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The effect of the crystal field on magnetization steps due to exchange-coupled Eu^{2+} open and closed triplets in $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$

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Abstract. The values of the magnetic fields at which magnetization steps (MSs) occur due to exchange-coupled open and closed triplets of Eu^{2+} ions ($S = 7/2$) are calculated for a $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$ single crystal, taking into account the crystal-field (CF)-interaction, which causes the isotropic separation between two consecutive MSs, $\Delta B = B_{l+1} - B_l$ ($l = 1, 2, \dots, 6$), where B_l is the value of the l th MS, that exists in the absence of the crystal field to become anisotropic with respect to the orientation of the external magnetic field (\mathbf{B}). The contribution of the single-ion anisotropic CF by an exchange-coupled open triplet (OT) leads to an average separation, ΔB_{av}^{OT-CF} , 10% higher than ΔB when $\mathbf{B} \parallel [100]$, and 5 and 8% lower than ΔB for $\mathbf{B} \parallel [110]$ and $\mathbf{B} \parallel [111]$, respectively. As for the exchange-coupled closed triplet (CT), it was estimated that ΔB_{av}^{CT-CF} is 7.0% higher than ΔB when $\mathbf{B} \parallel [100]$, and 3.4 and 4.1% lower than ΔB when $\mathbf{B} \parallel [110]$ and $\mathbf{B} \parallel [111]$, respectively. Furthermore, the values of ΔB_l^{OT-CF} and ΔB_l^{CT-CF} were found to depend on l ($l = 1, \dots, 6$ for OT, and $l = 1, \dots, 9$ for CT), varying by up to about 40%.

1. Introduction

As the strength of the external magnetic field is increased, energies of different levels of a paramagnetic ion change in different manners when the ion is imbedded in a single crystal depending upon the orientation of the magnetic field with respect to the crystal axes. Magnetization steps (MSs) are the consequence of crossings of the energy levels with increasing magnetic field, each energy level being characterized by its unique magnetization moment. At liquid-helium temperatures, such that $k_B T \ll \Delta$ (Δ is the smallest energy splitting between adjacent levels in the absence of external magnetic field and k_B is the Boltzmann constant), a crossing results in an abrupt change, referred to as an MS, in the magnetization of the ground-state manifold of energy levels due to the differences in the Boltzmann populations of the various energy levels. From MS positions of the external magnetic field, interesting information, like the strength of the exchange interaction between two paramagnetic ions, and the energy-level splittings of the paramagnetic ion due to the crystal field, as well as the absolute signs of the spin-Hamiltonian parameters can be obtained [1].

Magnetization and electron paramagnetic resonance (EPR) measurements have been extensively used to study magnetic properties and electronic structures of II–VI and IV–VI diluted magnetic semiconductors (DMSs) [1–4], which have been mainly studied via the Mn^{2+} and Co^{2+} ions serving as paramagnetic probe ions [5–7]. The magnetization of a sample is expressed by a Brillouin function, modified by an antiferromagnetic exchange interaction between the Mn^{2+} , or Co^{2+} , ions. Usually, this antiferromagnetic interaction is caused by the superexchange interaction mediated via anions. Typical values of the antiferromagnetic exchange interaction between Mn^{2+} ions in II–VI compounds are $J_P/k_B \geq 10$ K [8–11]. The (antiferromagnetic) exchange interaction between Co^{2+} ions in II–VI compounds has been determined by magnetic-susceptibility and Raman-scattering measurements, its value being $J_P/k_B \geq 35$ K [12–14]. On the other hand, not many investigations have been made on the IV–VI compounds with transition-metal rare-earth ions serving as paramagnetic probe ions. Magnetic susceptibility measurements on an $\text{Sn}_{1-x}\text{Eu}_x\text{Te}$ sample exhibited a weak antiferromagnetic coupling between Eu^{2+} ions [15, 17], in good agreement with the magnetization and magnetic susceptibility measurements of Anderson *et al* [3] and those of Savage and Rhyne [16] on $\text{Pb}_{1-x}\text{Gd}_x\text{Te}$, indicating a small antiferromagnetic exchange interaction between the Gd^{3+} ions. Recently, magnetization measurements by Bindilatti *et al* [18] revealed the presence of well resolved MSs in $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$ ($x = 1.3, 3.0$ and 4.1%) at 30 mK. A comparison between the measured magnetization and theoretical estimations allowed for an estimate of J_P , the nearest-neighbour (NN) exchange interaction. Magnetization steps due to isolated Eu^{2+} ions, not influenced by any exchange interactions, were also observed.

