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Ligand Field Theory of Metal Sandwich Complexes. Second Order Effects in the Magnetic Behaviour of d^x Configurations

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Calculations have been made of second order contributions to the magnetic susceptibilities of transition metal sandwich complexes, using the pseudo-axial ($C_{\infty v}$) ligand field model. The temperature independent paramagnetism, due to second order Zeeman interactions between the ground state and excited levels, has been evaluated for all d^x systems, and for non-orbitally degenerate ground states the magnetic consequences of a zero field splitting, due to second order spin–orbit interactions, have been investigated.

Introduction

For sandwich complexes of the transition metals the pseudo-axial ($C_{\infty v}$) ligand field model, introduced by Scott and Matsen,[1] has proved to be of great utility. Thus the *d–d* spectra have been interpreted using the appropriate d^x strong field energy matrices,[2–4] whilst the magnetic properties of such systems have also been investigated using this approach.[5] This latter treatment however considered only contributions to the susceptibilities arising from within the ground state manifold, and also restricted attention to those ground levels which possessed an orbital degeneracy. The purpose of the present work is therefore twofold: first are calculated the temperature independent susceptibilities, due to second order Zeeman interactions between the ground and excited states, and thereafter more detailed consideration is given to orbitally non-degenerate ground levels. For these latter systems the spin degeneracy may in some cases be lifted by second order spin–orbit coupling effects, and the consequences of this are examined, both as regards deviations of the average susceptibility from the spin-only value, and also with respect to the resulting anisotropies in the principal molecular susceptibilities.

Theory and Calculations

In a pseudo-axial ligand field the *d*-orbital set is split into three irreducible representations, $\sigma(d_{z^2})$, π (d_{xz}, d_{yz}), and δ ($d_{x^2-y^2}$, d_{xy}), which in the metallocenes and bis-arene complexes follow the one-electron energy sequence $\delta<\sigma\ll\pi$. In the absence of a magnetic field the appropriate perturbation Hamiltonian, H′, is

$$H' = \sum_{i<j} \frac{e^2}{r_{ij}} + \sum_i \xi(r_i) l_i \cdot s_i + \sum_i V_{LF}(r_i)$$

representing respectively the interelectronic coulombic repulsions, the spin–orbit interactions, and the pseudo-axial ligand field. Calculations in the strong field scheme[2–4] show that for the metallocenes the ground states, as listed in Table I, always show a purity of 98% or greater, and the inclusion of spin–orbit coupling leads to admixtures of no more than about 1%.

Consequently, in the original treatment of the magnetic properties of sandwich complexes,[5] the susceptibilities could adequately be calculated using the zero order ground state spin–orbit wave functions, and the familiar Van Vleck equation

$$\chi_\alpha = \frac{N\sum_i \left[\frac{(E_i^I)^2}{kT} - 2E_i^{II}\right] e^{-E_1^\circ/kT}}{\sum_i e^{-E_i^\circ/kT}}$$

where $E_i^I = \langle\psi_i | k'L_\alpha + 2S_\alpha | \psi_i\rangle\beta$, $E_i^{II} = \sum_{j\neq i}(\langle\psi_i | k'L_\alpha + 2S_\alpha | \psi_j\rangle\beta)^2/(E_i^\circ - E_j^\circ)$, with $\alpha = z$ ($H_{||}$) or x, y ($H_\perp$), and k′ is the orbital reduction factor through which allowance may be made for the delocalisation of electrons from the metal *d*-orbitals onto the ligands.

The second order Zeeman effects due to interaction between the ground and excited states are however readily evaluated since for such terms only the orbital contributions can be non-vanishing. Moreover, in $C_{\infty v}$ symmetry the operators L_z and L_x, L_y transform respectively as Σ^- and as Π, and for non-zero terms the direct product $\psi_{gr} \cdot L_\alpha \cdot \psi_{ex}$ must contain Σ^+. In addition the excited levels must also be of the same spin multiplicity as the ground state and must differ in only one orbital occupation. Finally all matrix elements of the type $\langle\sigma | L_\alpha | \delta\rangle$ vanish, yielding the interacting excited states as shown in Table I; all L_z

TABLE I. Second Order Zeeman Contributions to $\chi_\perp$ for $C_{\infty v}$ Ground States.[a]

