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Impurity spin resonance of Mn^{2+} in antiferromagnetic $FeBr_2$

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Electron spin resonance of substitutional Mn^{2+} ions in antiferromagnetic $FeBr_2$ host has been investigated in the liquid-helium temperature range using a conventional homodyne spectrometer. Experimental results show that the exchange constants between the impurity and the host are weaker than the host ones. Therefore, the impurity spin behaves nearly as a "paramagnetic" spin in an effective molecular field. From the experimental results, we have deduced an effective-spin Hamiltonian of the impurity. The leading term is the impurity-host effective field, its value being 2900 G. Moreover, the deviations $\Delta g'_{\parallel} = -0.06$ and $\Delta g'_{\perp} = -0.49$ of the spectroscopic factor, and the anisotropy term $D' = -770$ G are unusually large. A theoretical analysis including the effect of the exchange interactions between the impurity and the host has allowed us to get the physical origin of the various terms of the spin Hamiltonian. The values of diagonal exchange impurity-host parameters have been found (approximately 1 cm^{-1}). We have shown that $\Delta g'_{\parallel}$ and $\Delta g'_{\perp}$ were, respectively, proportional to the susceptibilities $\chi_{\parallel}$ and $\chi_{\perp}$ of the host, and that the large negative value of the anisotropy term resulted from large nondiagonal exchange impurity-host coupling.

INTRODUCTION

We have studied the low-energy excitations of a substitutional magnetic S impurity (Mn^{2+}), in the antiferromagnetic $FeBr_2$ host.

The magnetic excitations associated with the impurities are closely connected with the magnitude of the magnetic interactions between the impurity and the host spins.

In the most usual case, when the magnetic properties of the impurity and host are similar, the presence of impurities slightly disturbs the host excitation spectrum, so that it is difficult to get experimental evidence of physical features associated with the impurities. On the other hand, if the magnetic interactions between the impurity spin and host are very different compared with those between the host spins themselves, it is possible to get well-defined impurity localized modes.

Two cases may then be observed. First, the energy of the localized mode is large compared with that of the host spin waves. This situation has been widely investigated using optical techniques, for instance Ni^{2+} impurities in MnF_2.[1,2] Secondly, the energy of the impurity mode is weaker than that of the host spin waves. There are only few studies of that case.[3-5] We present here detailed results on Mn^{2+} impurities in the antiferromagnetic phase of $FeBr_2$.

A survey of the theoretical treatment of the localized impurity spin states in the case of an ordered magnetic host has been given by Cowley and Buyers and Izumov and Medvedev.[6]

We have experimentally studied the impurity excitations, first measuring the associated anomalies of the specific heat and the magnetic susceptibility between 0.3 and 7 K,[7] and then using electron-paramagnetic-resonance-spectroscopy techniques at liquid-helium temperatures in the 15-GHz microwave range.

Impurity spin-resonance experiments have been carried out by Motokawa and Date[3] in $FeCl_2$ using antiferromagnetic resonance techniques in pulsed magnetic fields with very high frequencies in the 80-GHz range. Our more sensitive paramagnetic resonance techniques and the weak concentration of impurities in our samples give narrower lines. So an extensive angular study has allowed us to determine the fine-structure terms of the spin Hamiltonian.

In Sec. I we give the crystallographic and magnetic properties of $FeBr_2$. Section II describes the experimental results of the impurity spin resonance of Mn^{2+} in $FeBr_2$. In Sec. III we show that these experimental results are well described by an effective-spin Hamiltonian of the impurity. Finally, in Sec. IV, taking into account the magnetic properties of the impurity and the antiferromagnetic host, we point out the physical meaning of the various terms of the effective-spin Hamiltonian.

I. CRYSTALLOGRAPHIC AND MAGNETIC PROPERTIES OF $FeBr_2$

Ferrous bromide is an ionic crystal isomorphous to CdI_2, with space group $P\bar{3}m1$ (D_{3d}^3). The structure is hexagonal with one molecule per unit cell. The lattice constants are $a = 3.74$ Å and $c = 6.17$ Å. The ferrous ions occupy $1a$ positions (0, 0, 0) while the bromine ions are situated at $2c$ positions $\{\pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{4})\}$. The diamagnetic surroundings of a ferrous ion form a slightly distorted octahedron, the point group being $\bar{3}m$. The resulting layer structure consists of sheets of ferrous ions sandwiched between two sheets of bromine ions perpendicular to the hexagonal c axis of the crystal, which is also the trigonal distortion axis. The crystal structure is illustrated in Fig. 1.

Many experimental and theoretical studies of $FeCl_2$ and $FeBr_2$ have been carried out in the past several decades, and the main properties of the ferrous halides are now well known.[8-17]

The magnetic structure of $FeBr_2$ was first investigated by Wilkinson *et al.*[18] In zero magnetic field and for temperature lower than $T_N = 14.2$ K, one observes an antiferromagnetic ordering which consists of sheets of ferromagnetically aligned Fe^{2+} spins directed along the c axis with antiferromagnetic ordering between adjacent sheets. So, the ferrous ions belong to two equivalent magnetic sublattices denoted α and β. This magnetic order essentially arises from intralayer ferromagnetic coupling and interlayer antiferromagnetic coupling. In the molecular-field approximation with spins along the c axis, these couplings are characterized by two effective interaction parameters, $J_1 > 0$ and $J_2 < 0$, between one ion and the two magnetic sublattices ($J_1 = 4.4$ cm^{-1} and $J_2 = -5.3$ cm^{-1}).[19]

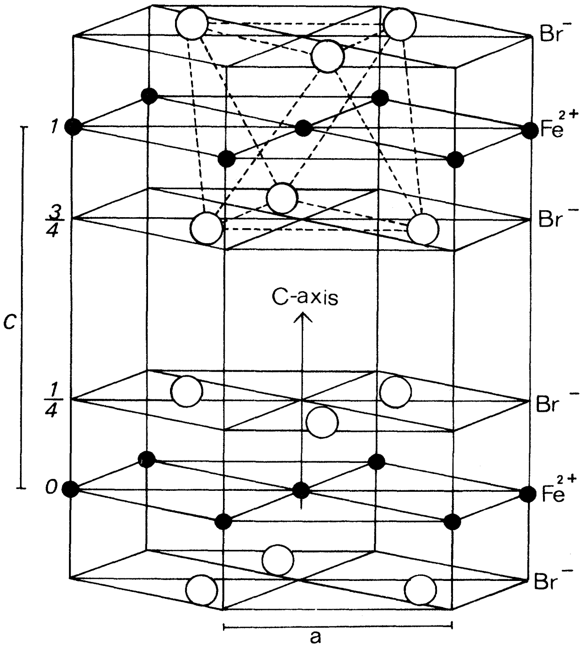

FIG. 1. Crystal structure of $FeBr_2$.

