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Magnetism in MnPSe₃: a layered 3d⁵ antiferromagnet with unusually large *XY* anisotropy

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Abstract. The anisotropic magnetic susceptibilities of single crystals of the isostructural layered antiferromagnets, MnPS₃ ($T_N = 78$ K) and MnPSe₃ ($T_N = 74$ K), have been measured as functions of temperature. In both compounds, divalent manganese is present in the high-spin $S = 5/2$ state. The anisotropies in the susceptibilities of the two are, however, very different; while the susceptibility of MnPS₃ is isotropic, that of MnPSe₃ shows a large *XY* anisotropy, unusual for a manganese compound. The anisotropic susceptibilities are described by the zero-field spin Hamiltonian: $\mathcal{H} = DS_{iz}^2 - \sum J_{ij} \vec{S}_i \cdot \vec{S}_j$ with the quadratic single-ion anisotropy term introducing anisotropy in an otherwise isotropic situation. The exchange J and the single-ion zero-field-splitting (ZFS) parameter D were evaluated using the correlated effective-field theory of Lines. For MnPSe₃, $J/k = -5.29$ K and $D/k = 26.6$ K, while for isotropic MnPS₃, $J/k = -8.1$ K. It is suggested that the large value of the ZFS parameter for MnPSe₃ as compared to MnPS₃ could be due to the large ligand spin-orbit contribution of the heavier selenium.

1. Introduction

Among low-dimensional magnetic systems, the insulating layered transition metal chalcogenophosphates, MPX₃ ($M = \text{Mn, Fe, Ni}$ and $X = \text{S or Se}$) are unique; they represent one of the few known layered systems in which both the magnetic and the crystallographic lattices are two dimensional (2D) [1, 2]. Unlike most other 2D magnetic systems wherein magnetic layers are separated by diamagnetic layers, in the metal chalcogenophosphates the magnetic MPX₃ layers are separated by a van der Waals gap. The presence of the gap rules out superexchange pathways and, since the interlayer metal-metal distance is of the order of ~ 6.5 Å, direct exchange, too, would be negligible; the chalcogenophosphates are hence nearly perfect 2D magnetic systems.

Anisotropic magnetic susceptibilities of MPS₃, $M = \text{Mn, Fe and Ni}$, have been reported [3]. All three are insulating antiferromagnets with the magnetic lattice being the 2D honeycomb. A remarkable feature of the magnetism in these compounds is that, although they are isostructural, the spin dimensionalities of the three are different. While MnPS₃ is best described by the isotropic Heisenberg Hamiltonian, FePS₃ is most effectively treated by the Ising model and NiPS₃ by the anisotropic or *XY* Heisenberg Hamiltonian [3]. In the transition metal chalcogenophosphates, metal-ligand interactions are ionic [4] and the d-electron manifold is adequately described by ligand-field theory [5]. The magnetic anisotropy was shown to be a consequence of zero-field splitting (ZFS) of the metal-ion ground state arising from a combination of spin-orbit coupling and the axial crystal field due to a trigonal distortion of

the MS_6 octahedra. The effective spin Hamiltonian for such a system is

$$\mathcal{H} = - \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j + \sum_i D S_{iz}^2 \quad (1)$$

with the ZFS term, $D S_{iz}^2$, introducing anisotropy in an otherwise isotropic situation. Depending on the sign and magnitude of D , a preference for the spins to align parallel (Ising) or perpendicular (XY) to the z -axis can be established.