Ground State	$\sigma \rightarrow \pi$ Excitations		$\delta \rightarrow \pi$ Excitations	
	Configuration	Excited States	Configuration	Excited States
$d^1, {}^2\Delta\ (\delta)$	–	–	(π)	$^2\Pi(2)$
$d^2, {}^3\Sigma^-\ (\delta^2)$	–	–	$(\pi\delta)$	$^3\Pi(4)$
$d^2, {}^3\Delta\ (\sigma\delta)$	$(\pi\delta)$	$^3\Pi(3), {}^3\Phi(3)$	$(\sigma\pi)$	$^3\Pi(2)$
$d^3, {}^4\Sigma^-(\sigma\delta^2)$	$(\pi\delta^2)$	$^4\Pi(6)$	$(\sigma\pi\delta)$	$^4\Pi(4)$
$d^4, {}^3\Delta(\sigma\delta^3)$	$(\pi\delta^3)$	$^3\Pi(3), {}^3\Phi(3)$	$(\sigma\pi\delta^2)$	$3\ {}^3\Pi(1, 1, 2), {}^3\Phi(2)$
$d^5, {}^6\Sigma^+(\sigma\pi^2\delta^2)$	–	–	–	–
$d^5, {}^2\Sigma^+(\sigma\delta^4)$	$(\pi\delta^4)$	$^2\Pi(6)$	$(\sigma\pi\delta^3)$	$2\ {}^2\Pi(8, 0)$
$d^5, {}^2\Delta(\sigma^2\delta^3)$	$(\sigma\pi\delta^3)$	$2\ {}^2\Pi(3/2, 9/2), 2\ {}^2\Phi(3/2, 9/2)$	$(\sigma^2\pi\delta^2)$	$2\ {}^2\Pi(1, 3), {}^2\Phi(2)$
$d^6, {}^1\Sigma^+(\sigma^2\delta^4)$	$(\sigma\pi\delta^4)$	$^1\Pi(12)$	$(\sigma^2\pi\delta^3)$	$^1\Pi(8)$
$d^7, {}^2\Pi(\sigma^2\pi\delta^4)$	$(\sigma\pi^2\delta^4)$	$^2\Sigma^+(3/2), {}^2\Sigma^-(9/2), {}^2\Delta(3)$	$(\sigma^2\pi^2\delta^3)$	$^2\Sigma^+(1), {}^2\Sigma^-(1), 2^2\Delta(1, 3)$
$d^8, {}^3\Sigma^-(\sigma^2\pi^2\delta^4)$	$(\sigma\pi^3\delta^4)$	$^3\Pi(6)$	$(\sigma^2\pi^3\delta^3)$	$^3\Pi(4)$
$d^9, {}^2\Pi(\sigma^2\pi^3\delta^4)$	$(\sigma\pi^4\delta^4)$	$^2\Sigma^+(3)$	$(\sigma^2\pi^4\delta^3)$	$^2\Delta(2)$

[a] Values shown in units of $N\beta^2/\Delta E$, assuming $k'^2 = 1$.

TABLE II. Magnetic Susceptibilities for Non-Orbitally Degenerate Ground States in $C_{\infty v}$ Symmetry.

$d^8, {}^3\Sigma^-$ $(\alpha = D/kT)$

$$\chi_\parallel = \frac{2N\beta^2}{kT} g_\parallel^2 \left\{ \frac{e^{-\alpha}}{1 + 2e^{-\alpha}} \right\} ; \quad \chi_\perp = \frac{2N\beta^2}{kT} g_\perp^2 \left\{ \frac{1-e^{-\alpha}}{\alpha(1 + 2e^{-\alpha})} \right\}$$

$d^3, {}^4\Sigma^-$ $(\alpha = 2D/kT)$

$$\chi_\parallel = \frac{N\beta^2}{4kT} g_\parallel^2 \left\{ \frac{1 + 9e^{-\alpha}}{1 + e^{-\alpha}} \right\} ; \quad \chi_\perp = \frac{N\beta^2}{2kT} g_\perp^2 \left\{ \frac{2 + 3\alpha^{-1}(1-e^{-\alpha})}{1 + e^{-\alpha}} \right\}$$

$d^5, {}^6\Sigma^+$ $(\alpha = 2D/kT)$

$$\chi_\parallel = \frac{N\beta^2}{4kT} g_\parallel^2 \left\{ \frac{1 + 9e^{-\alpha} + 25e^{-3\alpha}}{1 + e^{-\alpha} + e^{-3\alpha}} \right\} ; \quad \chi_\perp = \frac{N\beta^2}{4kT} g_\perp^2 \left\{ \frac{9 + 16\alpha^{-1}(1-e^{-\alpha}) + 5\alpha^{-1}(e^{-\alpha}-e^{-3\alpha})}{1 + e^{-\alpha} + e^{-3\alpha}} \right\}$$

contributions are thus zero, and the temperature independent susceptibility due to these second order Zeeman terms therefore arises only from the L_x, L_y operators.