Liquid-helium-temperature electron paramagnetic resonance (EPR) studies in the X-band on $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$ ($x = 1.3\%$) have been recently reported by Isber *et al* [19a] and by Misra *et al* [19b] the values of the spin-Hamiltonian parameters g , b_4 and b_6 were estimated. The positive absolute sign of b_4 was confirmed from the variation in the relative intensities of EPR transitions at 300 K and 4.2 K; this was in conformity with that determined by MS observed at 50 mK [18]. Usually, the value of the exchange constant in IV–VI materials is very small. To interpret MS data correctly, it is necessary to take into account the effect of the crystal field on different possible configurations of the various coupled clusters, formed by the probe paramagnetic ions, i.e. closed and open triplets in addition to exchange-coupled pairs, which have been well investigated.

It is the purpose of the present paper to report a detailed theoretical calculation of the effect of the crystal field on MSs due to exchange-coupled closed and open triplets of Eu^{2+} ions in $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$.

2. Energies of the various exchange-coupled configurations in the absence of a crystal field

2.1. Exchange-coupled pairs

The ‘single- J ’ model of energy levels, without taking into account the crystal field, has been well investigated [17–22]. For the sake of continuity this case will be briefly described. In this model, only the pair exchange interaction between the nearest neighbours is considered. Additional possible cluster configurations formed by exchange-coupled ions are open triplets, closed triplets and configurations consisting of more than three ions. More recently, quartet configurations have been also investigated by Liu *et al* [23]. The magnetic moment of a free Eu^{2+} ion is $M = -g\mu_B(S + L)$, where g is the Landé factor; $S = 7/2$ and $L = 0$ are, respectively, the spin and orbital momentum for Eu^{2+} . The resulting magnetization

can be described as a function of the magnetic field by a Brillouin function [17, 19a, 21]. No MS can be observed in this case. However, when the same ion is subjected to a crystal field, MSs due to crossing of the energy levels, which now become possible, are observed [2, 18, 24]. As for an Eu^{2+} exchange-coupled pair, figure 1(a) shows the calculated magnetization at 60 mK in the absence of a crystal field using the values $g = 1.980$ and $J_P/k_B = -0.24$ K [24]. Occurrences of seven MSs due to exchange pairs can be clearly observed at the magnetic fields B_n , such that

$$2n|J_P| = g\mu_B B_n \quad n = 1, 2, \dots, 7. \quad (1)$$

Figure 1(a) shows that at low magnetic fields the magnetization value due to the pair is equal to zero, corresponding to the $|S_T = 0, m_T = 0\rangle$ state. (Here $S_T = S_1 + S_2$; $0 \leq S_T \leq 2S$, where S_1 and S_2 are the spins of the two ions constituting the pair; for Eu^{2+} $S_1 = S_2 = 7/2$.) At $B = B_1 = 2|J_P|/g\mu_B$, the ground state (lowest energy level) changes to $|1, -1\rangle$ from $|0, 0\rangle$. This magnetization step ($k_B T \ll |J_P|$) results in an increase in the magnetic moment of the ground state as B is increased. At low temperatures, when $B > 14|J_P|/g\mu_B$ the magnetization becomes constant at the value $M_S = 7g\mu_B$, and remains constant for further increase in the magnetic field, since no crossing of the energy levels now takes place.

