



Spin dimer analysis of the three-dimensional antiferromagnetic ordering in the quaternary manganese sulfides $BaLn_2MnS_5$ ($Ln = La, Ce, Pr$)

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Abstract

The quaternary manganese sulfides $BaLn_2MnS_5$ ($Ln = La, Ce, Pr$) consist of $(MnS_4)^{6-}$ anions separated with short $S \cdots S$ distances slightly longer than the van der Waals distance. Nevertheless, these sulfides are known to undergo a three-dimensional (3D) antiferromagnetic ordering at a reasonably high temperature (i.e., $T_N = 58.5, 62.0$ and 64.5 K for $Ln = La, Ce$ and Pr , respectively). The origin of this observation was probed by studying the $Mn-S \cdots S-Mn$ super-superexchange interactions of $BaLn_2MnS_5$ on the basis of spin dimer analysis. The non-bonding $S \cdots S$ contacts in the vicinity of the van der Waals distance are found essential in determining the strengths of the $Mn-S \cdots S-Mn$ super-superexchange interactions. The antiferromagnetic spin exchange between adjacent $(MnS_4)^{6-}$ anions along the c -direction (J_2) is calculated to be stronger than that in the ab -plane (J_1) by a factor of ~ 10 , so that the strongly interacting spin units of $BaLn_2MnS_5$ ($Ln = La, Ce, Pr$) are 1D chains made up of the exchange paths J_2 . The relative strengths of the spin exchange interactions for the J_1 and J_2 paths are consistent with the finding that the Néel temperatures of $BaLn_2MnS_5$ are reasonably high, and they increase in the order $BaLa_2MnS_5 < BaCe_2MnS_5 < BaPr_2MnS_5$.

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1. Introduction

Quaternary manganese sulfides $BaLn_2MnS_5$ ($Ln = La, Ce, Pr$) consist of LnS and $BaMnS_4$ layers parallel to the ab -plane [1,2]. Each LnS layer has S^{2-} ions at the centers of $(Ln^{3+})_4$ squares, and $(Ln^{3+})_4$ squares share their corners to form bent $S-Ln-S$ linkages (Fig. 1a). Each $BaMnS_4$ layer has the NaCl-type arrangement of Ba^{2+} ions and tetrahedral $(MnS_4)^{6-}$ anions elongated along the c -direction (Fig. 1b). The crystal structures of $BaLn_2MnS_5$ result when the LnS layers alternate with the $BaMnS_4$ layers along the c -direction (Fig. 1c). The shortest $S \cdots S$ distances between adjacent tetrahedral $(MnS_4)^{6-}$ anions are slightly longer than the van der Waals distance (i.e., 3.60 \AA) (Fig. 2a and b). Thus the tetrahedral $(MnS_4)^{6-}$ anions of $BaLn_2MnS_5$ are well separated from one another, and so are the Mn^{2+} (d^5)

ions that are in the high-spin state ($S = 5/2$) [2]. Nevertheless, the Mn^{2+} ions undergo a three-dimensional (3D) antiferromagnetic ordering at a reasonably high temperature (i.e., the Néel temperature $T_N = 58.5, 62.0$ and 64.5 K for $Ln = La, Ce$ and Pr , respectively) [2]. This means that the $Mn-S \cdots S-Mn$ super-superexchange interactions of $BaLn_2MnS_5$ are substantial not only in the ab -plane but also along the c -direction.

The magnetic properties of $BaLn_2MnS_5$ present several important questions to probe. As depicted in Fig. 2, there are three adjacent super-superexchange paths, J_1, J_2 and J_3 , to consider in $BaLn_2MnS_5$ [3]. The interlayer spin exchange J_2 (between the Mn^{2+} ions along the c -direction, Fig. 2b) takes place through the intervening LnS layer. Thus it is important to ask if the intervening LnS layer is essential for the spin exchange J_2 . The powder neutron diffraction study of $BaLa_2MnS_5$ at 7 K reveals that the antiferromagnetic transition doubles the unit cell along each crystallographic direction [3]. The analysis of its Néel temperature T_N