The required wave functions for the excited states were as previously described,[2-4] and for each given ground state the second order Zeeman contribution is listed in units of $N\beta^2/\Delta E$ after the appropriate excited level. Where the latter contain a repeated irreducible representation for any orbital occupation, the contributions are listed following the ordering used in the coulombic repulsion matrices previously given.[2-4]

Within the limits of the earlier treatment,[5] non-orbitally degenerate ground states (*e.g.* $^4\Sigma^-$ $(\sigma\delta^2)$, $^2\Sigma^+$ $(\sigma\delta^4)$, $^6\Sigma^+$ $(\sigma\pi^2\delta^2)$, and $^3\Sigma^-$ $(\sigma^2\pi^2\delta^4)$) should show simply the spin-only moments, but closer scrutiny reveals that anisotropic magnetic behaviour may arise from two effects. In the first place the g values may deviate from the isotropic value of 2, due to spin–orbit interactions. For the $^2\Sigma^+$ $(\sigma\delta^4)$ system the matrix elements of H_{SO} and H_{Zeeman} with the ground state are both non-vanishing only for the $^2\Pi(\pi\delta^4)$ level, leading to the result $g_\parallel = 2.00$ and $g_\perp = 2.00 - 6\ \xi/\Delta E$, where $\Delta E = E(^2\Pi) - E(^2\Sigma^+)$. This system was not though investigated further since with a single Kramers' doublet it can show no zero field splitting. For the remaining systems however the first order separations produced by the magnetic field may be comparable with the second order spin–orbit interactions which produce the zero field splitting, and the appropriate perturbation treatment[6] has been used by Prins and Van Voorst[7] to obtain expressions for the g values for the d^3, $^4\Sigma^-$ and d^8, $^3\Sigma^-$ systems, exemplified by vanadocene and nickelocene respectively, whilst for

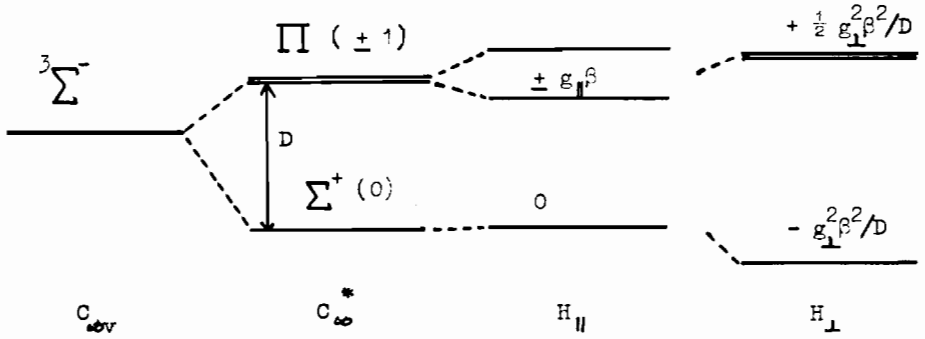

Figure 1. Zero field splitting for d^8, $^3\Sigma^-$, ground states.