In this paper we report that for the manganese compound, MnPX_3 , changing X from S to Se causes a change in the spin dimensionality. Both are $S = 5/2$ antiferromagnets, with $T_N = 78$ K and 74 K respectively. The in-layer structures of MnPS_3 and MnPSe_3 are identical; they differ only in the layer-stacking sequence [2, 6]. Earlier neutron diffraction studies had shown that the magnetic moments of the two compounds are similar and the orderings in the Néel state identical [6–8]. We have carried out single-crystal magnetic susceptibility measurements on MnPS_3 and MnPSe_3 . The paramagnetic susceptibility of MnPS_3 is isotropic; that of MnPSe_3 , however, shows a marked XY anisotropy. The results are interesting since the zero-field splitting for the orbital singlet 6S ground state of the Mn^{2+} ion is usually small, and consequently the magnetism in manganese compounds is isotropic and the behaviour is well described by the Heisenberg Hamiltonian ($D = 0$ in equation (1)) [9]. These two isostructural compounds provide a rare example in which changing the ligand causes no change in the magnetic properties other than a change in spin dimensionality.

2. Experimental procedure

MnPS_3 and MnPSe_3 were synthesized under vacuum from the corresponding elements [1, 2]. Single crystals were grown by chemical vapour transport in a two-zone furnace using excess chalcogen or iodine as the transporting agent. For MnPS_3 the temperatures of the two zones were 630 K and 580 K while for MnPSe_3 they were 650 K and 600 K. Large hexagonal platelet crystals were obtained: transparent pale green crystals of MnPS_3 and transparent wine-red crystals of MnPSe_3 . Low-temperature optical spectra were recorded on a Hitachi U3400 spectrophotometer. The band-gap energies found from the optical absorption spectra are 2.7 eV for MnPS_3 and 2.4 eV for MnPSe_3 .

Magnetic susceptibility measurements were made on a Faraday magnetic balance. Temperatures in the range 30–340 K were obtained using a closed-cycle cryostat (Air Products). The susceptometer was calibrated using $\text{Hg}[\text{Co}(\text{NCS})_4]$ as a standard. The crystals were suspended from the balance by an arrangement similar to that reported in [10]. The arrangement allowed measurements of the susceptibilities for different orientations of the crystal with respect to the field. The susceptibilities reported are for two directions—the field parallel and perpendicular to the trigonal axis. The trigonal axis in MnPX_3 ($X = S, Se$), the axis of distortion of the MX_6 polyhedra, is perpendicular to the layers.

3. Results and discussion

The temperature variation of the magnetic susceptibility of MnPS_3 is shown in figure 1. Above 100 K the susceptibility is isotropic while below 100 K it is typical of 3D antiferromagnetic ordering, χ_{\parallel} showing a sharp decrease, with χ_{\perp} remaining essentially constant. The antiferromagnetic axis is thus collinear with the trigonal axis, in agreement with neutron diffraction data [7]. The Néel temperature, defined as the temperature at which the slope of the χ - T curve is maximum, is 78 K. The broad maximum of 120 K is due to spin–spin correlation typical of low-dimensional magnetic systems. The exchange parameter, J , may be evaluated by fitting