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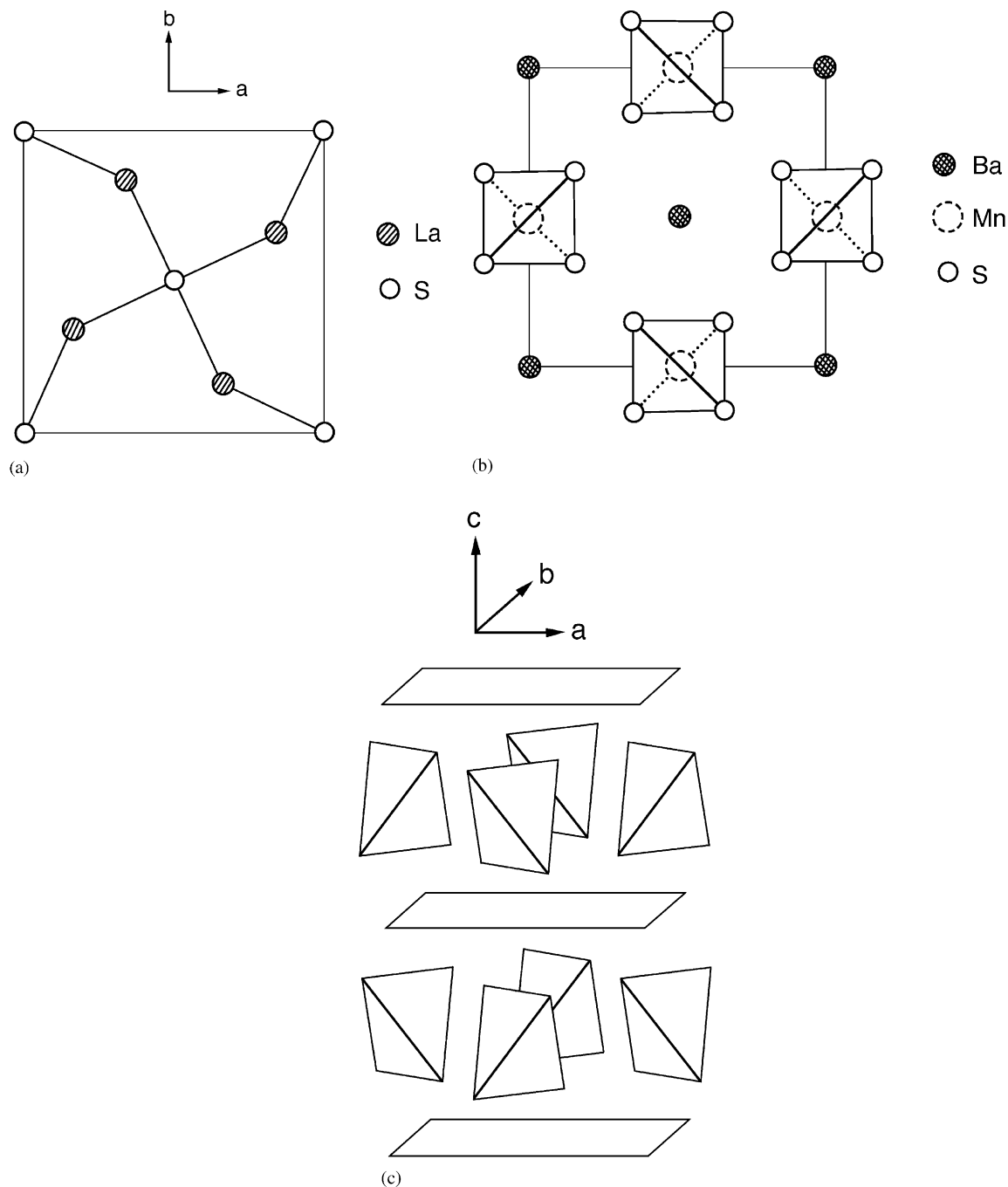


Fig. 1. (a) Arrangement of the Ln and S atoms in the LnS layer of $BaLn_2MnS_5$. (b) Arrangement of the Ba^{2+} ions and tetrahedral $(MnS_4)^{6-}$ anions in the $BaMnS_4$ layer of $BaLn_2MnS_5$. The $(MnS_4)^{6-}$ anions are elongated along the c -direction, so that the $\angle S-Mn-S$ angles pointed along the c -direction are 94.8° , 93.8° and 92.6° for $Ln=La, Ce$ and Pr , respectively. (c) Schematic view of the arrangement of the LnS and $BaMnS_4$ layers in $BaLn_2MnS_5$, where the LnS layers were represented by planes and Ba^{2+} ions of the $BaMnS_4$ layers were omitted for simplicity.