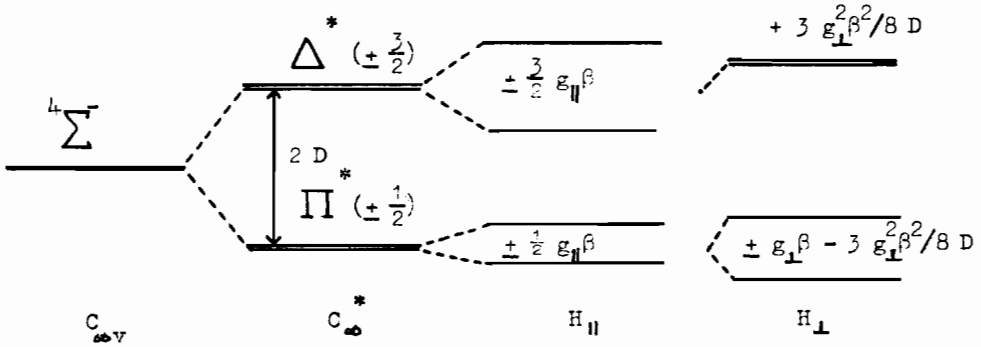

Figure 2. Zero field splitting for d^3, $^4\Sigma^-$, ground states.

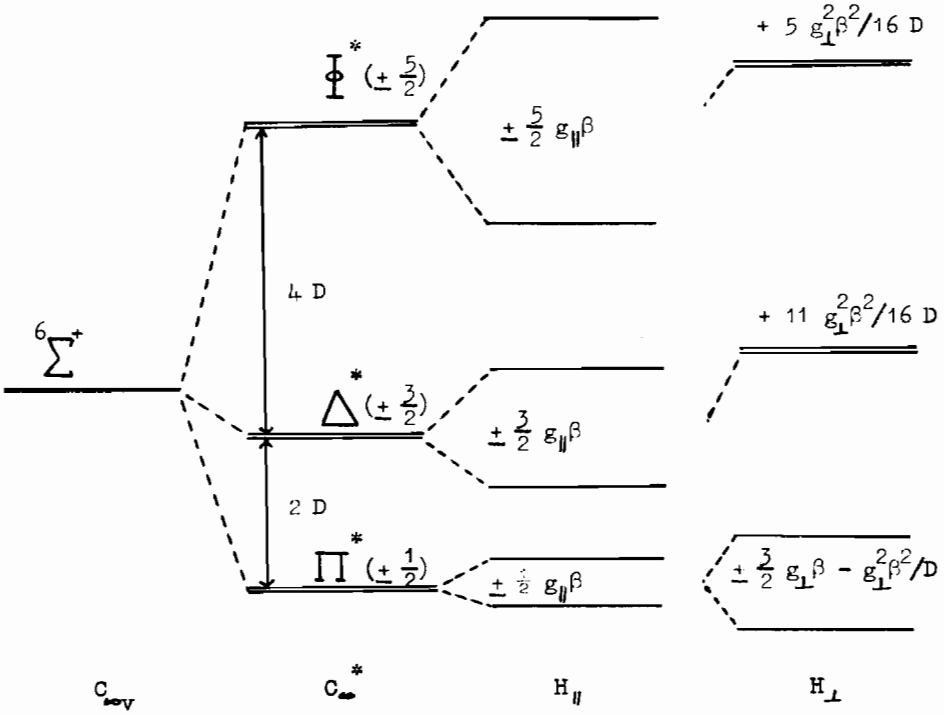

Figure 3. Zero field splitting for d^5, $^6\Sigma^+$, ground states.

the high-spin $^6\Sigma^+$ ground state of the d^5 manganocene similar equations have been derived by Krieger and Voitländer.[8]

Nevertheless, the observed g values do not differ greatly from 2, nor are they markedly anisotropic, and in this the orbital singlets resemble the orbitally degenerate ground states for which second order spin–orbit effects also exert only a relatively small influence on the g values.[9,10] Consequently, this effect alone should not produce substantial deviations from the spin-only behaviour, but the d^8, $^3\Sigma^-$, d^3, $^4\Sigma^-$, and d^5, $^6\Sigma^+$, systems should now all be described by the effective Hamiltonian

$$H' = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + D(S_z^2 - \tfrac{1}{3}S(S+1))$$

where D is the zero field splitting parameter. From the matrix elements within the respective ground state manifolds the energy levels of Figures 1–3 and the $\chi_{\parallel}$ and $\chi_{\perp}$ expressions of Table II are found, and from these results the corresponding magnetic moments may be derived using the Curie formula, $\chi = N\mu_{eff}^2/3$ kT, and the average from the relationship $\langle\mu\rangle = [\frac{1}{3}(\mu_{\parallel}^2 + 2\mu_{\perp}^2)]^{1/2}$.