Furthermore, $FeBr_2$ exhibits a single-ion uniaxial anisotropy $D = 9.7$ cm^{-1},[19] the easy axis being the c axis. Many unusual magnetic properties of these compounds result from the fact that the single-ion anisotropy is of the same order of magnitude as the magnetic couplings.

At low temperature, in a magnetic field parallel to the c axis, a characteristic metamagnetic behavior is observed, corresponding to a transition from an antiferromagnetic phase to a paramagnetic one. The value of the critical field $H_c = 29$ kG gives the antiferromagnetic exchange coupling parameter: $J_2 = -g_{\parallel}\mu_B H_c$.[15]

The crystalline anisotropy and the antiferromagnetic exchange interactions involve the existence of a gap in the magnon spectrum in zero magnetic field: $\hbar\omega_0 = 17.5$ cm^{-1}.[16,17]

When a magnetic S ion (Mn^{2+}) is substituted for a ferrous ion in $FeBr_2$, we will see that the impurity resonance spectrum can be clearly explained using the assumption that the exchange constants between the impurity and the host are consequently weaker than the host exchange constants (1 cm^{-1} compared with 10 cm^{-1}). The same situation was observed by Motokawa and Date in $FeCl_2$.[3] This indicates that the energy of the impurity excitation modes of about 1 cm^{-1} is small compared with that of host excitation modes of about 17.5 cm^{-1}. Therefore, the impurity spin behaves nearly as a "paramagnetic" spin in an effective molecular field.

II. EXPERIMENT

The measurements were made using a conventional homodyne spectrometer. Various resonance frequencies were used in the 12–25-GHz range. The cavity was immersed in a helium cryostat and measurements were generally made at 1.6 K. The magnetic field given by a 12-in. Varian magnet could be swept between 0 and 10 000 G. The field was measured with a proton magnetometer. Using small gear wheels, the sample could be rotated inside the cavity. Using this rotation and the rotating base of the magnet, precise alignment of the crystal could be made, with the crystal being at helium temperature. The angular dependence of the spectrum was used to obtain this alignment.

The hyperfine structure of the Mn^{2+} ion was observed for some orientations of the magnetic field relative to the crystal c axis [see Fig. 2(b)]. However, one does not evaluate directly the hyperfine

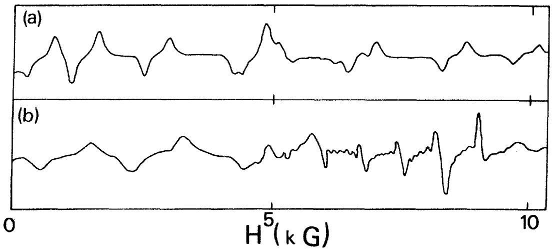

FIG. 2. Resonance spectra of Mn^{2+} in $FeBr_2$ at 4.2 K and with 15.5-GHz microwave frequency for two angles θ between the magnetic field and the c axis: (a) $\theta = 0°$; (b) $\theta = 60°$.

constant A_{zz} since the structure is not well resolved. This allowed a safe identification of the spectrum. This identification was confirmed using crystals of various Mn^{2+} concentrations. The latter were measured by atomic absorption, neutron activation, and mass spectrometry. Most of the measurements were made on a crystal which was not intentionally doped but naturally contained five Mn^{2+} ions for 10 000 Fe^{2+} ions. A crystal with a Mn^{2+} atomic concentration of 1.3% was also examined. At this concentration, the EPR lines were broadened.

Figure 2(a) shows a typical spectrum. The microwave frequency was 15.5 GHz and the magnetic field was aligned along the c axis of the crystal. For this orientation of the field, the linewidth is approximately equal to the hyperfine splitting, and this gives rise to a peculiar, trapezoidlike line shape.

Two groups of five resonance lines each are identified. They are due to Mn^{2+} ions substituted in one or the other of the two sublattices. This assignment is confirmed by measurements made at various microwave frequencies as shown in Fig. 3. Data shown in Fig. 3 also show that the Zeeman structures are linear functions of the magnetic field, with $g'_{\parallel} = 1.94$. This leads us to introduce only one term $g'_{\parallel}\mu_B H_z S'_z$ in the phenomenological spin Hamiltonian and to neglect terms of higher order in H_z. Figure 4 shows how the resonance fields change when the magnetic field is rotated with respect to the c axis. These spectra were observed to depend only on the angle θ which the magnetic field makes with the c axis of the crystal. Hence they have a cylindrical symmetry and not the lower trigonal symmetry allowed for the site of the Mn^{2+} ion in the lattice.

For all these measurements, the resonance field was taken as the center of the hyperfine pattern. An additional line observed at a field corresponding to a g value of 2 was assigned to some unknown impurity.

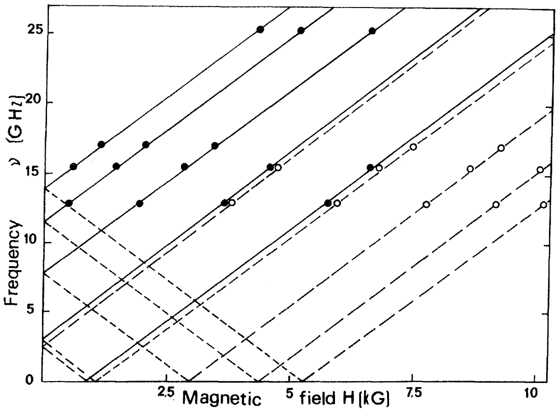

FIG. 3. Frequency-field diagram of the resonance points of Mn^{2+} impurity spin resonance at 4.2 K ($H \parallel c$ axis). The effective g' value is 1.94.

III. EFFECTIVE-SPIN HAMILTONIAN

All these experimental results are well explained (see Fig. 4) by the simple effective-spin Hamiltonian below:

$$\mathcal{H}_{\text{eff}} = \epsilon g'_{\parallel}\mu_B H_{\text{int}} S'_z + D'[S'^2_z - \tfrac{1}{3} S'(S'+1)] + \epsilon a_3 S'^3_z$$
$$+ \tfrac{1}{60} B^0_4 O^0_4 + g'_{\parallel}\mu_B H_z S'_z + g'_{\perp}\mu_B (H_x S'_x + H_y S'_y) ,$$

with

$$O^0_4 = 35 S'^4_z - 30 S'(S'+1) S'^2_z + 25 S'^2_z$$
$$- 6 S'(S'+1) + 3 S'^2 (S'+1)^2 ,$$

where μ_B is the Bohr magneton, H_z, H_x, and H_y are the components of the applied magnetic field, S'_z, S'_x, and S'_y are the components of the Mn^{2+} im-