(58.5 K) and Weiss constant θ (-96 K) using the molecular field approximation leads to the estimates, $(2J_1 + J_2)/k_B = -6.6$ K and $J_3/k_B = 0.80$ K [3]. Although both J_1 and J_2 are found to be antiferromagnetic [3], their individual values are unknown. Can we estimate the relative magnitudes of J_1 and J_2 , which are essential in understanding the 3D antiferromagnetic

ordering of $BaLn_2MnS_5$? The Néel temperatures T_N of $BaLn_2MnS_5$ increase in the order, $BaLa_2MnS_5$ ($T_N = 58.5$ K) $<$ $BaCe_2MnS_5$ ($T_N = 62.0$ K) $<$ $BaPr_2MnS_5$ ($T_N = 64.5$ K) [2]. Does this trend mean that the strengths of J_1 and J_2 increase in the same order? In the present work we will probe the questions raised above by studying the spin exchange interactions of

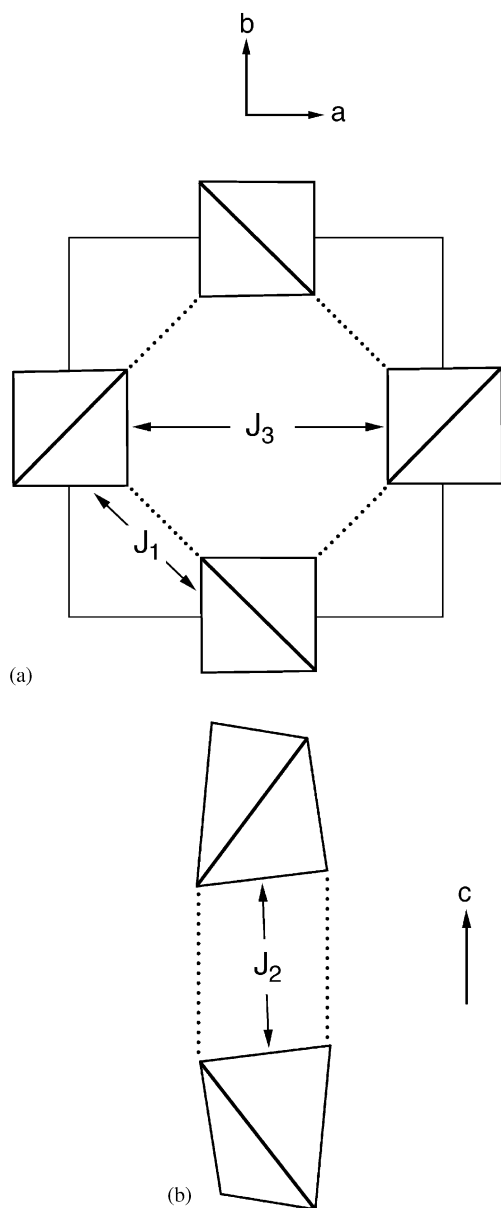


Fig. 2. Spin exchange paths of $\text{BaLn}_2\text{MnS}_5$ (a) within the BaMnS_4 plane and (b) along the c -direction. The dotted lines refer to the short $\text{S}\cdots\text{S}$ contacts. The $\text{S}\cdots\text{S}$ distances in (a) are 3.864, 3.869 and 3.905 Å for $Ln = \text{La}, \text{Ce}$ and Pr , respectively, and those in (b) are 3.754, 3.737 and 3.671 Å for $Ln = \text{La}, \text{Ce}$ and Pr , respectively.

$\text{BaLn}_2\text{MnS}_5$ ($Ln = \text{La}, \text{Ce}, \text{Pr}$) on the basis of spin dimer analysis.