In Figures 1–3 the levels of smaller $|S_z|$ are assumed to lie lower, corresponding to a positive D, and the calculations of Prins and Van Voorst[7] support this for the d^8 and d^3 systems, indicating $\Sigma^+ < \Pi$ and $\Pi^* < \Delta^*$ respectively. For the d^5, $^6\Sigma^+$ ground state however Krieger and Voitländer[8] found D to be negative with $\Phi^* < \Delta^* < \Pi^*$. For all three systems the expressions given in Table II reduce to the spin-only results, 8 $N\beta^2/3$ kT, 5 $N\beta^2$/kT, and 35 $N\beta^2/3$ kT respectively, for $g_{\parallel} = g_{\perp} = 2.00$, as $T \to \infty$ ($\alpha \to 0$), whilst for $\alpha \to +\infty$ and $\alpha \to -\infty$ (D positive or negative) the limiting values are easily derived from the formulae of Table II.

Results and Discussion

For the systems of pseudo-axial symmetry considered above the temperature independent susceptibilities to be added to the $\chi_{\perp}$ values, obtained as previously described,[5] are easily evaluated from the results of Table I. To assess their importance these terms are now calculated for the d^x metallocenes of the 3*d* series (x = 3–8), for which sufficient spectroscopic data are available to locate the excited levels involved. Thus the results of Prins and Van Voorst[7] were used for $V(Cp)_2$ and $Ni(Cp)_2$, those of Sohn, Hendrickson, and Gray[11] for $Fe(Cp)_2^+$, and the data of Ammeter and Swalen[9] for $Co(Cp)_2$. For $Cr(Cp)_2$ the results cited by Krieger and Voitländer[8] were used, and in all cases the assignments suggested in a recent review[12] were adopted. Finally, even the formally diamagnetic d^6, $^1\Sigma^+$ system, $Fe(Cp)_2$, should show a small residual paramagnetism, due to second order Zeeman effects, and here again the data of Sohn *et al.*[11] were used.

From these results the temperature independent susceptibilities are calculated to be 135, 145, 215, 210, 220, and 150×10^{-6} cgsu for $V(Cp)_2$, $Cr(Cp)_2$, $Fe(Cp)_2^+$, $Fe(Cp)_2$, $Co(Cp)_2$, and $Ni(Cp)_2$ respectively. Thus, even at room temperature, the temperature independent term is unlikely to constitute a significant fraction of $\chi_{\perp}$ (and of $\langle\chi\rangle$), except for the system with the smallest magnetic moment – the d^7, $Co(Cp)_2$. Even here however it is possible that its magnitude has been overestimated since the second order Zeeman terms arise from the orbital part of the $k'L_{x,y} + 2S_{x,y}$ operator, and the results should in all cases be multiplied by the factor k'^2. For $Co(Cp)_2$ the esr data of Ammeter and Swalen[9] suggest that the appropriate reduction factor, $k_{\perp}$, may be as small as 0.5, thereby reducing the temperature independent contribution to a quarter of the value given above. Thus the second order terms seem unlikely to make appreciable contributions to the measured susceptibility, although the residual paramagnetism of the $^1\Sigma^+$ $Fe(Cp)_2$ should amount to some 50×10^{-6} cgsu, even assuming $k_{\perp}$ to be as small as for $Co(Cp)_2$. However, although $Fe(Cp)_2$ is found to show a susceptibility of -125×10^{-6} cgsu, it is difficult therefrom to estimate the residual paramagnetism since the diamagnetic corrections derived using Pascal's constants amount to very much the same order.

In contrast to the second order Zeeman terms, second order spin–orbit effects, although relatively unimportant for Π and Δ ground states, may produce significant zero field splittings of orbitally non-degenerate ground levels, thereby leading to appreciable deviations from the isotropic spin-only behaviour predicted by the simple treatment.[5] Since the effects due to the anisotropy of the g values are comparatively small the influence of the zero field splitting on the magnetic behaviour is most conveniently represented diagramatically in terms of the dependence of the moments ($\mu_{\parallel}$, $\mu_{\perp}$, and $\langle\mu\rangle$) on the parameter α, as defined in Table II, assuming for simplicity $g_{\parallel} = g_{\perp} = 2.00$. For all three systems $\langle\mu\rangle$ attains its maximum (and the spin-only) value et $\alpha = 0$, and $\mu_{\parallel}$ similarly shows maxima as $\alpha \to \infty$ (D negative); for $\mu_{\perp}$ however differentiation shows the respective maxima deduced for the d^8, d^3, and d^5 systems to occur at $\alpha = 1.036$, 1.725, and 1.200, with D positive.

