

## EFFECT OF ZERO-FIELD SPLITTING ON THE MAGNETIC SUSCEPTIBILITY OF BINUCLEAR COMPLEXES OF IRON(III)

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*The effect of zero-field splitting on the magnetic susceptibility of binuclear complexes formed by high-spin iron(III) ions was studied. An analytic expression describing the magnetic susceptibility of such systems is presented. It was shown that in dimers with weak magnetic exchange the experimental data only fit adequately if the effect of zero-field splitting (ZFS) is taken into account. The effect of ZFS on the accuracy of the values obtained for the exchange parameters with various D/J ratios is discussed.*

**Key words:** polynuclear complexes, magnetic exchange, zero-field splitting.

Considerable attention has been paid in recent years to development of the scientific principles for the design of compounds capable of acting as carriers of information at the molecular level [1-7]. In the literature such compounds have often been called molecular magnetics, molecular magnets, or molecule-domains. To display molecule-domain characteristics dominant ferromagnetic exchange interactions must exist within the molecule, and the ground state of the molecule must consequently be ferromagnetic. Existing strategies for the creation of molecular magnets include the following: The production of molecules with a large number of uncompensated spins in the ground state (polyspin molecules) [1, 3], the design of systems with indeterminate spin [1, 3, 8] or with concurrent antiferromagnetic interactions resulting in the emergence of ferromagnetic ordering in the molecule [1, 8-11], the production of bulk exchange clusters with significant magnetic anisotropy [2], which in molecular subjects arises as a result of the appearance of zero-field splitting in the individual ions constituting the molecule. In addition, it was recently shown [12] that during the creation of molecules with a ferromagnetic ground state it is also necessary to take account of the possible existence of zero-field splitting (ZFS) of the spin levels that arises in systems with spin multiplicity greater than unity on account of spin-orbital coupling [12, 13]. On the curves for the temperature dependence of the magnetic susceptibility the ZFS effect as a rule appears in the low-temperature region ( $T < 20$  K). However, whereas investigation of the appearance of ZFS in the magnetic characteristics of mononuclear complexes is a fairly well developed routine procedure [14], such investigation for multinuclear complexes still presents certain difficulties. The recently published review [12] covers the main approaches that make it possible to take the ZFS effect into account during the modelling of the experimental magnetochemical data obtained during investigation of a wide range of both mononuclear and multinuclear compounds. Unfortunately, the results obtained during investigation of magnetic properties of polynuclear complexes of

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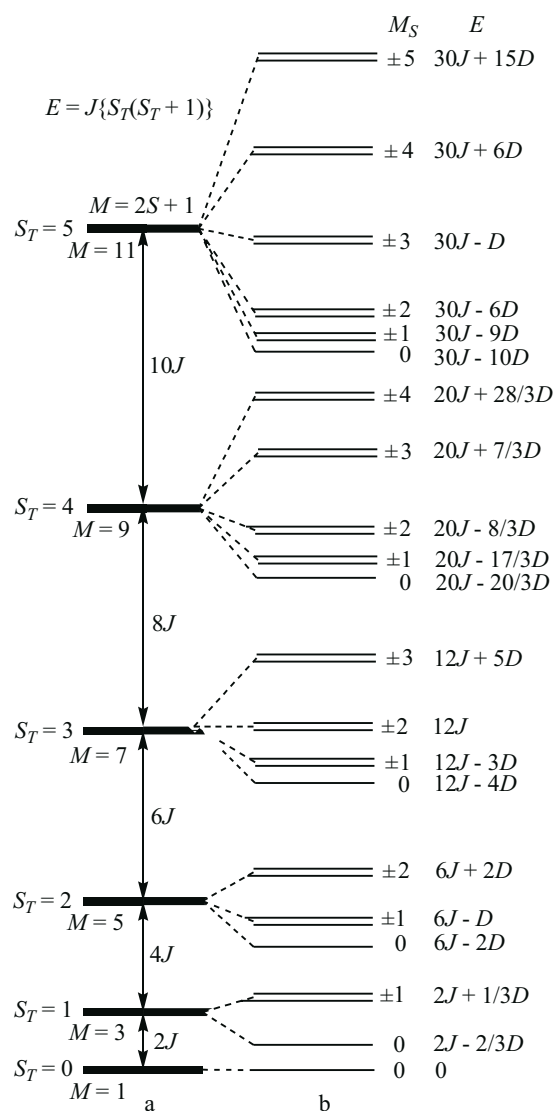


Fig. 1. The splitting of the spin levels in binuclear complexes of iron(III) ( $S = 5/2$ ) displaying antiferromagnetic interaction without (a) and with (b) the ZFS effect.