2. Spin dimer analysis

The strengths of spin exchange interactions can be determined from first-principles electronic structure calculations either for the high- and low-spin states of spin dimers (i.e., structural units consisting of two spin sites) [4–6] or for various ordered spin arrangements of a magnetic solid [7]. In explaining trends in spin exchange

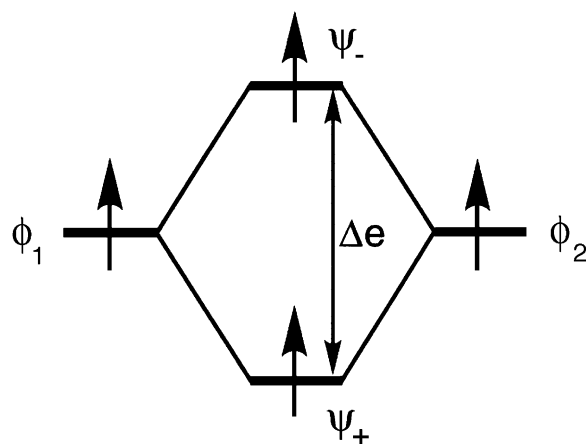


Fig. 3. Spin orbital interaction energy Δe of a spin dimer with two equivalent spin sites.

interactions of magnetic solids, it is sufficient to estimate the relative magnitudes of their J values [8–14]. In general, a spin exchange parameter J is written as $J = J_F + J_{AF}$, where the ferromagnetic term J_F (> 0) is small so that the spin exchange becomes ferromagnetic (i.e., $J > 0$) when the antiferromagnetic term J_{AF} (< 0) is negligibly small in magnitude. Thus antiferromagnetic spin exchange interactions (i.e., $J < 0$) can be discussed by focusing on the antiferromagnetic terms J_{AF} [9–14].

Consider a spin dimer in which each spin site contains one unpaired electron, and the two spin sites are equivalent and represented by non-orthogonal magnetic orbitals (i.e., singly occupied molecular orbitals of the spin monomers) ϕ_1 and ϕ_2 . Provided that S_{12} and Δe are, respectively, the overlap integral and the spin orbital interaction energy (Fig. 3) between ϕ_1 and ϕ_2 , then the antiferromagnetic term J_{AF} varies as $J_{AF} \propto -(\Delta e)^2 \propto -(S_{12})^2$ [8,9]. When each spin site of a spin dimer has M unpaired spins, the overall spin exchange parameter J of the spin dimer is described by [15]

$$J = \sum_{\mu=1}^M \sum_{\nu=1}^M \frac{J_{\mu\nu}}{M^2}. \quad (1)$$

From the viewpoint of non-orthogonal spin orbitals localized at the spin sites, the antiferromagnetic contribution J_{AF} from each off-diagonal term $J_{\mu\nu} (\mu \neq \nu)$ is negligible because the overlap integral between two adjacent spin orbitals of different symmetry is either zero or negligible. Consequently, for the discussion of antiferromagnetic spin exchange interactions, only the M diagonal $J_{\mu\mu}$ terms can contribute significantly to the antiferromagnetic term J_{AF} [13,14]. Consequently,

$$J \approx \sum_{\mu=1}^M \frac{J_{\mu\mu}}{M^2}. \quad (2)$$

Table 1

Exponents ζ_i and valence shell ionization potentials H_{ii} of Slater-type orbitals χ_i used for extended Hückel tight-binding calculation^a

Atom	χ_i	H_{ii} (eV)	ζ_i	C^b	ζ'_i	C'^b
Mn	4s	-9.75	1.844	1.0		
Mn	4p	-5.89	1.350	1.0		
Mn	3d	-11.67	5.767	0.3898	2.510	0.7297
S	3s	-20.0	2.662	0.5990	1.688	0.5246
S	3p	-13.3	2.388	0.5377	1.333	0.5615

^a H_{ii} 's are the diagonal matrix elements $\langle \chi_i | H^{\text{eff}} | \chi_i \rangle$, where H^{eff} is the effective Hamiltonian. In our calculations of the off-diagonal matrix elements $H^{\text{eff}} = \langle \chi_i | H^{\text{eff}} | \chi_j \rangle$, the weighted formula was used. Source: See Ammeter et al. [21].

^b Contraction coefficients used in the double-zeta Slater-type orbital.