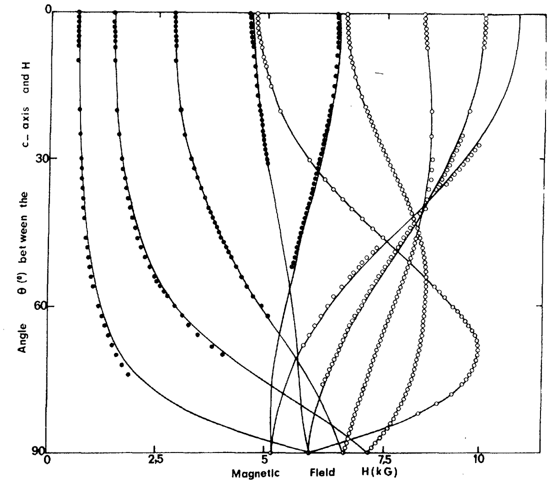

FIG. 4. Angular dependence of Mn^{2+} spin resonance in antiferromagnetic state of $FeBr_2$, at 4.2 K and with 15.5 GHz. The experimental points are circles. Solid lines are the calculated curves.

purity spin $\vec{S}'$ ($S'=\frac{5}{2}$), z being the c axis. ϵ takes the value $+1$ or -1 according into which magnetic sublattice the Mn^{2+} ion is substituted. As shown by the results of Fig. 3, it is not necessary to introduce terms in H_z^2 or any higher power. We will assume that the same is true for the x and y components of the magnetic field. Other terms (for instance $S_z'^5$ or $S_x' S_z' H_x$) would be allowed by the symmetry of the site. It is not necessary to introduce such additional terms in the simple Hamiltonian in order to fit all the experimental results within the experimental accuracy of 10 or 20 G.

The spectrum obtained for $\theta=0$ (field parallel to the c axis) allows us to calculate all the parameters except $g'_\perp$, which is given by the angular dependence of the spectrum.

The different coefficients are evaluated as

$$g'_\parallel = 1.94 \pm 0.01\ ,$$

$$g'_\perp = 1.51 \pm 0.01\ ,$$

$$H_{\mathrm{int}} = 2900 \pm 30\ \mathrm{G}\ ,$$

$$D'/g'_\parallel \mu_B = -770 \pm 20\ \mathrm{G}\ ,$$

$$a_3/g'_\parallel \mu_B = -70 \pm 3\ \mathrm{G}\ ,$$

$$B_4^0/g'_\parallel \mu_B = 15 \pm 4\ \mathrm{G}\ .$$

The signs of D' and B_4^0 are obtained by using the temperature dependence of the spectrum for $\theta=0$ in the 4.2–1.6 K range. The signs of H_{int} and a_3 cannot be determined, only their relative sign is known.

IV. THEORY

In this section, we shall find the physical origin of the various terms of the effective-spin Hamiltonian. For this, we shall start from the physical Hamiltonian of the antiferromagnetic $\mathrm{FeBr_2}$ host and one Mn^{2+} impurity, and we shall use a perturbation theory.

A. Hamiltonian of one impurity and the host

Assuming that one can neglect interactions between the Mn^{2+} impurities, this Hamiltonian can be written

$$H = H_0 + H_1\ ,$$

with

$$H_0 = H_{\mathrm{host}} + H^c_{\mathrm{imp}} + H_{\mathrm{hole}}\ ,$$

$$H_1 = H_i + H_{hi}\ .$$

H_{host} is the Hamiltonian of the $\mathrm{FeBr_2}$ host. H^c_{imp} describes the Mn^{2+} free-ion while H_{hole} is that of the hole when substituting the Mn^{2+} ion for one Fe^{2+} ion.

$H_i = -\vec{H}\cdot\vec{\mu} \simeq 2\mu_B \vec{H}\cdot\vec{S}'$ represents the Zeeman term of the Mn^{2+} impurity with spin $S'=\frac{5}{2}$. H_{hi} represents the so-called "magnetic" interactions (exchange and dipolar interactions) between the host and the impurity.

Note that we have not written the electric crystalline-field-interaction terms between host and impurity. Indeed, these interactions influence the fundamental level energy only in high order of the perturbation theory[20,21] and give rise to a small correction of the g' factor and to a fine structure constant D' much smaller than 100 G,[22] this value itself being weak compared with the experimental D' one. We neglect these corrective terms and the contribution of the crystalline field to the B_4^0 constant.

H_{hi} contains the exchange and dipolar interactions between the impurity spin $\vec{S}'$ and the host spins $\vec{S}_i$. For the exchange coupling we take the most general bilinear form

$$-2\vec{S}_i \cdot \overleftrightarrow{J}'_i \cdot \vec{S}'\ .$$

Indeed, the large negative experimental D' value can only be explained assuming large nondiagonal exchange terms $-2J'^{xz} S_x S_z'$ and $-2J'^{yz} S_y S_z'$. A parallel situation has been found for Mn^{2+} impurities in $\mathrm{CoCl_2\text{-}2H_2O}$ by Fujii *et al.*[4] and Tachiki.[23]

Therefore, the expression of H_{hi} is

$$H_{hi} = -\sum_i 2\vec{S}_i \cdot \overleftrightarrow{J}'_i \cdot \vec{S}' + \sum_i \vec{\mu}_i \cdot \overleftrightarrow{A}'_i \cdot \vec{\mu}'\ ,$$

where $\overleftrightarrow{A}'_i$ is the dipolar interaction tensor,

$$\overleftrightarrow{A}'_i = r_i'^{-3}(\overleftrightarrow{u} - 3\vec{r}_i' \cdot \vec{r}_i' r_i'^{-2})\ ,$$

and $\overleftrightarrow{u}$ is the unit tensor, $\vec{r}_i'$ is the vector joining the impurity to the Fe^{2+} spin site i.

B. Principle of the perturbation method

The substitution of a Mn^{2+} impurity to a Fe^{2+} ion does not modify very much the eigenstates of the $\mathrm{FeBr_2}$ host. So we shall neglect H_{hole} compared with H_{host}.

The nondegenerate fundamental antiferromagnetic state of the host and its energy are, respectively, denoted $|f\rangle$ and E_f, the excited states and their energies being $|e\rangle$ and E_e.

The lowest level of H^c_{imp} ($L'=0$) is $(2S'+1)$-fold degenerate. The six eigenstates are denoted $|M'\rangle$. The excited levels of the free-ion Mn^{2+} ($L'\neq 0$) are much higher than those of the host and are not taken into account in the perturbation theory.

Furthermore, the eigenvalues of H_1 (about $1\ \mathrm{cm}^{-1}$) are smaller than the gap of the spin-wave spectrum of the $\mathrm{FeBr_2}$ host, about $17.5\ \mathrm{cm}^{-1}$.