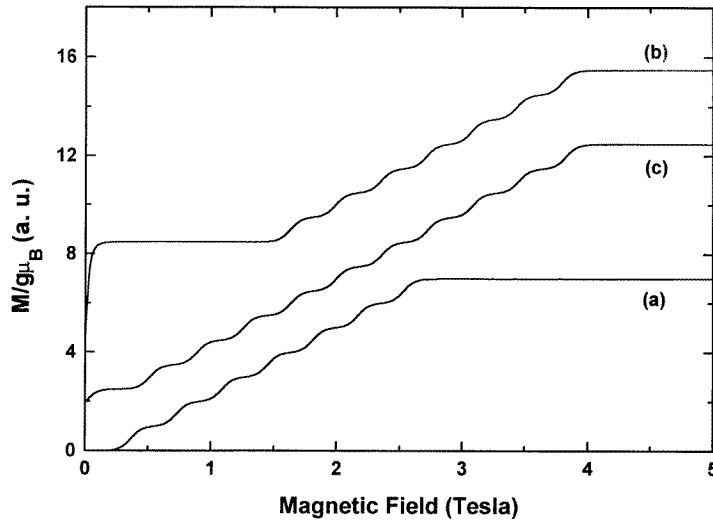


Figure 1. Calculated magnetization curves for $Pb_{1-x}Eu_xSe$ at $T = 60$ mK in the absence of the crystal field for (a) exchange-coupled pairs, (b) exchange-coupled open triplets and (c) exchange-coupled closed triplets; the value of the isotropic exchange constant used was $J_P/k_B = -0.24$ K. The curves for closed triplets and open triplets have been displaced by two and four units, respectively. The same arbitrary units (au) of magnetization have been used in figures 1–4.

2.2. An open triplet

An open triplet (OT) is a cluster wherein three magnetic ions, with spins S_1 , S_2 and S_3 , are exchange coupled to each other in such a way that there are only two nearest-neighbour (NN) couplings, i.e. those of S_1 and S_2 and S_2 and S_3 . The positions B_l of the MSs due to an OT are given by

$$2l|J_P| = g\mu_B B_l \quad l = 9, 11, 13, \dots, 21. \quad (2)$$

Figure 1(b) exhibits the calculated magnetization of an exchange-coupled OT, displaced by four units above that for an exchange-coupled pair. The ground state for an open triplet ($\uparrow\downarrow\uparrow$), wherein two Eu^{2+} spins are pointing in the same direction while the third one is pointing in the opposite direction, have the spin $S = 7/2$, and the OT magnetization can be represented, to a good approximation, by a Brillouin function with $S = 7/2$ for the value of the external magnetic field $B < 7|J_P|/g\mu_B$.

2.3. A closed triplet

In a closed triplet, all three ions are exchange coupled to each other, i.e. there exist NN couplings between S_1 and S_2 , S_2 and S_3 and S_1 and S_3 . The ground state for a closed triplet of an Eu^{2+} ion ($S = 7/2$) is $S_T = 1/2$ ($S_T = S_1 + S_2 + S_3$). The ten possible MS positions are given by

$$2m|J_P| = g\mu_B B_m \quad m = 3, 5, \dots, 21. \quad (3)$$

Figure 1(c) exhibits the calculated magnetization of a closed triplet displaced by two units above that for an exchange-coupled pair.

In conclusion, the spacings between any two successive MS due to pairs, and open and closed triplets are the same. However, their overall values are different from each other.

3. The effect of the crystal field on MSs corresponding to the various exchange-coupled configurations of Eu^{2+} ions in $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$

3.1. Uncoupled single ions

The spin Hamiltonian which describes an isolated Eu^{2+} ($^8S_{7/2}$) ion in the presence of a crystal field at the cubic site symmetry of $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$ can be expressed as [15, 25, 26]

$$H_{SI-CF} = g\mu_B \mathbf{B} \cdot \mathbf{S} + B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4). \quad (4)$$

In (4), O_4 and O_6 are the fourth- and the sixth-order spin operators characteristic of cubic symmetry; $b_4 = 60B_4$ and $b_6 = 1260B_6$ are the corresponding crystal-field coefficients, which depend on the paramagnetic ion and the configuration of the host lattice. In zero magnetic field, the $^8S_{7/2}$ state of the Eu^{2+} ion splits into two doublets, Γ_6 and Γ_7 , and one quadruplet, Γ_8 . Figure 2(a) shows the EPR spectrum of $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$ for the magnetic-field orientation parallel to the [100] direction at 4.2 K. Seven allowed EPR transitions ($\Delta M = \pm 1$, where M is the electronic magnetic quantum number of the Eu^{2+} ion) were observed [19a,b]. The energy levels for a single Eu^{2+} ion in $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$ as functions of the external Zeeman field intensity, as calculated by a numerical diagonalization of the H_{SI-CF} matrix with the values of the parameters $g = 1.980$, $b_4 = 0.270$ GHz and $b_6 = -0.0026$ GHz, determined from EPR measurements in the X-band (9.56 GHz) [19], are shown in figure 2(b). Figure 2(c) shows the calculated magnetization of the Eu^{2+} single ion in PbSe at 30 mK. As the magnetic field strength was increased to $B_{cr} = 2$ kOe a magnetization step was observed due to crossing of the two levels $M = -5/2$ and $M = -7/2$. No crossing of the $M = -5/2 \leftrightarrow -7/2$ levels was observed for the orientation of the external magnetic field \mathbf{B} parallel to the [110], or [111], directions. The estimated magnetizations for an uncoupled Eu^{2+} ion for $\mathbf{B} \parallel [110]$ and $\mathbf{B} \parallel [111]$ at 30 mK are displayed in figure 3. No MSs occur for these directions of \mathbf{B} .