Fe(III) were not reflected in the review. This may in part result from the widely held view that the splitting of energy levels in  $d^5$  systems [the high-spin state of iron(III)] resulting from ZFS is small (in the order of tenths of  $\text{cm}^{-1}$ ) and hardly makes any contribution to the magnetic susceptibility against the background of the prevailing exchange interactions [15]. This assertion only holds [1] rigorously for the high-spin compounds of iron(III) with ideal octahedral environment but is not fulfilled so rigorously in compounds where the coordination unit is distorted. Recently it was found that ZFS must often be taken into account during modelling of the temperature dependence of magnetic susceptibility for a series of binuclear complexes of iron(III) with small exchange parameters  $J$ . Applied software packages that make it possible to make such corrections automatically by diagonalization of the respective spin matrices are often used for such purposes. An alternative to this approach may be to derive equations that take account of the effect of the parameter  $D$  on the temperature dependence of the magnetic susceptibility. In the light of the fundamental importance of the binuclear complexes of iron(III) as elementary units

for the construction of multispin molecules and molecule-domains the present paper is devoted to the examination of the effect of ZFS on their magnetic behavior.

The value of the magnetic susceptibility for a given temperature is obtained from van Vleck's equation:

$$\chi = \frac{Ng^2\beta^2}{3kT} \frac{\sum_n a_n \exp(-E_n/kT)}{\sum_n b_n \exp(-E_n/kT)} = \frac{Ng^2\beta^2}{3kT} \frac{A}{B} \quad (1)$$

where  $N$  is the Avogadro number,  $k$  is the Boltzmann constant,  $g$  is the Lande factor,  $\beta$  is the Bohr magneton,  $E_n$  is the energy of the spin level,  $T$  is temperature,  $a_n$  and  $b_n$  are coefficients taking account of the multiplicity of the spin level:  $a_n = 6M_S^2$ ;  $b_n = 1$  for  $M_S = 0$  and  $b_n = 2$  if  $M_S \neq 0$ .

Modelling of the temperature dependence of the magnetic susceptibility involves finding values for the energy of each state at a given temperature such that the experimental and calculated curves coincide when these values are substituted in Eq. (1).

In an external magnetic field the coupling of the spin moments  $S$  of a pair of iron(III) ions ( $d^5$ ,  $S = 5/2$ ), which are linked by a bridging ligand into a binuclear complex, is described by the isotropic spin Hamiltonian (2) and leads to the set of spin levels with the energies given in Fig. 1a:

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 \quad (2)$$

where  $J$  is the exchange parameter, and  $\hat{S}_1$  and  $\hat{S}_2$  are the spin operators of the iron atoms.

Use of the isotropic spin Hamiltonian is justified in this case since each of the  $\text{Fe}^{3+}$  ions ( $d^5$ ,  $S = 5/2$ ) is located in an octahedral field and, as was demonstrated earlier [1, 15, 16], most such systems are described quite adequately in terms of this model. The eigenvalues of the spin Hamiltonian give the required energy values (Fig. 1a shows the spin ladder levels for the case of antiferromagnetic exchange), substitution of which in (1) gives the classical equation for calculating the magnetic susceptibility of iron(III) dimers.

As mentioned above, spin-orbital coupling results in removal of the degeneracy in the high-multiplicity spin levels (ZFS), leading to the appearance of a new system of spin levels (Fig. 1b). The effect of zero field splitting in the dimer consisting of two atoms of iron(III) can be described to a first approximation (the applied magnetic field is parallel to the principal symmetry axis of the molecule, which has an inversion center) by the spin Hamiltonian [1, 13]:

$$\hat{H} = -2J\hat{S}_1\hat{S}_2 + D[M_S^2 - 1/3S_T(S_T + 1)] \quad (3)$$

where  $D$  is the zero-field splitting parameter,  $M_S$  is the spin quantum number which varies in the range of  $-S_T, -(S_T - 1), \dots, (S_T - 1), S_T$ , and  $S_T$  is the total spin. Since most iron(III) dimers have a symmetrical structure with an inversion center, Eq. (3) must describe the properties of such molecules adequately without allowance for anisotropic exchange.

The energies of the spin levels obtained according to (3) are given in Fig. 1b, which shows how the spin multiplets of the binuclear complexes of iron are split in the zero field. It should be noted that Fig. 1b is generally qualitative in nature, and with  $|D|/J > 1$  the ground state will no longer be  $S_T = 0$  but  $S_T = 1$ ,  $M_S = 0$ .