Therefore, the antiferromagnetic spin exchange parameters J can be related to the average of the spin orbital interaction energy squares $\langle (\Delta e)^2 \rangle$ [13],

$$\langle (\Delta e)^2 \rangle = \sum_{\mu=1}^M \frac{(\Delta e_{\mu\mu})^2}{M^2}, \quad (3)$$

where $\Delta e_{\mu\mu}$ is the spin orbital interaction energy associated with the two singly filled molecular orbitals of a spin dimer that result from the spin orbitals ϕ_{μ} from the two spin sites. Since J_{AF} is proportional to $-\langle (\Delta e)^2 \rangle$, it can be written as $J_{\text{AF}} = -\gamma \langle (\Delta e)^2 \rangle$. For antiferromagnetic spin exchange interactions, the proportionality constant γ can be estimated by comparing the calculated $\langle (\Delta e)^2 \rangle$ values with the corresponding J values determined experimentally. Then the constant γ has the meaning of $1/U_{\text{eff}}$, where U_{eff} is the effective on-site repulsion [8,9,16].¹

3. Results and discussion

In reproducing trends in spin exchange interactions of magnetic solids in terms of Δe values obtained from extended Hückel calculations [17],² it is found necessary [10–14] to employ double-zeta Slater type orbitals [19] for both the 3d orbitals of the transition metal and the sp orbitals of the surrounding ligand atoms. The atomic orbital parameters of Mn and S employed for our extended Hückel tight-binding calculations are listed in Table 1.

The Mn^{2+} ion of a tetrahedral $(\text{MnS}_4)^{6-}$ anion is in the high spin state [2], so that the magnetic orbitals of $(\text{MnS}_4)^{6-}$ are its five d-block levels (Fig. 4), and $M = 5$ in Eq. (3). The spin dimers for the intralayer spin exchange paths J_1 and J_3 are represented by $[(\text{MnS}_4)^{6-}]_2$, which are made up of two isolated $(\text{MnS}_4)^{6-}$ anions. The spin dimer for the interlayer spin exchange path J_2 is also represented by $[(\text{MnS}_4)^{6-}]_2$ if

the intervening LnS layer is neglected, but by $[(\text{MnS}_4)^{6-}]_2(\text{S}^{2-})_2$ if we include the two S^{2-} anions of the LnS layer lying closest to the dimer $[(\text{MnS}_4)^{6-}]_2$. Results of our calculations of $\langle (\Delta e)^2 \rangle$ for the three compounds $\text{BaLa}_2\text{MnS}_5$, $\text{BaCe}_2\text{MnS}_5$ and $\text{BaPr}_2\text{MnS}_5$ are summarized in Table 2. To compare the relative strengths of the antiferromagnetic spin exchange interactions in these compounds, the relative J_{AF} values were calculated using the formula $J_{\text{AF}} = -\langle (\Delta e)^2 \rangle / U_{\text{eff}}$ with respect to the largest $\langle (\Delta e)^2 \rangle$ value (calculated for $\text{BaPr}_2\text{MnS}_5$) under the assumption that U_{eff} is constant.

Table 2 shows that the magnitude of the interlayer interaction J_2 is determined primarily by the direct Mn–S...S–Mn super–superexchange paths (Fig. 2b). The $\langle (\Delta e)^2 \rangle$ values for J_2 calculated by using the spin dimer $[(\text{MnS}_4)^{6-}]_2(\text{S}^{2-})_2$ are slightly smaller than those calculated by using the spin dimer $[(\text{MnS}_4)^{6-}]_2$. Thus the LnS layer is not essential in determining the strength of the interlayer superexchange interaction J_2 . It is clear from Table 2 that the interlayer spin exchange J_2 is stronger than the intralayer spin exchange J_1 (by a factor of ~ 10). This can be easily accounted for because the path J_2 has two short S...S contacts whereas the path J_1 has one and also because the S...S contacts of the path J_2 are shorter than that of the path J_1 (Fig. 2). Thus the strongly interacting spin units of $\text{BaLn}_2\text{MnS}_5$ ($Ln = \text{La, Ce, Pr}$) are 1D chains made up of the exchange paths J_2 , and these 1D chains interact weakly via the exchange paths J_1 . Although the exchange interaction through J_2 is stronger than that through J_1 , the latter is not negligible compared with the former. This explains why the Néel temperatures T_N of $\text{BaLn}_2\text{MnS}_5$ are reasonably high. Table 2 shows that the relative strengths of J_{AF} for the J_2 path increase in the order $\text{BaLa}_2\text{MnS}_5 < \text{BaCe}_2\text{MnS}_5 < \text{BaPr}_2\text{MnS}_5$, those for the J_1 path increase in the order $\text{BaLa}_2\text{MnS}_5 < \text{BaCe}_2\text{MnS}_5 \leq \text{BaPr}_2\text{MnS}_5$, and the differences in J_{AF} are more pronounced in the J_2 paths than in the J_1 paths. In general, the presence of stronger antiferromagnetic spin exchange interactions implies the occurrence of magnetic ordering at a high temperature. Consequently, the above results are consistent with the experimental finding that the Néel temperatures T_N