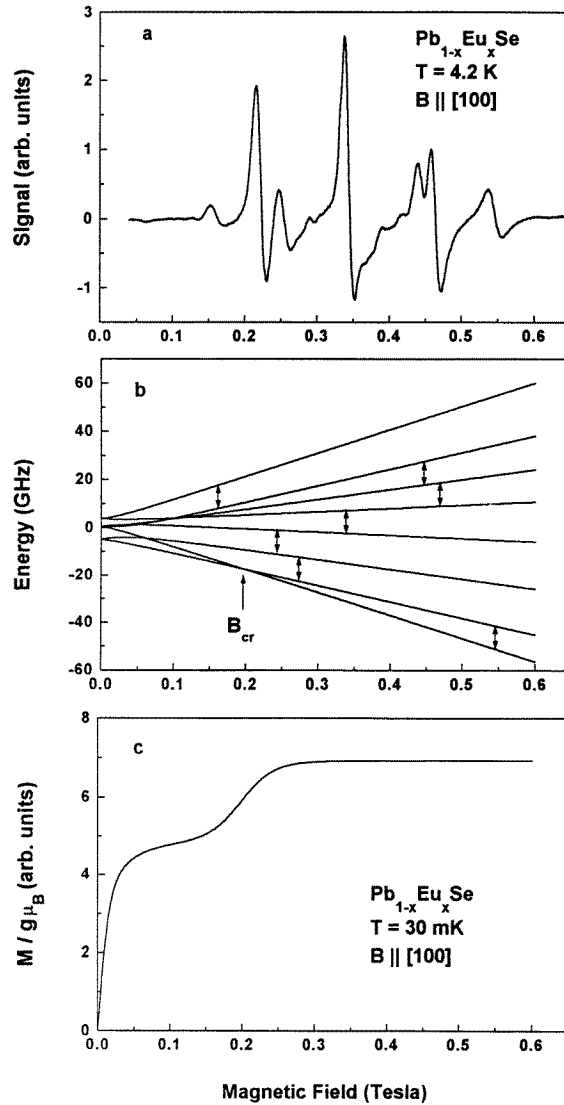


Figure 2. (a) Eu^{2+} EPR spectrum in $Pb_{1-x}Eu_xSe$ for $B \parallel [100]$ at 4.2 K, (b) the energy levels of Eu^{2+} in PbSe as calculated by a numerical diagonalization of the spin-Hamiltonian matrix H_{SI-CF} given by (4) as functions of the intensity of the external magnetic field parallel to the [100] direction, and (c) the calculated magnetization curve for an isolated Eu^{2+} ion in PbSe at 30 mK for $B \parallel [100]$. The same arbitrary units (au) of magnetization have been used in figures 1–4.

3.2. An exchange-coupled pair

The dominant exchange interaction of $Eu^{2+}-Eu^{2+}$ pairs in $Pb_{1-x}Eu_xSe$ was determined to be equal to $J_P/k_B = -0.24\text{ K}$ [24]. The various states of an exchange-coupled Eu^{2+} pair have the energies $2J_P$, $6J_P$, $12J_P$, $20J_P$, $30J_P$, $42J_P$ and $56J_P$ for the electronic spin