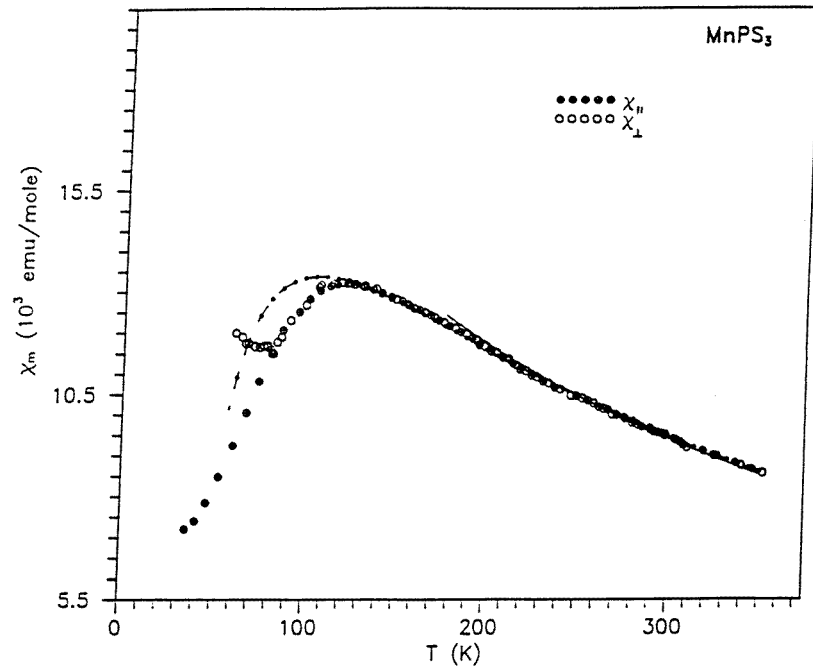


Figure 1. Magnetic susceptibilities of MnPS₃ single crystals parallel (χ_{\parallel}) and perpendicular (χ_{\perp}) to the trigonal axis. The dot-dashed curve is the fit to the HTSE susceptibility expression for $J/k = -8.1$ K and $g = 2.01$. The solid curve is the calculated CEF susceptibility for the same values of J/k and g .

the high-temperature series expansion (HTSE) susceptibility of a $S = 5/2$ 2D Heisenberg antiferromagnet [11] to the experimental data [3]. The expression for the HTSE susceptibility is

$$\chi_M = \frac{Ng^2\beta^2 S(S+1)}{3kT} \left(1 + \sum_{i=1}^6 (-1)^i b_i (|J|/kT)^i \right)^{-1}. \quad (2)$$

The b_i are the expansion coefficients and for a honeycomb lattice may be evaluated using the formulae of Rushbrook and Wood [11]. The dashed curve in figure 1 is the best fit obtained for $J/k = -8.1$ K and $g = 2.01$.

The temperature-dependent susceptibility of MnPSe₃, figure 2, shows a marked anisotropy; even at the highest temperature, $\chi_{\perp} > \chi_{\parallel}$ (the susceptibilities are defined with respect to the trigonal axis of the MSe₆ octahedra which is perpendicular to the basal plane). The susceptibility shows a broad maximum at 100 K and an antiferromagnetic Néel temperature of 74 K. In contrast to the case for MnPS₃, it is χ_{\perp} which drops sharply below 100 K, with χ_{\parallel} remaining essentially constant, implying that the antiferromagnetic axis in MnPSe₃ lies in the basal plane, perpendicular to the trigonal axis. The results are in agreement with neutron diffraction data, which showed that while the magnetic ordering is identical for MnPS₃ and MnPSe₃, in the latter the moments lie in the basal plane while in the former they lie along the c -axis [6–8].

The anisotropy in the magnetic susceptibility of MnPSe₃ originates from the ZFS of the manganese ion arising from the axial trigonal distortion of the MnSe₆ octahedra. Neutron diffraction [6], as well as the present susceptibility values, indicates that the divalent manganese