¹ This expression is valid when spin exchange parameters of a spin Hamiltonian are written as J instead of $2J$.

² Our calculations were carried out by employing the CAESAR program package [18].

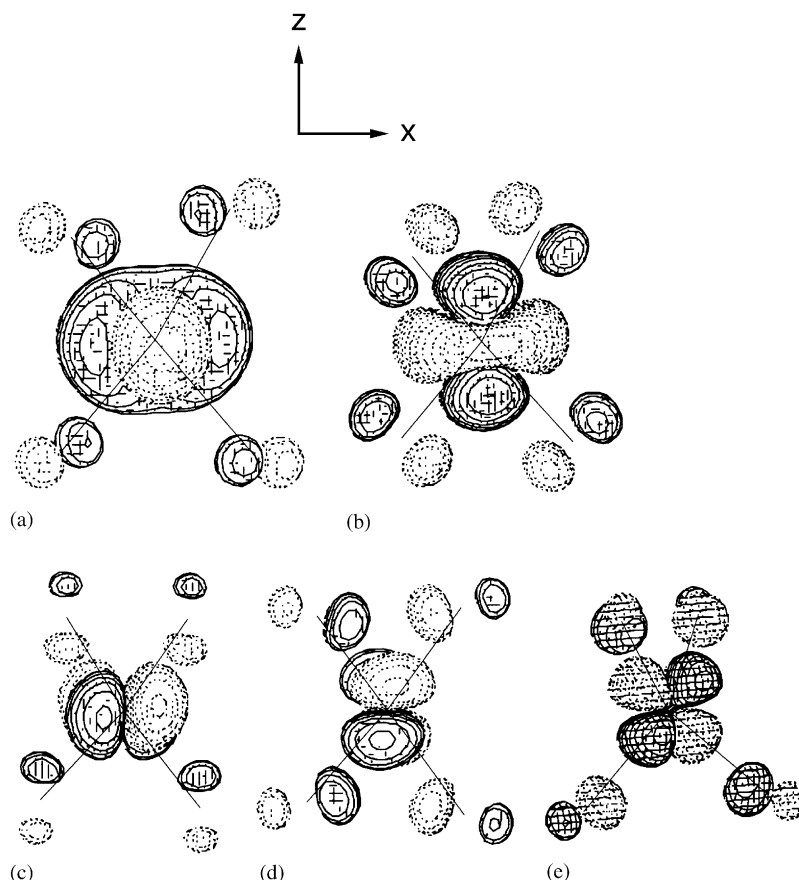


Fig. 4. 3D surface representations of the five magnetic orbitals of a tetrahedral $(\text{MnS}_4)^{6-}$ anion: (a, b) e_g orbitals; (c–e) t_{2g} orbitals.