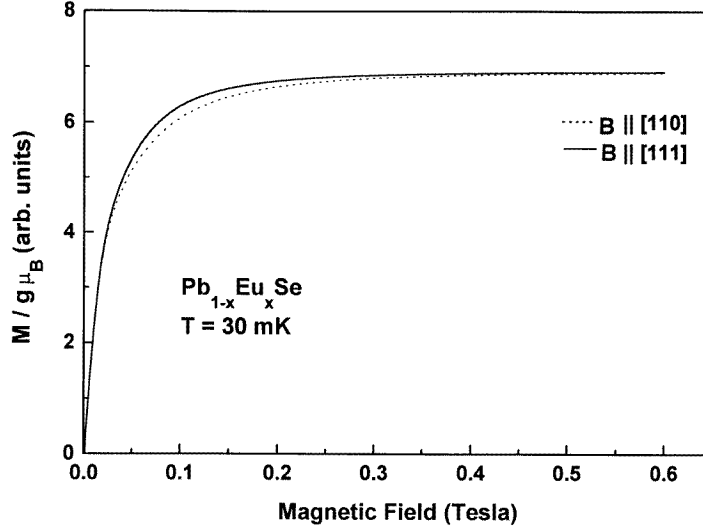


Figure 3. Calculated magnetization curves for an uncoupled Eu^{2+} ion in $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$ at 30 mK for $B \parallel [110]$ and for $B \parallel [111]$. The same arbitrary units (au) of magnetization have been used in figures 1–4.

$S = 7/2$ of the Eu^{2+} ion. Since the overall zero-field splitting of the ground state for a single Eu^{2+} ion is equal to $\Delta = 32b_4 - 8b_6 = 0.42$ K, which is rather significant, it is necessary to take into account the effect of the crystal field.

The spin Hamiltonian for an exchange-coupled Eu^{2+} pair in $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$ subjected simultaneously to the exchange interaction (EI) and crystal field (CF) is

$$H_{EI-CF}^P = g\mu_B(\mathbf{S}_1 + \mathbf{S}_2) \cdot \mathbf{B} - 2J_P \mathbf{S}_1 \cdot \mathbf{S}_2 + [B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4)]_{|1\rangle} + [B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4)]_{|k\rangle}. \quad (5)$$

In (5), the basis vectors in the direct-product representation, with the matrix dimension (64×64) , are $|M_1 = 1, M_2 = k\rangle = |1, k\rangle$ with $1, k = -7/2, -5/2, \dots, 5/2, 7/2$. The energy levels can be calculated by a numerical diagonalization of the H_{EI-CF}^P matrix, as given by (5) with $J_P = -0.24$ K, $g = 1.982$, $b_4 = 0.270$ GHz, $b_6 = -0.0026$ GHz [19]. The elements of the pair matrix $M_{(i,j)}^P(B)$ for H_{EI-CF}^P can be deduced from those for the H_{SI-CF} , S_x , S_y and S_z matrices for a single ion ($S = 7/2$) using the following equivalence:

$$M_{(i,j)}^P(B) = -J_P[S_{x_{m_i, n_j}} S_{x_{p_i, q_j}} + S_{y_{m_i, n_j}} S_{y_{p_i, q_j}} + S_{z_{m_i, n_j}} S_{z_{p_i, q_j}}] + H_{m_i, n_j}^{SI-CF}(B)\delta_{p_i, q_j} + H_{p_i, q_j}^{SI-CF}(B)\delta_{m_i, n_j} \quad (6)$$

where $i, j = 0, 1, \dots, 63$, and m_i, n_j are the values of $(i/8)$ rounded to an integer, as follows: m_i, n_j take the values 0 for $i, j = 0, 1, \dots, 7$, and 1 for $i, j = 8, 9, \dots, 15$, etc; while p_i and q_j take on the values 0, 1, \dots , 7, for $i, j = 0, 1, \dots, 7$ and 0, 1, \dots , 7 for $i, j = 8, 9, \dots, 15$, etc; $\delta_{i,j}$ is the Kronecker-delta function: $\delta_{i,j} = 1$ for $i = j$ and $\delta_{i,j} = 0$ for $i \neq j$; $H^{SI-CF}(B)$ is the matrix representing the Zeeman and crystal-field interactions for an isolated Eu^{2+} ion. Figure 4(a) exhibits the calculated magnetization of an exchange-coupled pair of Eu^{2+} ions in the presence of a crystal field for $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$ for the orientations of the external magnetic field along the [100], [110] and [111] directions; the curves for $B \parallel [110]$ and $B \parallel [111]$ have been displaced above that for $B \parallel [100]$;