Therefore we can consider H_1 as a perturbation in the sixfold-degenerate manifold $\{|fM'\rangle\}$

$\equiv \{|f\rangle |M'\rangle\}$ of the unperturbed Hamiltonian H_0. Then, we have to diagonalize H_1 in this manifold. We improve this first-order perturbation calculation by considering the part of H_1 which connects the eigenstates of the manifold $\{|fM'\rangle\}$ to the excited eigenstates of the manifolds $\{|eM'\rangle\}$. So, we shall use the effective-Hamiltonian formalism (see Pryce,[24] and Abragam and Pryce[25]), modified in order to take into account the host-impurity magnetic interactions. This problem has been treated by Hutchings *et al.*[26,27] without the host-lattice interaction term and their results have been applied by many authors to paramagnets.[28-31] We have extended this approach to antiferromagnets.

Within the fundamental impurity manifold $\{|M'\rangle\}$, the effective Hamiltonian can be written as follows:

$$\mathcal{H}_{\text{eff}} = \langle f|H_1|f\rangle + \sum_e \frac{\langle f|H_1|e\rangle\langle e|H_1|f\rangle}{E_f - E_e} \quad .$$

This calculation of the effective Hamiltonian is correct to higher-order perturbation terms $|H_1|^2/\Delta E$. Another source of error is the choice of the antiferromagnetic host states $|f\rangle$ and $|e\rangle$. These states are given in the Appendix.

C. Physical origin of the effective-spin Hamiltonian

First, we can describe the physical origin of the principal parameters H_{int}, $\Delta g'_{\parallel}$, $\Delta g'_{\perp}$, and D' entering into $\mathcal{H}_{\text{eff}}$ using a simplified model. We shall assume a Heisenberg exchange between the impurity and the host and we shall neglect the dipolar interactions.

So H_1 is written

$$H_1 = 2\mu_B \vec{\mathrm{H}} \cdot \vec{\mathrm{S}}' - 2J'_\alpha \vec{\mathrm{S}}^\alpha \cdot \vec{\mathrm{S}}' - 2J'_\beta \vec{\mathrm{S}}^\beta \cdot \vec{\mathrm{S}}' \quad .$$

In order to reduce the notations, we have assumed that the impurity spin $\vec{\mathrm{S}}'$ is only coupled with one nearest-neighbor host spin of each sublattice α and β.

We first consider the first-order term of $\mathcal{H}_{\text{eff}}$. In a magnetic field parallel to the x axis, $\mathcal{H}_{\text{eff}}$ is written

$$\mathcal{H}_{\text{eff}} = 2\mu_B H_x S'_x - 2(J'_\alpha \langle f|S^\alpha_x|f\rangle + J'_\beta \langle f|S^\beta_x|f\rangle)S'_x \quad .$$

The two matrix elements in the bracket are proportional to H_x so that the bracket gives rise to a correction $\Delta g'_\perp$ to the g' value.

Within each manifold of a Fe^{2+} host ion, we introduce an effective spin $\vec{\mathrm{s}}$, so that

$$\vec{\mathrm{S}} = \overleftrightarrow{\alpha} \cdot \vec{\mathrm{s}} \quad \text{and} \quad \vec{\mu} = -\mu_B \overleftrightarrow{\mathrm{g}} \cdot \vec{\mathrm{s}} \quad .$$

Within the lowest-effective-spin $s = 1$ triplet, we have the following relations:

$$\langle f|S^\alpha_x|f\rangle = \langle f|S^\beta_x|f\rangle = -(\alpha_\perp / g_\perp \mu_B)\langle f|\mu^\alpha_x|f\rangle \quad ,$$

$$\langle f|\mu^\alpha_x|f\rangle = \langle f|\mu^\beta_x|f\rangle = \chi_\perp H_x \quad ,$$

where $\chi_\perp$ is the perpendicular susceptibility per ion of the host, and with

$$\alpha_\perp \simeq \tfrac{3}{2} \quad \text{and} \quad g_\perp \simeq \tfrac{7}{2}$$

(see Appendix). Then, the effective Hamiltonian is

$$\mathcal{H}_{\text{eff}} = 2\mu_B H_x S'_x + (2\alpha_\perp / g_\perp \mu_B)(J'_\alpha + J'_\beta)\chi_\perp H_x S'_x \quad .$$

So we have the variation of the perpendicular spectroscopic factor:

$$\Delta g'_\perp = (2\alpha_\perp / g_\perp \mu_B^2)(J'_\alpha + J'_\beta)\chi_\perp \quad .$$

In a magnetic field parallel to the z axis, the Zeeman term and the effect of the exchange are given by

$$\mathcal{H}_{\text{eff}} = 2\mu_B H_z S'_z - 2(J'_\alpha \langle f|S^\alpha_z|f\rangle + J'_\beta \langle f|S^\beta_z|f\rangle)S'_z \quad .$$

To the first order of a perturbation calculation

$$\langle f|S^\alpha_z|f\rangle = -\langle f|S^\beta_z|f\rangle = -\alpha_\parallel \simeq -\tfrac{3}{2} \quad .$$

To the second order of perturbation one has to consider the mixing by the magnetic field of the lower $s = 1$ states and the excited states $s = 2$. It is this mixing which gives rise to a nonzero Van Vleck parallel susceptibility per ion $\chi_\parallel$. So one understands that the second-order correction to the matrix elements $\langle f|S^{\alpha,\beta}_z|f\rangle$ is proportional to both the H_z component of the magnetic field and the susceptibility per ion $\chi_\parallel$:

$$\langle f|S^{\alpha,\beta}_z|f\rangle = \mp\alpha_\parallel - (\chi_\parallel / \beta_\parallel \mu_B)H_z \quad ,$$

where the signs $-$ and $+$ apply, respectively, to the sublattices α and β. It is easy to show that we have (see Appendix)

$$\beta_\parallel = 3 \quad .$$

Then $\mathcal{H}_{\text{eff}}$ becomes

$$\mathcal{H}_{\text{eff}} = 2\mu_B H_z S'_z + g'_\parallel \mu_B H_{\text{int}} S'_z + \Delta g'_\parallel \mu_B H_z S'_z \quad ,$$

with the effective molecular field and the variation of the parallel spectroscopic factor being given by

$$H_{\text{int}} = (2\alpha_\parallel / g'_\parallel \mu_B)(J'_\alpha - J'_\beta) \quad ,$$

$$\Delta g'_\parallel = (2/\beta_\parallel \mu_B^2)(J'_\alpha + J'_\beta)\chi_\parallel \quad .$$

In the second-order term of the effective Hamiltonian, we consider only the excited host states of the triplet $s = 1$, because the excited states $s = 2$ are much higher ($2\lambda' = 180\ \mathrm{cm}^{-1}$).

