{SAT}}m_{\mathrm{Ce}}+m_{\mathrm{Se}}$. Na is the Avogadro number, g is the effective Landé factor determined from the EPR measurement ($g=1.354\pm0.003$), $\tilde{S}$ is the effective spin of the doublet Γ_7, x_{SAT} was obtained from the saturation magnetization, and $B_{\tilde{S}}(\xi)$ is the Brillouin function:

$$B_{\tilde{S}}(\xi)=\frac{2\tilde{S}+1}{2\tilde{S}}\coth\left(\frac{2\tilde{S}+1}{2\tilde{S}}\,\xi\right)-\frac{1}{2\tilde{S}}\coth\left(\frac{\xi}{2\tilde{S}}\right),$$

where

$$\xi=\frac{\tilde{S}g\mu_B H}{k_B T} \tag{5}$$

and k_B is the Boltzmann constant.

The pairs contribution is

$$M_P=\frac{1}{2}\,M_0x_2\,\frac{\Sigma_{S=0}^{S_{\max}}\exp[(J_{\mathrm{ex}}/k_BT)S(S+1)]S(\sinh\{[(2S+1)/2S]x_P\})B_S(x_P)}{\Sigma_{S=0}^{S_{\max}}\exp[(J_{\mathrm{ex}}/k_BT)S(S+1)](\sinh\{[(2s+1)/2S]x_P\})} \tag{6}$$

with $\xi_P=Sg\mu_BH/k_BT$, $S_{\max}=2\tilde{S}$, and J_{ex} is the NN exchange parameter. The open and the closed triplet contributions are

$$M_{\mathrm{OT}}=M_0x_{\mathrm{OT}}\langle S_Z\rangle_{\mathrm{OT}}\quad\text{with}\quad\langle S_Z\rangle_{\mathrm{OT}}=\frac{\Sigma_{S_a,S_b,m}m\,\exp[-E_{\mathrm{OT}}(S_a,S_b,m)/k_BT]}{\Sigma_{S_a,S_b,m}\exp[-E_{\mathrm{OT}}(S_a,S_b,m)/k_BT]} \tag{7}$$

and $E_{\mathrm{OT}}=-mg\mu_BH+J_{\mathrm{ex}}[S_b(S_b+1)-S_a(S_a+1)-\tilde{S}(\tilde{S}+1)]$:

$$M_{\mathrm{CT}}=M_0x_{\mathrm{CT}}\langle S_Z\rangle_{\mathrm{CT}}\quad\text{with}\quad\langle S_Z\rangle_{\mathrm{CT}}=\frac{\Sigma_{S_a,S_b,m}m\,\exp[-E_{\mathrm{CT}}(S_a,S_b,m)/k_BT]}{\Sigma_{S_a,S_b,m}\exp[-E_{\mathrm{CT}}(S_a,S_b,m)/k_BT]} \tag{8}$$

and $E_{\mathrm{CT}}=-mg\mu_BH+J_{\mathrm{ex}}[S_b(S_b+1)+3\tilde{S}(\tilde{S}+1)]$:

$$0\leqslant S_a\leqslant1,\quad |S_a-1/2|\leqslant S_b\leqslant S_a+1/2,\quad |m|\leqslant S_b.$$

The probabilities to find magnetic ions in singles, pairs, or triangle clusters, assuming a random distribution, are given by[17]

$$P_S=(1-x_{\mathrm{SAT}})^{12},$$

$$P_P=12x_{\mathrm{SAT}}(1-x_{\mathrm{SAT}})^{18},$$

$$P_{\mathrm{OT}}=18x_{\mathrm{SAT}}2(1-x_{\mathrm{SAT}})^{23}[2+5(1-x_{\mathrm{SAT}})],$$

$$P_{\mathrm{CT}}=1-P_S-P_P-P_{\mathrm{OT}}.$$

Each cluster-type composition is deduced from these expressions with $x_i=x_{\mathrm{SAT}}\,P_i$ $(i=S,P,\mathrm{OT},\mathrm{CT})$. A phenomenological parameter T_0 is introduced in the temperature, taking account of the long-distance magnetic interaction.