without such displacement the saturated values at higher magnetic fields for all three curves would be the same. The energy levels, ε_{ij} were calculated by a numerical diagonalization of the H_{E1-CF}^P matrix. The value of the magnetization was calculated by the use of the thermodynamic definition:

$$\text{mag}_P = -k_B N T \frac{\partial \ln(Z)}{\partial B} \quad (7)$$

where Z is the partition function, given by

$$Z = \sum_{i,j} \exp(-\varepsilon_{i,j}/k_B T). \quad (8)$$

In the calculation, only the eleven lowest-lying levels were taken into consideration. The values of $\Delta B_j = B_{j+1} - B_j$ in the absence of the crystal field are the same for all j : $\Delta B_j = 0.360$ T. On the other hand, when the crystal field is present, the average separations, ΔB_{av} , are different for the three orientations of \mathbf{B} . It is found that ΔB_{av} is 9% higher than ΔB for $\mathbf{B} \parallel [100]$, and 4% and 7% lower than ΔB for $\mathbf{B} \parallel [110]$ and $[111]$, respectively, where ΔB represents the case for the absence of the crystal field, which is independent of the orientation of \mathbf{B} .

3.3. An exchange-coupled open triplet

The spin Hamiltonian for an open triplet of Eu^{2+} ions in $Pb_{1-x}Eu_xSe$ in the presence of the crystal field is given by

$$\begin{aligned} H_{E1-CF}^{OT} = & g\mu_B(\mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3) \cdot \mathbf{B} - 2J_P \mathbf{S}_1 \cdot \mathbf{S}_2 - 2J_P \mathbf{S}_1 \cdot \mathbf{S}_3 \\ & + [B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4)]_{|l\rangle} \\ & + [B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4)]_{|k\rangle} \\ & + [B_4(O_4^0 + 5O_4^4) + B_6(O_6^0 - 21O_6^4)]_{|m\rangle}. \end{aligned} \quad (9)$$

The basis vectors in the direct-product representation are $|l, k, m\rangle$ where $l, k, m = -7/2, -5/2, \dots, 5/2, 7/2$, with the matrix dimensions of H_{E1-CF}^{OT} 512×512 . The matrix elements of H_{E1-CF}^{OT} can be determined from those for the single and pair spin-Hamiltonian matrices. Defining $\mathbf{S}_{123} = \mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3$ and $\mathbf{S}_{23} = \mathbf{S}_2 + \mathbf{S}_3$, one obtains

$$-2J_P[\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_1 \cdot \mathbf{S}_3] = J_P[\mathbf{S}_1^2 - \mathbf{S}_{123}^2 + \mathbf{S}_{23}^2]. \quad (10)$$

The matrix elements for an open triplet are given by

$$\begin{aligned} M_{(ii,jj)}^{OT}(B) = & M_{(m_{ii},n_{jj})}^z(B)\delta_{p_{ii},q_{jj}} + M_{p_{ii},q_{jj}}^{SI-CF}(B)\delta_{m_{ii},n_{jj}} \\ & + J_P[\mathbf{S}_{1(ii,jj)}^2 - \mathbf{S}_{123(ii,jj)}^2 + \mathbf{S}_{23(ii,jj)}^2] \end{aligned} \quad (11)$$

where $\mathbf{S}_1^2 = S(S+1)\mathbf{I} = \frac{63}{4}\mathbf{I}$, where \mathbf{I} is the unit matrix; $\mathbf{S}_{1(ii,jj)}^2 = S(S+1)\delta_{ii,jj} = (63/4)\delta_{ii,jj}$; m_{ii} and n_{jj} are the values of $(ii/8)$ and $(jj/8)$, respectively ($ii, jj = 0, 1, \dots, 511$) rounded to integral values over 8. $M_{(m_{ii},n_{jj})}^z$ is the pair Hamiltonian matrix including terms other than those due to exchange coupling. Figure 4(b) shows the calculated magnetization of an open triplet in the presence of the crystal-field interaction for $Pb_{1-x}Eu_xSe$; the curves for $\mathbf{B} \parallel [110]$ and $\mathbf{B} \parallel [111]$ have been displaced above that for $\mathbf{B} \parallel [100]$; without such displacement the saturated values at higher magnetic fields for all three curves would be the same. The MS positions, B_l^{OT} , depend upon the orientation of the magnetic field. The average separation between two successive MSs, ΔB_{av}^{OT} , is 10% higher than ΔB for $\mathbf{B} \parallel [100]$, and 5 and 8% lower than ΔB for $\mathbf{B} \parallel [110]$ and $[111]$, respectively, where ΔB is the separation in the absence of the crystal field independent of