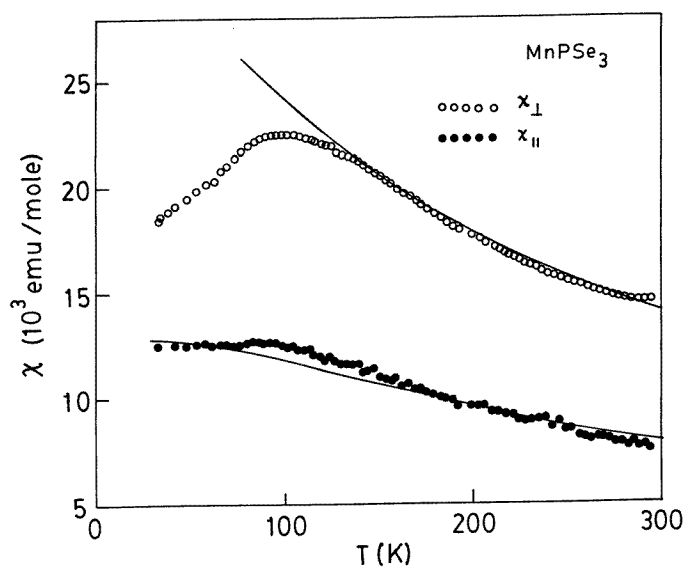


Figure 2. Magnetic susceptibilities of MnPSe₃ single crystals for magnetic fields applied parallel (χ_{\parallel}) and perpendicular (χ_{\perp}) to the trigonal axis. The solid curve is the best fit to the CEF susceptibility expression for $J/k = -5.29$ K, $D/k = 26.6$ K, $g_{\parallel} = 2.01$ and $g_{\perp} = 2.45$.

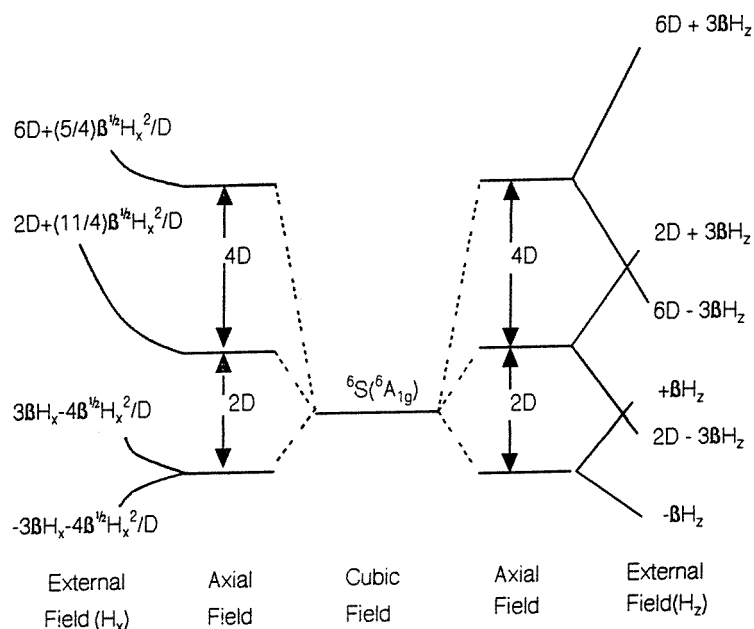


Figure 3. Energy levels of an isolated Mn²⁺ ion ($S = 5/2$) in a trigonal crystal field for magnetic fields applied parallel (H_z) and perpendicular (H_x) to the trigonal axis. The zero-field splitting parameter is D .

ion is present in the high-spin $S = 5/2$ (6S) state. Although the orbital angular momentum for such a state is zero, it has been clearly established that a combination of spin-orbit and

crystal-field effects can couple the ⁶S states to higher-lying multiplets, thereby giving rise to the ZFS [12–15]. For example, while the D₃ symmetry of the MnSe₆ polyhedra leaves the ⁶A_{1g}(⁶S) state unchanged, it lifts the degeneracy of the higher-lying ⁴T₁ state. Inclusion of spin–orbit coupling mixes the quartet and sextet states, since under D₃^{*} they span the same irreducible representations [15]. Such models have indeed been successful in accounting for the ZFS of Mn²⁺ and Fe²⁺ ions doped in ionic crystals [12]. The effective spin Hamiltonian describing magnetism in such systems is equation (1).

Any model used for estimating the ZFS and exchange parameters of MnPSe₃ must be able to account for the complicated energy level structure of the Mn²⁺ ion due to the ZFS (figure 3), while at the same time it must be able to account for spin correlations which in these low-dimensional systems are manifested at temperatures much higher than T_N. In this paper we have used the correlated effective-field (CEF) approximation developed by Lines [16, 17] to analyse the anisotropic susceptibility data for MnPSe₃ and evaluate the ZFS and exchange parameters, D and J. The CEF formalism is ideally suited for systems for which the excited crystal-field energies, exchange energies and thermal energies are all of the same order of magnitude. The model has been successfully used in analysing the high-temperature susceptibility of RbFeBr₃ [18] and RbFeCl₃ [19] as well as that of the transition metal thiophosphates [20, 21].