The first fitting of total magnetization was made using two fitting parameters x and T_0 and only the contribution of the single ions and the diamagnetic part of the PbSe lattice. We found $x_{\mathrm{SAT}}=0.0405$, $T_0=-0.2$ K at 1.5 K, and $x_{\mathrm{SAT}}=0.041$, $T_0=-0.21$ K at 4.2 K. These parameters are used for the second fit (with all the contributions) of the magnetization measurements data where the only fitting parameter is J_{ex}. The NN exchange interaction was found to be antiferromagnetic and temperature independent; $J_{\mathrm{ex}}/k_B=-0.715\pm0.005$ K.

B. Magnetic susceptibility

The susceptibility of Ce^{3+} is obtained from the experimental susceptibility minus the diamagnetic susceptibility of the PbSe lattice $[\Delta\chi=\chi(\mathrm{Pb}_{1-x}\mathrm{Ce}_x\mathrm{Se})-\chi_d]$. The reciprocal susceptibility of $\mathrm{Ce}^{3+}(\Delta\chi^{-1})$ vs the temperature shown in Fig. 3 is strongly dependent on the temperature. A Curie-Weiss behavior exists only approximately at a temperature above 100 K. This behavior is reproduced by a fit using the parameters deduced from EPR and magnetic measurements and the following expression:

$$\Delta\chi(T)=\frac{Nax}{m(x)}\,\frac{\mu_{\mathrm{Ce}}^2\mu_B^2}{3k_B(T-\theta)}, \tag{9}$$

where $\mu_{\mathrm{Ce}}=g_J\sqrt{J(J+1)}$ is the effective moment of Ce^{3+}. In this case, $\mu_{\mathrm{Ce}}=2.4\mu_B$, $J=5/2$, and $g_J=0.812$. x is the nominal composition of Ce^{3+} deduced from the saturation of the magnetization. The asymptotic Curie-Weiss temperature deduced from the linear part of the reciprocal susceptibility is found to be strongly negative, $\theta=-165$ K. The pronounced negative curve of the $\Delta\chi^{-1}$ plots vs temperature shows that the cubic crystal field affects the magnetic properties of the cerium $^2F_{5/2}$ ground state above 70 K. A determination of the splitting Δ between the doublet Γ_7 and the quadruplet Γ_8 energy levels can be deduced from the Jones law[18,19] as follows:

$$\frac{C}{\chi}-\theta=\frac{21T(1+2e^{-\delta})}{[5+26e^{-\delta}+(32/\delta)(1-e^{-\delta})]}\quad\text{with}\quad\delta=\frac{\Delta}{k_BT}. \tag{10}$$