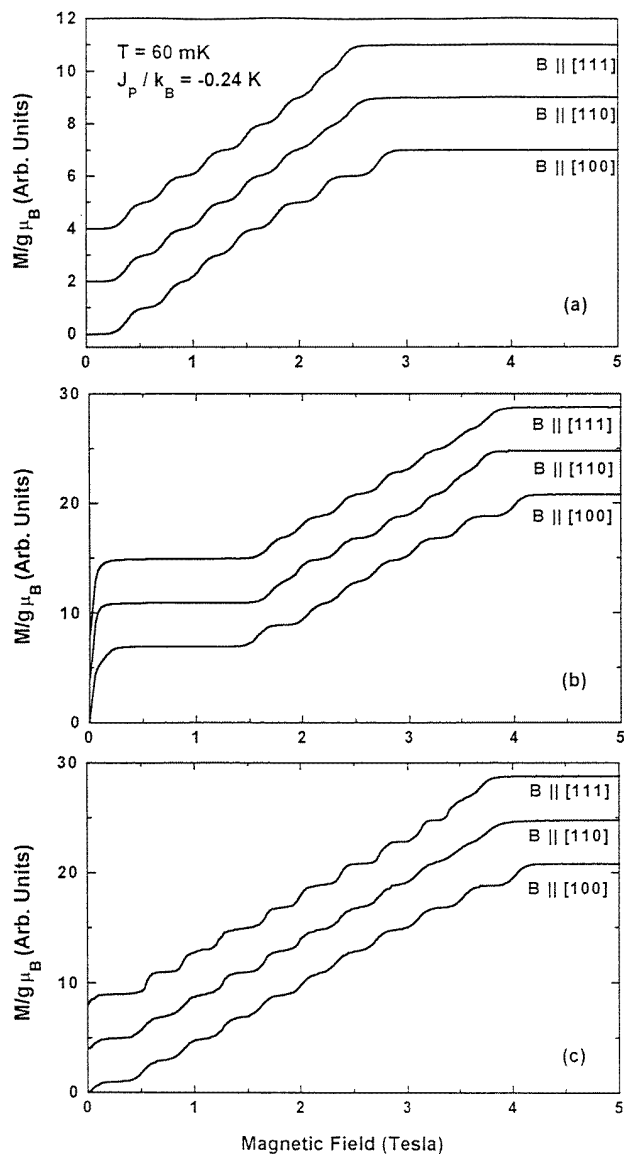


Figure 4. Calculated magnetization curves for $\text{Pb}_{1-x}\text{Eu}_x\text{Se}$ at 60 mK taking into account the effect of the crystal-field terms for three orientations of the external magnetic field: $B \parallel [100]$, $B \parallel [110]$ and $B \parallel [111]$: (a) exchange-coupled pairs; (b) an exchange-coupled open triplet; (c) an exchange-coupled closed triplet. In each figure, the curves for $B \parallel [110]$ and $B \parallel [111]$ have been displaced above that for $B \parallel [100]$ for better viewing, since the saturated values at higher magnetic fields for the three curves are identical. The same arbitrary units (au) of magnetization have been used in figures 1–4.

the orientation of B . Furthermore, $\Delta B_l^{OT} = B_{l+1}^{OT} - B_l^{OT}$ depend upon the value of l , and can change as much as about 40%, as compared to the case for the absence of the crystal field.