Therefore, the second-order term of $\mathcal{H}_{\text{eff}}$ in zero magnetic field (see Sec. IV D 4) is

$$\mathcal{H}_{\text{eff}} = \frac{1}{E_f - E_e} (J'^2_\alpha \langle f|S^-_\alpha S'^+|e\rangle\langle e|S^+_\alpha S'^-|f\rangle + J'^2_\beta \langle f|S^-_\beta S'^+|e\rangle\langle e|S^+_\beta S'^-|f\rangle) \quad .$$

Using the following relations,

$$\langle 1-1|S_\alpha^- S'^+|10\rangle\langle 10|S_\alpha^+ S'^-|1-1\rangle$$
$$= (\langle 1-1|S_\alpha^-|10\rangle)^2 S'^+ S'^- ,$$

and

$$\langle 1-1|S_\alpha^-|10\rangle = \alpha\langle 1-1|s_\alpha^-|10\rangle = \sqrt{2}\,\alpha ,$$
$$S'^+ S'^- = \vec{S}'^2 - S_z'^2 + S_z' ,$$

$\mathcal{H}_{\text{eff}}$ is given by

$$\mathcal{H}_{\text{eff}} = \frac{2\alpha^2}{E_e - E_f}\,(J_\alpha'^2 + J_\beta'^2)\,[S_z'^2 - S_z' - S'(S'+1)] .$$

The anisotropy term D' is then

$$D' = \frac{2\alpha^2}{E_e - E_f}\,(J_\alpha'^2 + J_\beta'^2) .$$

Therefore, in the Heisenberg exchange assumption, the D' value is positive. Besides, we observe a small correction to the effective molecular field H_{int}.

The above simple considerations illustrate the physical origin of the parameters H_{int}, $\Delta g_\parallel'$, $\Delta g_\perp'$, and D' of the effective-spin Hamiltonian.

A more-detailed analysis will allow us to estimate the order of magnitude of the different exchange integrals J', and to show the importance of dipolar interactions and exchange anisotropy. This analysis involves the determination of the different parameters $\alpha_\parallel$, $g_\parallel$, $\chi_\parallel$, and so on, of the FeBr$_2$ host, which implies the choice of a model to describe the host states $|f\rangle$ and $|e\rangle$.

D. Detailed calculation of the effective-spin Hamiltonian

The eigenstates and the eigenenergies of the host Hamiltonian are obtained in the molecular-field approximation (see Appendix). The fundamental state of the host ions is written as

$$|f\rangle = \prod_{i\in\alpha} |-1\rangle_i' \prod_{j\in\beta} |+1\rangle_j' ,$$
$$|f\rangle = |f_0\rangle + a|f_0'\rangle + a_z H_z|f_z\rangle + a_x H_x|f_x\rangle ,$$

with

$$|f_0\rangle = \prod_{i\in\alpha} |1-1\rangle_i \prod_{j\in\beta} |11\rangle_j ,$$
$$|f_0'\rangle = \sum_{i'\in\alpha} |2-1\rangle_{i'} \prod_{i\in\alpha}{}' |1-1\rangle_i \prod_{j\in\beta} |11\rangle_j - \sum_{j'\in\beta} |21\rangle_{j'} \prod_{i\in\alpha} |1-1\rangle_i \prod_{j\in\beta}{}' |11\rangle_j ,$$
$$|f_z\rangle = \sum_{i'\in\alpha} |2-1\rangle_{i'} \prod_{i\in\alpha}{}' |1-1\rangle_i \prod_{j\in\beta} |11\rangle_j + \sum_{j'\in\beta} |21\rangle_{j'} \prod_{i\in\alpha} |1-1\rangle_i \prod_{j\in\beta}{}' |11\rangle_j ,$$
$$|f_x\rangle = \sum_{i'\in\alpha} |10\rangle_{i'} \prod_{i\in\alpha}{}' |1-1\rangle_i \prod_{j\in\beta} |11\rangle_j + \sum_{j'\in\beta} |10\rangle_{j'} \prod_{i\in\alpha} |1-1\rangle_i \prod_{j\in\beta}{}' |11\rangle_j ,$$
$$a = -(\sqrt{5}/9)\Delta g_\parallel ,$$
$$a_z = (\sqrt{5}/9\mu_B)\chi_\parallel ,$$
$$a_x = -(\sqrt{2}/7\mu_B)\chi_\perp .$$

With this state $|f\rangle$, we can now calculate the first term of the effective-spin Hamiltonian, the applied magnetic field being in the zx plane:

$$\langle f|H_1|f\rangle = 2\mu_B H_z S_z' + 2\mu_B H_x S_x' + \mathcal{H}_{\text{eff}}^{(1)} + \mathcal{H}_{\text{eff}}^{(2)} + \mathcal{H}_{\text{eff}}^{(3)} ,$$

with:

$$\mathcal{H}_{\text{eff}}^{(1)} = \langle f_0|H_{hi}|f_0\rangle - (\sqrt{5}/9)\Delta g_\parallel(\langle f_0'|H_{hi}|f_0\rangle + \langle f_0|H_{hi}|f_0'\rangle) .$$
$$\mathcal{H}_{\text{eff}}^{(2)} = -(\sqrt{5}/9\mu_B)\chi_\parallel(\langle f_z|H_{hi}|f_0\rangle + \langle f_0|H_{hi}|f_z\rangle)H_z ,$$
$$\mathcal{H}_{\text{eff}}^{(3)} = -(\sqrt{2}/7\mu_B)\chi_\perp(\langle f_x|H_{hi}|f_0\rangle + \langle f_0|H_{hi}|f_x\rangle)H_x .$$

1. Determination of H_{int}

$\mathcal{H}_{\text{eff}}^{(1)}$ gives the following contribution to the spin Hamiltonian:

$$\mathcal{H}_{\text{eff}}^{(1)} = \Big(\sum_{i\in\alpha} [-2J_i'^{zz}(-\tfrac{3}{2} - \tfrac{1}{3}\Delta g_\parallel) - 2\mu_B^2 A_i'^{zz}(\tfrac{7}{2} + \Delta g_\parallel)] + \sum_{i\in\beta} [-2J_i'^{zz}(\tfrac{3}{2} + \tfrac{1}{3}\Delta g_\parallel) - 2\mu_B^2 A_i'^{zz}(-\tfrac{7}{2} - \Delta g_\parallel)]\Big)\, S_z' .$$

By symmetry, the Hamiltonian does not contain S_x' and S_y' terms.

So, we find a predominant term $2\mu_B H_{\text{int}} S_z'$ corresponding to a magnetic interaction effective field between the impurity and the host. The effective molecular field H_{int} changes its sign according to which sublattice the impurity belongs.