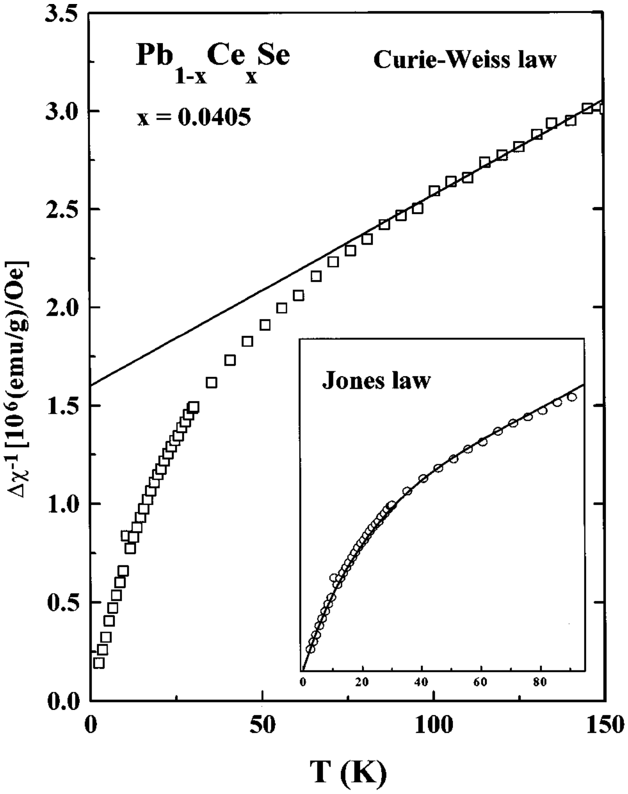

FIG. 3. Reciprocal magnetic susceptibility of Ce^{3+}, $(\Delta\chi)^{-1}$ vs temperature. In the insert is the Jones law fit with $\Delta = 268$ K.

An overall splitting of 268 K is sufficient in order to obtain reasonable agreement between the theoretical and experimental magnetic susceptibility (with $\theta = -0.2$ K). Using the value of the magnetic interaction between the NN Ce atoms, deduced from the magnetization curve, the Curie temperature θ at low temperature can be calculated as follows:[16]

$$\theta(x) = \left[\frac{2xJ(J+1)}{3k_B}\right] ZJ_{\text{ex}}.$$

Z is the number of sites on the coordination sphere ($Z = 12$).

We found a Curie temperature ($\theta = -0.17$ K) of the same magnitude as the Jones law one. The Curie-Weiss temperature $\theta = -165$ K, deduced from relation (9), can be seen as a manifestation of the Kondo effect on the susceptibility. It is well known that for components with diluted rare-earth-like cerium,[20,21] Ce^{3+} ions produce Kondolike anomalies in the physical properties. The Kondo effect of cerium is connected to the presence of a $4f$ level close to the Fermi level which produces a large resonant scattering effect. The resonant scattering mechanism of a conduction electron by localized atom impurities begins preponderant on the direct exchange between conduction electron spin and localized electrons. The interaction exchange J_{sf} is negative and large. For alloys with diluted magnetic impurities, the magnetic susceptibility obeys a Curie-Weiss law with $|\theta| \cong 4T_{\text{Kondo}}$.[22]

IV. CONCLUSION

From EPR measurements, we conclude that the Ce^{3+} substitute the Pb^{2+} ions in PbSe, i.e., the octahedral symmetry of the site is confirmed. The orbital reduction factor $(1-k)$ is closed to the value for ytterbium ions octahedral in PbSe.[5] At 4.2 K, the effective Landé factor is determined for this material and its value confirms that the doublet Γ_7 is the ground state. The magnetization measurements show a magnetic ordering at 1.5 K. The value of the nominal Ce composition x deduced from the saturation of the magnetization is very closed to the composition determined by microprobe analysis and the exchange interaction parameter is found to be antiferromagnetic in this material. At 1.5 and 4.2 K, the magnetization measurements confirm that the doublet Γ_7 is quite isolated. The low-field magnetic susceptibility is influenced by the PbSe crystal-field effect on the diluted cerium ions and shows the presence of the Kondo effect. For Ce^{3+} diluted in PbSe, Kondo temperature is found to be equal to 41 K. Measurement performed on a single crystal of γ-Ce gives 40 K for the Kondo temperature.[23] This value has been calculated by Cornut *et al.*[20] in the case of two levels. The splitting of the Ce^{3+} ground state into the doublet Γ_7 and quadruplet Γ_8 energy levels allows one to determine the unique value of the crystal parameter $b_4^0 \cong 40$ K (without tetragonal distortion). In the case of alloys with ytterbium impurities such as PbYbSe, PbYbTe, and PbYbS, the EPR measurements can give information about the nature of the ground state. Measurements performed by Isber *et al.*[5] confirm a cubic symmetry site and a doublet Γ_6 as a ground state for Yb^{3+} in PbSe, PbTe, and PbS. But no Kondo effect is present in these materials although many authors related its existence in the case of ytterbium impurity alloys.[22,24]

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