3.4. An exchange-coupled closed triplet

The spin Hamiltonian for an exchange-coupled closed triplet of Eu^{2+} ions in $Pb_{1-x}Eu_xSe$, taking into account the single-ion anisotropy, can be expressed as

$$H_{E1-CF}^{CT} = H_{E1-CF}^{OT} - 2J_P \mathbf{S}_2 \cdot \mathbf{S}_3. \quad (12)$$

Here, the basis vectors are the same as those used for the open-triplet case. One only needs to define $\mathbf{S}_{123} = \mathbf{S}_1 + \mathbf{S}_2 + \mathbf{S}_3$, for which

$$-2J_P[\mathbf{S}_1 \cdot \mathbf{S}_2 + \mathbf{S}_1 \cdot \mathbf{S}_3 + \mathbf{S}_2 \cdot \mathbf{S}_3] = J_P[3\mathbf{S}_1^2 - \mathbf{S}_{123}^2]. \quad (13)$$

The matrix elements for an open triplet are given by, noting that $\mathbf{S}_1^2 = \mathbf{S}_2^2 = \mathbf{S}_3^2$

$$M_{(ii,jj)}^{CT}(B) = M_{(m_{ii},n_{jj})}^z(B)\delta_{p_{ii},q_{jj}} + M_{(p_{ii},q_{jj})}^{SI-CF}(B)\delta_{m_{ii},n_{jj}} + J_P[3\mathbf{S}_{1(ii,jj)}^2 - \mathbf{S}_{123(ii,jj)}^2]. \quad (14)$$

Figure 4(c) shows the calculated magnetization curve for a closed triplet of Eu^{2+} ions in $Pb_{1-x}Eu_xSe$ taking into account the crystal-field interaction; the curves for $\mathbf{B} \parallel [110]$ and $\mathbf{B} \parallel [111]$ have been displaced above that for $\mathbf{B} \parallel [100]$; without such displacement the saturated values at higher magnetic fields for all three curves would be the same. It is found that the average separation, ΔB_{av}^{CT} , is 7.0% higher than ΔB for $\mathbf{B} \parallel [100]$, and 3.4 and 4.1% lower than ΔB for $\mathbf{B} \parallel [110]$ and $[111]$, respectively, as compared to the case for the absence of the crystal field, where ΔB is the separation in the absence of the crystal field, independent of the orientation of \mathbf{B} .

4. Concluding remarks

It is concluded from the present study that in $Pb_{1-x}Eu_xSe$ the crystal field alters the separation between the magnetization steps for the various exchange-coupled cluster configurations of Eu^{2+} ions. Further, it is shown that when the crystal-field splitting becomes comparable to the exchange interaction the experimental difference of the separation, ΔB , between two successive magnetization steps of pairs becomes anisotropic, not being the same for different orientations of the external magnetic field. They vary by about 12%, when the exchange interaction is taken into account over and above the crystal field. When compared to the case of the absence of crystal field, for which the separation ΔB is independent of the orientation of \mathbf{B} , it is found that for an open triplet the average separation in the presence of the crystal field, ΔB_{av}^{OT-CF} , is 10% higher than ΔB for $\mathbf{B} \parallel [100]$, and 5 and 8% lower than ΔB for $\mathbf{B} \parallel [110]$ and $\mathbf{B} \parallel [111]$, respectively. Likewise, for a closed triplet, in the presence of the crystal field, ΔB_{av}^{CT-CF} is 7.0% higher than ΔB for $\mathbf{B} \parallel [100]$, and 3.4 and 4.1% lower than ΔB for $\mathbf{B} \parallel [110]$ and $\mathbf{B} \parallel [111]$, respectively. Furthermore, ΔB_l^{OT-CF} and ΔB_l^{CT-CF} depend on l ($l = 1, \dots, 6$ for OT, and $l = 1, \dots, 9$) and can vary by about 40%. The hyperfine interaction has here not been taken into account because of its magnitude being less than 20% of the crystal-field splitting, and no hyperfine structure is manifested in the magnetization data.

The crystal-field effect is more prominent in the case of $Pb_{1-x}Eu_xS$ than in $Pb_{1-x}Eu_xSe$, being characterized by larger values of the spin-Hamiltonian parameters than those in $Pb_{1-x}Eu_xSe$, for which case the values have been cited following (5) above. More recent EPR data at low temperatures reveal that the values of the Eu^{2+} spin-Hamiltonian parameters $b_4 = 0.448$ GHz and $b_6 = -0.011$ GHz [27], with the exchange-interaction constant ($= -0.24$ K) being the same as that in the $Pb_{1-x}Eu_xSe$ lattice [28].

It is hoped that the present calculations would be found useful in the interpretation of EPR and MS data where exchange couplings between ions become important to affect the observed data significantly.

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