The "weighted" coefficients for  $D$  in van Vleck's equation were calculated according to the equation:

$$E(\text{ZFS}) = D[M_S^2 - 1/3S(S + 1)]. \quad (4)$$

By substituting the values of  $E$  (Fig. 1b) in (1) we obtain an expression for the temperature dependence of the magnetic susceptibility in the binuclear complexes of iron with allowance for ZFS, where  $A$  and  $B$  are obtained as follows:

$$A = 6 \exp [(2J + 1/3D)/kT] + 24 \exp [(6J + 2D)/kT] + 6 \exp [(6J - D)/kT] + 54 \exp [(12J + 5D)/kT] +$$

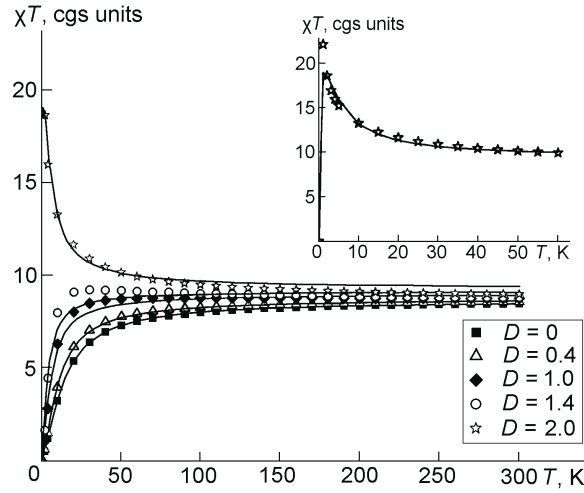


Fig. 2. The temperature dependence of  $\chi T$  for various values of  $D$  with constant  $g = 2.00$  and  $J = -1.0 \text{ cm}^{-1}$  (a marker). The solid lines correspond to the best simulations, which were obtained without allowance for the ZFS effect. The inset shows the low-temperature region for  $D = 2.0 \text{ cm}^{-1}$ .

$$\begin{aligned}
 & + 24 \exp [(12J)/kT] + 6 \exp [(12J - 3D)/kT] + 96 \exp [(20J + 28/3D)/kT] + \\
 & + 54 \exp [(20J + 7/3D)/kT] + 24 \exp [(20J - 8/3D)/kT] + 6 \exp [(20J - 17/3D)/kT] + \\
 & + 150 \exp [(30J + 15D)/kT] + 96 \exp [(30J + 6D)/kT] + 54 \exp [(30J - D)/kT] + \\
 & + 24 \exp [(30J - 6D)/kT] + 6 \exp [(30J - 9D)/kT], \tag{5}
 \end{aligned}$$

$$\begin{aligned}
 B = & 1 + 2 \exp [(2J + 1/3D)/kT] + \exp [(2J - 2/3D)/kT] + 2 \exp [(6J + 2D)/kT] + 2 \exp [(6J - D)/kT] + \\
 & + \exp [(6J - 2D)/kT] + 2 \exp [(12J + 5D)/kT] + 2 \exp [(12J)/kT] + 2 \exp [(12J - 3D)/kT] + \\
 & + \exp [(12J - 4D)/kT] + 2 \exp [(20J + 28/3D)/kT] + 2 \exp [(20J + 7/3D)/kT] + 2 \exp [(20J - 8/3D)/kT] + \\
 & + 2 \exp [(20J - 17/3D)/kT] + \exp [(20J - 20/3D)/kT] + 2 \exp [(30J + 15D)/kT] + 2 \exp [(30J + 6D)/kT] + \\
 & + 2 \exp [(30J - D)/kT] + 2 \exp [(30J - 6D)/kT] + 2 \exp [(30J - 9D)/kT] + 2 \exp [(30J - 10D)/kT]. \tag{6}
 \end{aligned}$$

If  $D = 0$  is substituted in the obtained expression, it is reduced to the classical equation describing the temperature dependence of  $\chi$  in the binary complexes of iron(III) in the absence of ZFS [13-15]:

$$\chi T = \frac{Ng^2\beta^2}{k} \frac{2\exp(2J/kT) + 10\exp(6J/kT) + 28\exp(12J/kT) + 60\exp(20J/kT) + 110\exp(30J/kT)}{1 + 3\exp(2J/kT) + 5\exp(6J/kT) + 7\exp(12J/kT) + 9\exp(20J/kT) + 11\exp(30J/kT)}. \tag{7}$$