Table 2

Values of $\langle(\Delta e)^2\rangle$ [in $(\text{meV})^2$] and relative J_{AF} values calculated for $\text{BaLn}_2\text{MnS}_5$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}$)^a

Path	$\text{BaLa}_2\text{MnS}_5$		$\text{BaCe}_2\text{MnS}_5$		$\text{BaPr}_2\text{MnS}_5$	
	$\langle(\Delta e)^2\rangle$	Rel. J_{AF}	$\langle(\Delta e)^2\rangle$	Rel. J_{AF}	$\langle(\Delta e)^2\rangle$	Rel. J_{AF}
J_1	216	−0.083	267	−0.102	273	−0.105
J_2	2074 ^b (1779) ^c	−0.794 (−0.681)	2278 ^b (1844) ^c	−0.872 (−0.706)	2612 ^b (2107) ^c	−1.000 (−0.087)
J_3	44	−0.017	59	−0.023	40	−0.015

^aThe relative J_{AF} values were calculated using the expression $J_{\text{AF}} = -\langle(\Delta e)^2\rangle/U_{\text{eff}}$ with respect to the largest $\langle(\Delta e)^2\rangle$ value (calculated for $\text{BaPr}_2\text{MnS}_5$) under the assumption that U_{eff} is constant.

^bCalculated by using $[(\text{MnS}_4)^{6-}]_2$ as the spin dimer for J_2 .

^cCalculated by using $[(\text{MnS}_4)^{6-}]_2(\text{S}^{2-})_2$ as the spin dimer for J_2 .

increase in the order, $\text{BaLa}_2\text{MnS}_5$ ($T_{\text{N}} = 58.5 \text{ K}$) < $\text{BaCe}_2\text{MnS}_5$ ($T_{\text{N}} = 62.0 \text{ K}$) < $\text{BaPr}_2\text{MnS}_5$ ($T_{\text{N}} = 64.5 \text{ K}$), and the J_2 paths should contribute more to the differences in the Néel temperatures than do the J_1 paths. The J_{AF} term of the intralayer spin exchange J_3 is practically zero. This is consistent with the experimental finding that J_3 is ferromagnetic in $\text{BaLa}_2\text{MnS}_5$ [3].

In each magnetic orbital of a $(\text{MnS}_4)^{6-}$ anion, the Mn 3d orbital is a major component and the S 3p orbitals are a minor component (Fig. 4). Such a minor p-orbital component of a magnetic orbital, referred to as the

p-orbital tail of the magnetic orbital, plays a crucial role in determining the sign and the magnitude of a spin exchange interaction [12]. Thus the strengths of the Mn–S⋯S–Mn super–superexchange interactions in $\text{BaLn}_2\text{MnS}_5$ are determined by the overlap between the p-orbital tails in the S⋯S contacts. All the short S⋯S contacts between adjacent $(\text{MnS}_4)^{6-}$ anions are slightly longer than the van der Waals distance. Nevertheless, from the observed 3D antiferromagnetic ordering in $\text{BaLn}_2\text{MnS}_5$ [2,3] and our spin dimer analysis, it is evident that the non-bonding S⋯S contacts in the

vicinity of the van der Waals distance are crucial for the Mn–S⋯S–Mn super–superexchange spin exchange interactions.

Finally, we note that the magnetic moments of the Mn²⁺ ions in BaLa₂MnS₅ are oriented along the *c*-direction [3]. This should be related to the spin–orbit coupling [20,21] associated with the anisotropic spin density distribution around each Mn²⁺ ion, which should be elongated along the *c*-direction because of the elongation of the tetrahedral (MnS₄)^{6−} anions.

4. Concluding remarks

The tetrahedral (MnS₄)^{6−} anions of BaLn₂MnS₅ (Ln = La, Ce, Pr) are well separated from one another, with the short S⋯S distances slightly longer than the van der Waals distance. The present spin dimer analysis shows that these non-bonding S⋯S contacts in the vicinity of the van der Waals distance are critical for the Mn–S⋯S–Mn super–superexchange interactions, and the LnS layer is not essential in determining the strength of the interlayer spin exchange J_2 . Our calculations predict that the interlayer spin exchange J_2 is stronger than the intralayer spin exchange J_1 by a factor of ~ 10 , and hence the strongly interacting spin units of BaLn₂MnS₅ (Ln = La, Ce, Pr) are 1D chains made up of the exchange paths J_2 . The relative strengths of the spin exchange interactions for J_1 and J_2 paths are consistent with the observation that the Néel temperatures of BaLn₂MnS₅ are reasonably high, and they increase in the order BaLa₂MnS₅ < BaCe₂MnS₅ < BaPr₂MnS₅.

Acknowledgments

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