For some purposes consideration of the temperature dependence of the susceptibilities may be preferable, and since $\chi_{\parallel}$ arises only from first order Zeeman splittings it is a function of α and T^{-1}. However, both first and second order terms may contribute to $\chi_{\perp}$ (see Figures 1–3), as in the d^3 and d^5 cases for which the first order terms are due to $\langle +^1/_2 \| -^1/_2 \rangle$ interactions, but for the d^8 configuration only second order

terms are involved in $\chi_\perp$, leading to a dependence upon α and D^{-1}, from which in principle the zero field splitting parameter could be determined. The data available for all three systems are now therefore considered.

d^8, $^3\Sigma^-$

Here expressions for $\chi_{\|}$ and $\chi_\perp$ equivalent to those of Table II were given by Prins, Van Voorst, and Schinkel,[14] who measured the bulk susceptiblity of $Ni(Cp)_2$ between 6.5 and 300 K. The Curie–Weiss law was followed down to 70 K, yielding a moment of 2.89 ± 0.15 B.M., but below this temperature $<\chi>$ became markedly smaller than the spin-only value, tending towards a temperature independent value as $T \rightarrow 0$. Using the ratio $g_\perp^2/D$ $(= 3<\chi>_{T=o}/4\ N\beta^2)$ thus obtained, the data were fitted[14] by the parameters $g_{\|} = 2.00$, $g_\perp = 2.06 \pm 0.10$, and $D = 25.6 \pm 3.0$ $cm.^{-1}$ However, even in the higher temperature range, calculations using these parameters show that the regular behaviour of $<\chi>$ conceals a substantial anisotropy in the principal molecular susceptibilities, which if defined as $|\chi_{\|}-\chi_\perp|/<\chi>$ amounts to nearly 12% at 300 K and exceeds 30% at 70 K. Consequently, measurement of the anisotropic susceptibilities for this system would enable D, and also $g_{\|}$ and $g_\perp$, to be determined with much greater accuracy, especially since $\chi_{\|}$ is indicated by differentiation to show a well marked maximum at $\alpha = 1.463$, which here corresponds to $T = 25.2$ K.

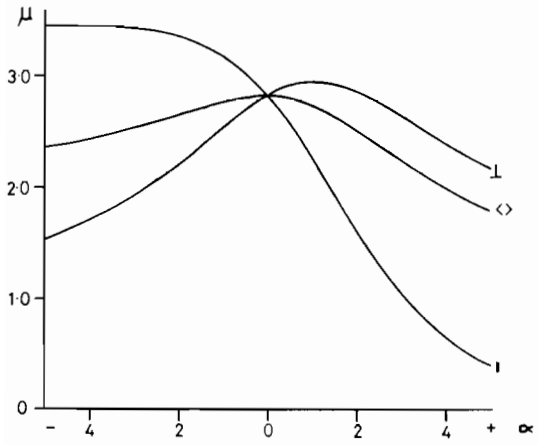

Figure 4. Variation of magnetic moments with zero field splitting for d^8, $^3\Sigma^-$ systems. Here and in Figures 5 and 6 $g_{\|} = g_\perp = 2.00$.

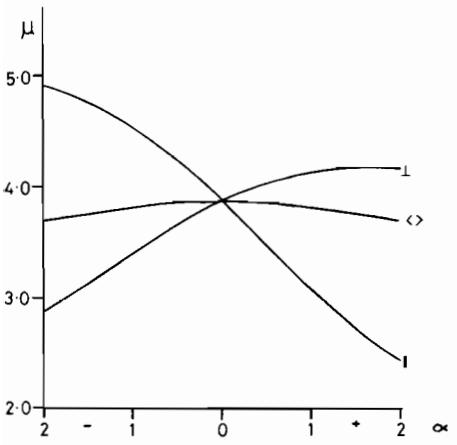

Figure 5. Variation of magnetic moments with zero field splitting for d^3, $^4\Sigma^-$ systems.