The CEF approximation is applicable to systems for which the total Hamiltonian may be written as equation (1). The CEF approximation attempts to reduce the many-body problem to a single-body non-interacting-ensemble form by the introduction of static, temperature-dependent spin-correlation parameters, α, which are evaluated by forcing consistency with the fluctuation-dissipation theorem [16]. In this model, the correlated effective field for the *i*th spin, S_{*i*}, is obtained by replacing each S_{*j*} in equation (1) by the sum of two contributions, one its ensemble average, ⟨S_{*j*}⟩, and the other a term proportional to the instantaneous deviation of S_{*i*} from its own averaged value ⟨S_{*i*}⟩, i.e.

$$S_j^\lambda \rightarrow \langle S_j^\lambda \rangle + \alpha^\lambda (S_i^\lambda - \langle S_i^\lambda \rangle) \quad (3)$$

where λ, in general, runs over the three cartesian coordinates, *x*, *y* and *z*, but because of the axial symmetry of equation (1), would be either parallel or perpendicular to \vec{z} for the MPX₃ compounds. Corresponding to this replacement, the effective Hamiltonian for the *i*th spin in the high-temperature paramagnetic phase, where ensemble averages are zero, is

$$\mathcal{H}_i^0(\text{eff}) = DS_{iz}^2 - \sum_\lambda \sum_j 2J_{ij}^\lambda \alpha^\lambda (S_i^\lambda)^2. \quad (4)$$

The eigenfunctions and eigenvalues of $\mathcal{H}_i^0(\text{eff})$ are readily calculated as functions of the correlation parameter, α^λ. The correlated effective-field Hamiltonian, $\mathcal{H}_i(\text{eff})$, may be obtained by considering a static applied field, \vec{H}_0 , in the direction λ. Since the susceptibility is diagonal in the coordinate system, all ensemble averages other than for the direction λ are zero:

$$\mathcal{H}_i(\text{eff}) = \mathcal{H}_i^0(\text{eff}) - g\beta H_0 S_i^\lambda - \sum_j 2J_{ij}^\lambda S_i^\lambda (\langle S_j^\lambda \rangle - \alpha^\lambda \langle S_i^\lambda \rangle). \quad (5)$$

By considering the last two terms as a perturbation, the perturbed eigenvalues and eigenfunctions are obtained using first-order perturbation theory, and the ensemble average ⟨S_{*i*}^λ⟩_H in the presence of the field calculated using Boltzmann statistics (the ensemble average ⟨S_{*i*}^λ⟩₀ in the absence of a field is zero in the paramagnetic phase):

$$kT \langle S_i^\lambda \rangle_H = g\beta H_0 \langle S_i^\lambda : S_i^\lambda \rangle_0 + \sum_j 2J_{ij}^\lambda [\langle S_j^\lambda \rangle_H - \alpha^\lambda \langle S_i^\lambda \rangle_H] \langle S_i^\lambda : S_i^\lambda \rangle_0. \quad (6)$$

The colon-product ensemble average in the above expression is defined by

$$\langle S_i^\lambda : S_i^\lambda \rangle_0 = \sum_n \rho_n \left(S_{nn}^\lambda S_{nn}^\lambda + 2kT \sum_{m \neq n} \frac{S_{nm}^\lambda S_{mn}^\lambda}{E_m - E_n} \right). \quad (7)$$