TABLE 1. The Model Data

Assigned values			Calculated values				
$g$	$J$	$D$	$G$	$J$	$D$	$\sigma^2$	$R^2$
2	-1	0.1	1.973 ± 0.001	-0.98 ± 0.01	0	0.00004	0.000000616
2	-1	0.2	1.976 ± 0.002	-0.92 ± 0.02	0	0.00024	0.00000386
2	-1	0.4	1.981 ± 0.001	-0.80 ± 0.01	0	0.00198	0.000279
2	-1	0.6	1.987 ± 0.001	-0.69 ± 0.01	0	0.00658	0.000221
2	-1	0.8	1.994 ± 0.002	-0.58 ± 0.01	0	0.01618	0.000236
2	-1	1.0	2.003 ± 0.003	-0.48 ± 0.01	0	0.03435	0.000484
2	-1	1.1	2.008 ± 0.04	-0.43 ± 0.01	0	0.04843	0.000669
2	-1	1.2	2.013 ± 0.04	-0.37 ± 0.02	0	0.06714	0.000908
2	-1	1.4	2.025 ± 0.05	-0.27 ± 0.02	0	0.12583	0.001627
2	-1	1.6	2.05 ± 0.02	-0.17 ± 0.04	0	0.25015	0.003055
2	-1	1.8	2.07 ± 0.02	-0.07 ± 0.1	0	0.684	0.007656
2	-1	2.0	2.25 ± 0.05	0.35 ± 0.04	0	0.2912	0.002475

**Note.**  $\sigma^2$  is the error variance in the determination of the parameters  $g$  and  $J$  [17];  $R^2 = \Sigma(\chi T_{\text{asgn}} - \chi T_{\text{calc}})^2 / \Sigma(\chi T_{\text{asgn}})^2$ .

The model was used to determine the effect of zero field splitting on the magnetic behavior of the binary complexes of iron by modelling the temperature dependence of the magnetic susceptibility by nonlinear regression with the Origin 6.0 software package (Microcal Software, Inc.). Since this effect must show up to the greatest degree in the case of weak magnetic exchange interaction (in view of the small values of  $D$ ), the theoretical curves were calculated for the hypothetical case with a fixed value of  $J = -1 \text{ cm}^{-1}$  (in all cases the value of the  $g$  factor of the  $\text{Fe}^{3+}$  ion was frozen at 2.00) with the  $D$  parameter varying from 0.1 to 2.0. The curves for the temperature dependence of the  $\chi T$  value obtained in this way are given in Fig. 2. Analysis of the obtained data makes it possible to state that contrary to the widespread opinion ZFS (positive values of  $D$ ) not only has a significant effect in the low-temperature region but also makes a significant contribution at higher temperatures, leading to an increase in the  $\chi T$  values.

We analyzed the adequacy of the description of the  $\text{Fe}_2(\text{III})$  system in which ZFS is present by means of the classical model that does not take account of this effect. For this purpose collections of data on the temperature dependence of  $\chi T$  for various values of  $D$  were modelled by means of Eq. (7). Analysis of the obtained data (Table 1) shows that the disregard of ZFS with ratios  $D/J < 1$  leads to the production of a  $g$  factor of  $< 2$  for  $\text{Fe}^{3+}$ , which has no physical meaning. With increase in the  $D/J$  ratio disregard of the effect of ZFS leads to substantial deterioration of the agreement between the observed and expected results of modelling. The appearance of a low-temperature peak with increase of the ratio  $D/J$  (Fig. 2) is significant. Thus, with  $D/J = 2$  the maximum value of  $\chi T$  for the binuclear complex of iron amounts to 22.18 cgs units, whereas the maximum theoretically possible value of  $\chi T$  without allowance for exchange interactions is only 8.74. This may lead to the result that disregard of ZFS with perceptible  $D/J$  ratios may lead to an incorrect interpretation as the presence of ferromagnetic interaction

between the two iron atoms in the polynuclear core. Similar arguments hold for the reverse situation – the case of weak ferromagnetic exchange with a negative value for the parameter  $D$ .

Thus, the analysis made in the present work showed that in the case of weakly exchanging Fe(III)–Fe(III) systems (the boundary region between weak antiferromagnetics and ferromagnetics) the experimental magnetochemical data can only be modelled and interpreted correctly if zero field splitting is taken into account. For this reason some caution is required in the use of existing correlations between the structural parameters of the binuclear complexes of iron(III) and the exchange parameters, since most of the  $J$  values used for the construction of such relationships were obtained with no allowance for ZFS.

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