For an ion in the sublattice α, we have

$$H_{\text{int}} = 3.39\,\frac{J_{\alpha\alpha}'^{zz} - J_{\alpha\beta}'^{zz}}{2\mu_B} - 4.08\mu_B(A_{\alpha\alpha}'^{zz} - A_{\alpha\beta}'^{zz}) ,$$

with

$$\sum_{i\in\alpha} J_i'^{zz} = J_{\alpha\alpha}'^{zz},\quad \sum_{i\in\beta} J_i'^{zz} = J_{\alpha\beta}'^{zz} ,$$
$$\sum_{i\in\alpha} A_i'^{zz} = A_{\alpha\alpha}'^{zz},\quad \sum_{i\in\beta} A_i'^{zz} = A_{\alpha\beta}'^{zz} .$$

We can calculate exactly the contribution to the effective field from dipolar interactions by a rapidly convergent summation method.[15,32] The dipolar sums correspond to our sample, which is approximately a flat disk perpendicular to the c axis:

$$A'^{zz}_{\alpha\alpha} = -2A'^{xx}_{\alpha\alpha} = -2A'^{yy}_{\alpha\alpha} = 2.130\times 10^{23}\ \text{cm}^{-3}\ ,$$

$$A'^{zz}_{\alpha\beta} = -2A'^{xx}_{\alpha\beta} = -2A'^{yy}_{\alpha\beta} = 0.021\times 10^{23}\ \text{cm}^{-3}\ .$$

This contribution for an α ion is evaluated as

$$H^{\alpha\ \text{dip}}_{\text{int}} = -8000\ \text{G}\ .$$

From the experimental value (evaluated with $g'_{\parallel} = 2$):

$$H_{\text{int}} = \pm 2800 \pm 30\ \text{G}\ ,$$

the contribution from the exchange interactions is

$$H^{\alpha\ \text{ex}}_{\text{int}} = 10\,800\ \text{G or } H^{\alpha\ \text{ex}}_{\text{int}} = 5200\ \text{G}\ .$$

Thus, we can get the two possible accurate values of the difference between the effective zz exchange couplings between an impurity and the two sublattices:

$$\frac{J'^{zz}_{\alpha\alpha} - J'^{zz}_{\alpha\beta}}{2\mu_B} = 3200 \pm 30\ \text{G or } 1500 \pm 30\ \text{G}\ .$$

2. *Determination of* $\Delta g'_{\parallel}$

$\mathcal{H}^{(2)}_{\text{eff}}$ is expressed as

$$\mathcal{H}^{(2)}_{\text{eff}} = -\frac{2}{3\mu_B}\chi_{\parallel}\Big(\sum_i (3\mu_B^2 A'^{zz}_i - J'^{zz}_i)\Big) H_z S'_z\ .$$

Thus, we obtain a deviation of the parallel spectroscopic factor directly connected to the host parallel susceptibility per ion:

$$\Delta g'_{\parallel} = -(2/3\mu_B^2)\chi_{\parallel}[3\mu_B^2(A'^{zz}_{\alpha\alpha} + A'^{zz}_{\alpha\beta}) - (J'^{zz}_{\alpha\alpha} + J'^{zz}_{\alpha\beta})]\ ,$$

$$\Delta g'_{\parallel} = (27/10\lambda')(J'^{zz}_{\alpha\alpha} + J'^{zz}_{\alpha\beta}) - (81/10\lambda')\mu_B^2(A'^{zz}_{\alpha\alpha} + A'^{zz}_{\alpha\beta})\ .$$

The value of $\Delta g'_{\parallel}$ resulting from dipolar interactions is

$$\Delta g'^{\ \text{dip}}_{\parallel} = -0.01\ .$$

The experimental result $\Delta g'_{\parallel} = -0.06 \pm 0.01$ allows us to evaluate the order of magnitude of the sum of the effective intralayer and interlayer zz exchange constants:

$$\frac{J'^{zz}_{\alpha\alpha} + J'^{zz}_{\alpha\beta}}{2\mu_B} = -17\,000 \pm 3500\ \text{G}\ .$$

The experimental values of H_{int} and $\Delta g'_{\parallel}$ give an estimation of the effective zz exchange couplings between an impurity and each sublattice. In spite of a somehow large error (±3500 G) proceeding from the $\Delta g'_{\parallel}$ measurement, we observe that in any case the exchange couplings are antiferromagnetic.

First possibility:

$$J'^{zz}_{\alpha\alpha} = J'^{zz}_{\beta\beta} = -6900\ \text{G}\ ,$$

$$J'^{zz}_{\alpha\beta} = J'^{zz}_{\beta\alpha} = -10\,000\ \text{G}\ .$$

Second possibility:

$$J'^{zz}_{\alpha\alpha} = -7800\ \text{G}\ ,$$

$$J'^{zz}_{\alpha\beta} = -9300\ \text{G}\ .$$

3. *Determination of* $\Delta g'_{\perp}$

$\mathcal{H}^{(3)}_{\text{eff}}$ is given by

$$\mathcal{H}^{(3)}_{\text{eff}} = -\frac{2}{7\mu_B}\chi_{\perp}\Big(\sum_i (7\mu_B^2 A'^{xx}_i - 3J'^{xx}_i)\Big) H_x S'_x\ .$$

The variation of the perpendicular spectroscopic factor is thus proportional to the host perpendicular susceptibility per ion:

$$\Delta g'_{\perp} = -(2/7\mu_B^2)\chi_{\perp}[7\mu_B^2(A'^{xx}_{\alpha\alpha} + A'^{xx}_{\alpha\beta}) - 3(J'^{xx}_{\alpha\alpha} + J'^{xx}_{\alpha\beta})]\ ,$$

$$\Delta g'_{\perp} = \frac{21}{2(D-2J_2)}(J'^{xx}_{\alpha\alpha} + J'^{xx}_{\alpha\beta}) - \frac{49}{2(D-2J_2)}\mu_B^2(A'^{xx}_{\alpha\alpha} + A'^{xx}_{\alpha\beta})\ .$$

The dipolar contribution

$$\Delta g'^{\ \text{dip}}_{\perp} = +0.06$$

is much weaker than the experimental value $\Delta g'_{\perp} = -0.49 \pm 0.01$. Therefore we have

$$\Delta g'^{\ \text{ex}}_{\perp} = -0.55 \pm 0.01\ ,$$

$$\frac{J'^{xx}_{\alpha\alpha} + J'^{xx}_{\alpha\beta}}{2\mu_B} = -11\,200 \pm 200\ \text{G}\ .$$

There is apparently an anisotropy of the host-impurity diagonal exchange.

4. *Determination of* D'

Finally, we study the second term of the effective-spin Hamiltonian:

$$\sum_e \frac{\langle f|H_1|e\rangle\langle e|H_1|f\rangle}{E_f - E_e} = \sum_e \frac{\langle f|H_{hi}|e\rangle\langle e|H_{hi}|f\rangle}{E_f - E_e}\ .$$

Expanding the eigenstates and the energies of the host as functions of the applied field, we get a predominant field-independent contribution. We can neglect the other field-dependent contributions which are smaller than the previous ones.