The S_{nm}^λ are the matrix elements of the λ th component of the i th spin connecting the n th and m th eigenstates, E_n and E_m are the eigen-energies of the respective levels and ρ_n is the density matrix:

$$\rho_n = (e^{-E_n/kT}) / \left(\sum_n e^{-E_n/kT} \right). \quad (8)$$

Using the fact that the zero-field averages $\langle S_i^\lambda : S_i^\lambda \rangle_0$ are site independent, equation (6) may be Fourier transformed to give

$$kT \langle S(q)^\lambda \rangle_H = g\beta H_0 \langle S_i^\lambda : S_i^\lambda \rangle_0 + 2[J(q)^\lambda - \alpha^\lambda J^\lambda(0)] \langle S(q)^\lambda \rangle_H \langle S_i^\lambda : S_i^\lambda \rangle_0 \quad (9)$$

where $S(q)$ and $J(q)$ are the Fourier transforms of the corresponding lattice quantities and the momentum q lies in the first Brillouin zone. The susceptibility, defined by $\chi^\lambda(q) = N \langle S(q)^\lambda \rangle / H_0$, may be written as

$$kT \chi_i(q)^\lambda = g_\lambda^2 \beta^2 \langle S_i^\lambda : S_i^\lambda \rangle_0 + U^\lambda(q) \quad (10)$$

where

$$U^\lambda(q) = \frac{2[J(q) - \alpha^\lambda J(0)] \langle S_i^\lambda : S_i^\lambda \rangle_0^2}{kT - 2[J(q) - \alpha^\lambda J(0)] \langle S_i^\lambda : S_i^\lambda \rangle_0}. \quad (11)$$

From the fluctuation theorem, we have $\sum_q U(q) = 0$ [16], which allows the complete determination of the correlation parameters, α^λ :

$$\alpha^\lambda = \left(\sum_q J(q) \{kT - 2[J(q) - \alpha^\lambda J(0)] \langle S^\lambda : S^\lambda \rangle\}^{-1} \right) \times \left(\sum_q J(0) \{kT - 2[J(q) - \alpha^\lambda J(0)] \langle S^\lambda : S^\lambda \rangle\}^{-1} \right)^{-1}. \quad (12)$$

Once α^λ is obtained, the uniform static susceptibility follows directly as

$$\chi_{\text{layer}}^\lambda = \frac{N g_\lambda^2 \beta^2 \langle S_i^\lambda : S_i^\lambda \rangle_0}{kT - 2z J(0) (1 - \alpha^\lambda) \langle S_i^\lambda : S_i^\lambda \rangle_0}. \quad (13)$$

The weak interlayer coupling between the MnPX₃ sheets was included using a mean-field approximation:

$$\chi^\lambda = \frac{\chi_{\text{layer}}^\lambda}{1 - 2J' \chi_{\text{layer}}^\lambda / N g_\lambda^2 \beta^2} \quad (14)$$

where J' is the interlayer coupling.

The susceptibilities were calculated using equation (12), after evaluation of the α -parameters. The equations for α^λ involve a summation over the Brillouin zone. We have used the special- k -point scheme of Chadi and Cohen [22] for obtaining the averages over the Brillouin zone. For MnPS₃ and MnPSe₃, in which the Mn²⁺ ions form a honeycomb lattice, the 6 k -point set obtained by Cunningham for a 2D hexagonal lattice was used [23]. In these compounds the direction λ is either parallel (\parallel) or perpendicular (\perp) to the trigonal axis.

The colon products $\langle S_i^\lambda : S_i^\lambda \rangle_0$ in equation (11) for a Mn²⁺ ion ($S = 5/2$) were evaluated from the eigenvalues and functions of \mathcal{H}_{eff} [17]. They are, for $D' = [D - zJ(\alpha^\parallel - \alpha^\perp)]/4kT$,

$$\langle S_i^\parallel : S_i^\parallel \rangle = \frac{(1/4)[\exp(-D') + 9 \exp(-9D') + 25 \exp(-25D')]}{\exp(-D') + \exp(-9D') + \exp(-25D')} \quad (15)$$

$$\langle S_i^\perp : S_i^\perp \rangle = \frac{\exp(-D')(9D' + 2) - (11/8) \exp(-9D') - (5/8) \exp(-25D')}{(4D')[\exp(-D') + \exp(-9D') + \exp(-25D')]} \quad (16)$$

The CEF susceptibility for MnPS₃ was calculated using equation (12) with the values of J and g which gave the best fit for the HTSE and $D = 0$. The solid curve in figure 1 shows that it compares well with the exact HTSE susceptibility.