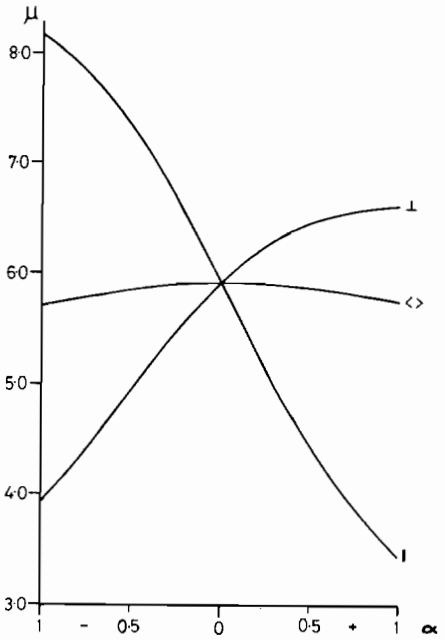

Figure 6. Variation of magnetic moments with zero field splitting for d^5, $^6\Sigma^+$ systems.

d^3, $^4\Sigma^-$

This system was investigated by Leipfinger,[15] who measured the average susceptibility at various temperatures between 430 and 1.5 K. Above 14.3 K $<\chi>$ was found to show Curie–Weiss behaviour, with a moment of 3.78 ± 0.19 B.M., close to the spin-only value, but between 1.5 and 4.2 K the susceptibility was appreciably smaller than expected, and although almost temperature independent showed a slight decrease as $T \rightarrow 0$. This behaviour cannot however be accommodated by the present treatment and it thus seems reasonable to follow Leipfinger[15] in attributing the low temperature effects to antiferromagnetism. In fact, using the dipolar interaction model,[16] the observed trend can be reproduced with an exchange integral, J,

of −1.5 to −2.0 cm^{-1}, although the fit is not very close and suggests a more complex interaction. More significant antiferromagnetic effects would however be expected for the d^3 system, with an $M_S = \pm 1/2$ lower level, than for the d^8 system, in which $M_S = 0$ lies lower.

The regular temperature dependence of $<\chi>$ above 14.3 K is nevertheless quite consistent with the esr results of Prins and Van Voorst,[7] who found $g_{\parallel} = 2.00$, $g_{\perp} = 1.99$, and $|D| = 2.7$ cm^{-1}, and calculated D to be positive. The deviation of $<\chi>$ from the spin-only value thereby calculated is less than 2% even at 15 K, and no information concerning D can thus be obtained from the $<\chi>$ *vs.* T plot, especially since in this case $<\chi>$ does not tend towards a simple function of D as $T \rightarrow 0$. However, the spin-only behaviour above 14.3 K does obscure a significant magnetic anisotropy, this time amounting to 5% at 70 K and over 28% at 15 K. Again then anisotropic data might afford a better estimate for D, although in this case $\chi_{\parallel}$ shows no convenient maximum (a point of inflection is indicated at $\alpha = 2.398$, but corresponds here to T = 3.25 K, below the temperature at which $V(Cp)_2$ ceases to be magnetically dilute). Similarly the maximum in $\mu_{\perp}$ is predicted at 4.5 K, as against 35.6 K for $Ni(Cp)_2$.

d^5, $^6\Sigma^+$

This system, exemplified by $Mn(Cp)_2$, presents a number of complicating features since the pink, high-spin, form of manganocene is not stable below 432 K, and the $^6\Sigma^+$ ground state is therefore not directly accessible for the low temperatures at which the effects of the zero field splitting on the susceptibility may be appreciable. However, diluted in suitable host lattices, $Mn(Cp)_2$ does show the $^6\Sigma^+$ $(\sigma\pi^2\delta^2)$ ground state, with a spin-only moment of 5.92 B.M. between 77 and 438 K,[17] and the g values for $Mn(Cp)_2$ in the high-spin form are close to 2.00 and almost isotropic,[8,10,18] with $|D|$ between 0.25 and 0.50 $cm.^{-1}$ Moreover, Krieger and Voitländer[8] have calculated D to be −0.24 cm^{-1}, but with this value for D any deviations of $<\chi>$ from the spin-only value should be immeasurably small (less than 1% even at 5 K), and with D negative no maximum should be observed for $\mu_{\perp}$. Nevertheless, the predicted anisotropy, although only 1.5% at 70 K, is almost 7.5% at 15 K, and would be significantly increased should $|D|$ prove to be as large as 0.50 cm^{-1}.

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