Furthermore, for simplicity, we neglect D/λ' corrective terms so that for the ground state we shall take

$$|f\rangle \simeq |f_0\rangle\ ,$$

while for the excited states, we shall consider one-ion excitations to the states $|10\rangle$ and $|11\rangle$ for an α ion and to the states $|10\rangle$ and $|1-1\rangle$ for a β ion. We shall not take into account the one-ion higher excited states $s=2$ (at $2\lambda'=180\ \mathrm{cm}^{-1}$) and $s=3$ (at $5\lambda'=450\ \mathrm{cm}^{-1}$).

Then, we obtain

$$\mathcal{H}_{\mathrm{eff}}^{(4)}=-\frac{1}{2(D+J_1-J_2)}\sum_i\left[(7\mu_B^2A_i'^{xz}-3J_i'^{xz})^2+(7\mu_B^2A_i'^{yz}-3J_i'^{yz})^2\right]S_z'^2\ ,$$

$$\mathcal{H}_{\mathrm{eff}}^{(5)}=-\frac{1}{2(D+J_1-J_2)}\sum_i\left[(7\mu_B^2A_i'^{xx}-3J_i'^{xx})^2+(7\mu_B^2A_i'^{yx}-3J_i'^{yx})^2\right]S_x'^2\ ,$$

$$\mathcal{H}_{\mathrm{eff}}^{(6)}=-\frac{1}{2(D+J_1-J_2)}\sum_i\left[(7\mu_B^2A_i'^{yy}-3J_i'^{yy})^2+(7\mu_B^2A_i'^{xy}-3J_i'^{xy})^2\right]S_y'^2\ .$$

By symmetry, the coefficients of $\mathcal{H}_{\mathrm{eff}}^{(5)}$ and $\mathcal{H}_{\mathrm{eff}}^{(6)}$ are equal, and we obtain a term proportional to

$$S_x'^2+S_y'^2=-S_z'^2+S'(S'+1)\ .$$

Finally, $\mathcal{H}_{\mathrm{eff}}^{(4)}$, $\mathcal{H}_{\mathrm{eff}}^{(5)}$, and $\mathcal{H}_{\mathrm{eff}}^{(6)}$ give a $D'S_z'^2$ contribution to the spin Hamiltonian which may account for the large negative experimental value $D'/g_{\parallel}'\mu_B=-770$ G. Neglecting dipolar interactions we have

$$\left(\sum_i\ (J_i'^{xz2}+J_i'^{yz2}-J_i'^{xx2}-J_i'^{yy2}-J_i'^{xy2}-J_i'^{yx2})\right)^{1/2}=5900\ \mathrm{G}\ .$$

It appears that the nondiagonal components of the exchange interactions have to be of the same order of magnitude as the diagonal ones.

Just as in the case theoretically studied by Tachiki,[23] it is shown that the $\mathcal{H}_{\mathrm{eff}}^{(4)}$ negative contribution due to J'^{xz} and J'^{yz} is predominant.

Furthermore, a significant contribution to the anisotropy term D' may arise from a biquadratic exchange between the host and the impurity (see Harris and Owen[33]):

$$-\sum_i j_i(\vec{S}_i\cdot\vec{S}')^2\ .$$

5. Other terms

The second term of the effective-spin Hamiltonian leads to other quadratic terms in spin components which are nondiagonal. By symmetry all these terms cancel except $-i(S_x'S_y'-S_y'S_x')=S_z$, which gives

$$\mathcal{H}_{\mathrm{eff}}^{(7)}=-\frac{1}{2(D+J_1-J_2)}\left(\sum_{i\in\alpha}B_i'-\sum_{i\in\beta}B_i'\right)S_z'\ ,$$

with

$$B_i'=\left[(7\mu_B^2A_i'^{xx}-3J_i'^{xx})(7\mu_B^2A_i'^{yy}-3J_i'^{yy})-(7\mu_B^2A_i'^{yx}-3J_i'^{yx})(7\mu_B^2A_i'^{xy}-3J_i'^{xy})\right]\ .$$

$\mathcal{H}_{\mathrm{eff}}^{(7)}$ gives a weak contribution to the effective field H_{int}.

This second-order perturbation technique may be extended to the third order. The third-order terms will give the missing spin Hamiltonian term $\epsilon a_3 S_z'^3$ which appears in $H_{hi}H_{hi}H_{hi}/(\Delta E)^2$. Its order of magnitude is $(10^4)^3/(20\times10^4)^2\simeq 25$ G in good agreement with the experimental value. The term $\frac{1}{60}B_4^0O_4^0$ may issue from the crystalline field or from higher-order perturbation terms.

CONCLUSION

Electron spin resonance of substitutional Mn^{2+} ions in antiferromagnetic FeBr_2 host has allowed us to evaluate the effective magnetic field describing the exchange and dipolar magnetic interactions between an impurity and the host.

Moreover, in the effective-spin Hamiltonian, we have pointed out some original features: the deviations $\Delta g_{\parallel}'$ and $\Delta g_{\perp}'$ of the spectroscopic factor are very large, and the single-ion uniaxial anisotropy term $D'S_z'^2$ is much larger than the crystalline-field contribution.

A theoretical analysis using the "Abragam-Pryce" formalism has allowed us to get the physical origin of the anomalies. We have shown the predominant part played by the host properties. So $\Delta g_{\parallel}'$ and $\Delta g_{\perp}'$ were, respectively, proportional to the host susceptibilities $\chi_{\parallel}$ and $\chi_{\perp}$.

The experimental values of H_{int} and $\Delta g_{\parallel}'$ have given two possible sets of values for the exchange parameters between an impurity and the two sublattices which are weaker than exchange couplings within the host:

$$J_{\alpha\alpha}'^{zz}=-0.64\ \mathrm{cm}^{-1},\ J_{\alpha\beta}'^{zz}=-0.94\ \mathrm{cm}^{-1}\ ,$$

or

$$J_{\alpha\alpha}'^{zz}=-0.73\ \mathrm{cm}^{-1},\ J_{\alpha\beta}'^{zz}=-0.87\ \mathrm{cm}^{-1}\ .$$

These results are significantly different from those obtained by Motokawa and Date[3] in FeCl_2 ($J_{\alpha\alpha}'^{zz}=+0.64\ \mathrm{cm}^{-1}$, $J_{\alpha\beta}'^{zz}=-0.41\ \mathrm{cm}^{-1}$) where one coupling is ferromagnetic.

Furthermore, the accuracy of our measurements has allowed us to point out the existence of an anisotropy of the diagonal exchange coupling and the presence of large nondiagonal exchange terms.

Note on new experimental data

Recent measurements at $T = 4.2$ K and $\nu = 14.5$ GHz have been carried out by Chamel using high magnetic fields (Service National des Champs Intenses de Grenoble). The value of the internal molecular field on an impurity in the paramagnetic phase of $FeBr_2$ is found to be

$$H_{\text{int}} = -55\,900 \pm 30 \text{ G}.$$

A rapid analysis of this result gives:

$$\frac{J'^{zz}_{\alpha\alpha} + J'^{zz}_{\alpha\beta}}{2\mu_B} = -14\,500 \text{ G},$$

in good agreement with the above determination resulting from the measurement of $\Delta g'_{\parallel}$:

$$\frac{J'^{zz}_{\alpha\alpha} + J'^{zz}_{\alpha\beta}}{2\mu_B} = -17\,000 \pm 3500 \text{ G}.$$

An extensive analysis of these EPR measurements of Mn^{2+} ions substituted in the saturated paramagnetic phase of $FeBr_2$ will be presented later.