The CEF susceptibility expression (equation (12)) was fitted to the experimental data for MnPSe₃ by a non-linear least-squares algorithm. The best fit, shown as a solid curve in figure 2, was obtained for $J/k = -5.29$ K, $D/k = 26.64$ K, $J'/k = -0.015$ K, $g_\parallel = 2.01$ and $g_\perp = 2.45$. At low temperatures the CEF susceptibilities diverge (177 K for MnPS₃ and 100 K for MnPSe₃), since the denominator in equation (11) goes to zero. This temperature, however, has no thermodynamic significance and should not be compared with experimental T_N -values since magnetic ordering in 2D isotropic and XY anisotropic systems is a consequence of weak interlayer coupling [9].

The large difference between the anisotropies in the magnetic susceptibilities of isostructural MnPS₃ and MnPSe₃ is rather puzzling. In both compounds the Mn 3d electrons are strongly correlated and localized, as reflected in their high spin-state values and the fact that both are insulators with large optical band gaps. These compounds are best viewed as salts of the chalcogenophosphate anion rather than as metal phosphorus sulphides or selenides [4]. In neither compound would the trigonal distortion of the MX₆ octahedra give rise to a ZFS unless the ground state is admixed with a higher-lying state due to spin-orbit coupling. It is the latter parameter, the spin-orbit interaction, which plays a crucial role in deciding the magnitude and the origin of the ZFS in MnPS₃ and MnPSe₃. The spin-orbit interaction for 3d^{*n*} ions in cubic fields involves two parameters, ξ and ξ' [24]. The former acts within the t₂ states and the latter between t₂ and e states. For a free ion, $\xi = \xi' = \xi_{3d}$. The spin-orbit constants may be evaluated using molecular orbital theory where t₂ and e orbitals are expressed as mixtures of the orbitals on the magnetic ion and those on the ligand:

$$\begin{aligned} \xi &= \xi_{3d} + \lambda_\pi^2 \xi_L \\ \xi' &= \xi_{3d} - (1/2)\lambda_\sigma \lambda_\pi \xi_L. \end{aligned}$$

In the above expressions, λ_π and λ_σ denote covalency parameters and ξ_{3d} and ξ_L are the spin-orbit constants of the 'free'-metal-ion 3d and ligand-ion 2p orbitals [24]. In situations where the metal ions are the same, large differences in spin-orbit constants could arise from changes in covalency and/or changes in the ligand contribution. In the case of MnPS₃ and MnPSe₃, covalency is likely to be stronger for the latter and, equally important, the spin-orbit constant ξ_L of Se²⁻ (1463 cm⁻¹) [25] is much larger than that of S²⁻ (382.4 cm⁻¹) [25] ($\xi_{Mn^{2+}} = 347$ cm⁻¹ [15]). As a consequence, even small changes in the covalency of the Mn-X interactions could still lead to a large change in the spin-orbit constants and hence a larger ZFS in MnPSe₃. The role of the ligand spin-orbit contribution has been pointed out by various authors [14, 26]; e.g. the large variation in the ZFS parameter D in the EPR spectra of Cr²⁺ ($S = 2$) doped in ZnS, ZnSe and ZnTe has been explained as arising from substantial changes in the ligand spin-orbit contribution on going from S to the heavier Te [26]. MnPS₃ and MnPSe₃, however, are probably the first examples in which changes in the ligand spin-orbit contribution cause a change in the anisotropy of the macroscopic magnetic susceptibility. The large ZFS of the Mn²⁺ ion gives rise to an unusually large XY anisotropy in the magnetism of MnPSe₃.

Acknowledgments

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