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APPENDIX: EIGENSTATES AND ENERGIES OF THE $FeBr_2$ HOST

The single-ion energy-level diagram has been widely developed by Ono *et al.*,[9] Carrara,[11] and Alben.[12]

We consider an assembly of magnetic Fe^{2+} free ions. Each magnetic ion is placed in the crystalline field of the diamagnetic ions and the molecular field describing in a mean-field theory the exchange and dipolar couplings with the other magnetic ions. Then we have a one-ion problem, the Hamiltonian being

$$V = H_c + V_c + V_{LS} + V_m + V_Z ,$$

where the various terms are, respectively, the free-ion Coulombian Hamiltonian, the crystalline-field, the spin-orbit coupling, the molecular-field Hamiltonian, and the Zeeman term.

First, the predominant cubic part K of the crystalline field V_c splits the free-ion spectral $3d^6(^5D)$ term, giving a lowest orbital $^5T_{2g}$ triplet with a fivefold spin degeneracy. In this orbital triplet, we introduce an effective angular momentum $\vec{l}$ $(l = 1)$, and then we have

$$\vec{L} = -\vec{l},$$

$$V_{LS} = \lambda' \vec{l} \cdot \vec{S},$$

$$T = -10D(l_z^2 - \tfrac{2}{3}),$$

where T is the residual trigonal component of the crystalline field.

In the case of $FeBr_2$, we can consider the trigonal field as a perturbation compared with the spin-orbit coupling. So, the $^5T_{2g}$ level is split by the spin-orbit interaction giving a triplet ground state characterized by an effective spin $s = 1$ $(\vec{s} = \vec{l} + \vec{S})$, a quintuplet $s = 2$ at $2\lambda' \simeq 180 \text{ cm}^{-1}$ (Ref. 13) and a septet $s = 3$ at $5\lambda' \simeq 450 \text{ cm}^{-1}$.

Neglecting the dipolar interactions, the residual terms of the Hamiltonian of an ion of the sublattice α are then

$$V_1 = -10D(l_z^2 - \tfrac{2}{3}) - (2J^{\alpha\alpha}\langle S_z^\alpha\rangle + 2J^{\alpha\beta}\langle S_z^\beta\rangle)S_z$$
$$-(2J^{\alpha\alpha}\langle S_x^\alpha\rangle + 2J^{\alpha\beta}\langle S_x^\beta\rangle)S_x - H_z\mu_z - H_x\mu_x ,$$

where exchange Heisenberg interactions are treated in the molecular-field approximation and $\langle S_z^\alpha\rangle \ldots$, are the mean values of $S_z^\alpha \ldots$, at $T = 0$ K.

Within the lowest triplet, the spin $\vec{S}$ and the magnetic momentum $\vec{\mu}$ of a Fe^{2+} ion are related to the effective spin $\vec{s}$ by

$$\vec{S} = \overleftrightarrow{\alpha} \cdot \vec{s}, \quad \vec{\mu} = -\mu_B \overleftrightarrow{g} \cdot \vec{s} .$$

At this order of the perturbation calculation, we have

$$\alpha_\parallel = \alpha_\perp = \tfrac{3}{2}, \quad g_\parallel = g_\perp = \tfrac{7}{2} .$$

The fundamental triplet $s = 1$ of the Hamiltonian $V_0 = H_c + K + V_{LS}$ is split by the perturbation term V_1. At $T = 0$ K and $H = 0$, an antiferromagnetic order is observed with

$$\langle s_z^\alpha\rangle = -\langle s_z^\beta\rangle = -1 \text{ and } \langle s_x^\alpha\rangle = \langle s_x^\beta\rangle = 0 .$$

The triplet is split into a fundamental singlet characterized by $s_z^\alpha = -1$ (state $|sm_s\rangle = |1-1\rangle$), a first excited singlet at $D + J_1 - J_2$ (state $|10\rangle$), and a second excited singlet at $2(J_1 - J_2)$ (state $|11\rangle$).

J_1 is the effective intralayer ferromagnetic exchange parameter, J_2 is the effective interlayer antiferromagnetic exchange parameter, and D is the single-ion uniaxial anisotropy constant. The values of these characteristic parameters are[15,19,34,35]

$$J_1 = 2\alpha_\parallel^2 J^{\alpha\alpha} = 4.4 \text{ cm}^{-1},$$

$$J_2 = 2\alpha_\parallel^2 J^{\alpha\beta} = 5.3 \text{ cm}^{-1},$$

$$D = 9.7 \text{ cm}^{-1} .$$

A higher-order perturbation calculation which includes the Zeeman Hamiltonian leads for an α ion to the following fundamental state in the basis $\{|sm_s\rangle\}$:

$$|-1\rangle' = |1\,-1\rangle + a|2\,-1\rangle + a_z H_z |2\,-1\rangle + a_x H_x |10\rangle \ ,$$

with

$$a = -(5D + J_1 - J_2)/2\sqrt{5}\lambda' \ ,$$

$$a_z = -9\mu_B/4\sqrt{5}\lambda' \ ,$$

$$a_x = -7\mu_B/2\sqrt{2}(D - 2J_2) \ .$$

Note that

$$\langle \mu_x^\alpha \rangle = {}'\langle -1|\mu_x|-1\rangle' = -\frac{7}{\sqrt{2}}\,\mu_B a_x H_x = \chi_\perp H_x \ ,$$

$$\langle \mu_z^\alpha \rangle = {}'\langle -1|\mu_z|-1\rangle' = \mu_B\left(\frac{7}{2} - \frac{9}{\sqrt{5}}\,a - \frac{9}{\sqrt{5}}\,a_z H_z\right)$$

$$= \mu_B\,(\tfrac{7}{2} + \Delta g_\parallel) + \chi_\parallel H_z \ ,$$

where $\chi_\perp$ and $\chi_\parallel$ are the perpendicular and the parallel one-ion susceptibilities at $T = 0$ K. Therefore

$$a = -(\sqrt{5}/9)\Delta g_\parallel \ ,$$

$$a_z = -(\sqrt{5}/9\mu_B)\chi_\parallel \ ,$$

$$a_x = -(\sqrt{2}/7\mu_B)\chi_\perp \ .$$

The fundamental state for a β ion is

$$|1\rangle' = |11\rangle - a|21\rangle + a_z H_z |21\rangle + a_x H_x |10\rangle \ .$$

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