Theory of Magnetism Close to the $^5T_2 - ^1A_1$ Crossover in Iron(II) Complexes

II. Full Configuration Interaction Calculation in a Cubic Field

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On the basis of the eigenvalues and the eigenvectors resulting from the diagonalization of the complete ligand field, Coulomb interaction, and spin-orbit coupling matrices, the magnetic susceptibility has been calculated for the $d^6$ configuration in a field of octahedral symmetry. The magnetic moment values $\mu_{\text{eff}}$ are presented as function of temperature and $10 \, \text{Dq}$ for a fixed set of values of the Racah parameters $B$, $C$ and the spin-orbit coupling constant $\zeta$. The region of the $^5T_2 - ^1A_1$ crossover is considered in detail and the application to relevant experimental data is discussed.

Introduction

In a previous paper [1] we have briefly reviewed the magnetic properties of iron(II) complexes in which a $^5T_2 - ^1A_1$ crossover is either established or supposedly involved. An attempt has been made to develop a semi-empirical theory suitable to reproduce the experimental magnetic data of such systems. It was shown that a modification of the two-level scheme including at least an axial field distortion and taking account of permanently paramagnetic material was needed. In all compounds studied in some detail, the axial field splitting of the $^5T_2$ term is such as to produce a low lying orbital singlet (i.e. $^5B_2$, if the distortion is tetragonal). This is equivalent to the axial field parameter $\delta$ being negative and varying, in actual compounds, between about $-200$ and $-1000 \, \text{cm}^{-1}$.

Based on a comparison of calculated and experimental magnetic data it was demonstrated that the energy separation $\epsilon$ between the centers of gravity of the $^5T_2$
and $^1A_1$ terms is strongly temperature-dependent. This result is consistent with the decrease of the Fe-ligand bond distance which is expected on change of the groundstate from $^5T_2(t^6e^2)$ to $^1A_1(t^6)$ [2]. In one case, the change of the Fe-ligand bond length has been demonstrated directly by X-ray structure methods [3]. Specific values for $\varepsilon = \varepsilon(T)$ were determined in two systems, viz. [Fe(mphen)$_3$]-[ClO$_4$]$^-$ and [Fe(mphen)$_3$](BF$_4$)$^-$ where mphen = 2-methyl-1,10-phenanthroline [4]. In these compounds, the parameter $\delta$ was estimated from the temperature dependence of the quadrupole splitting in the $^{57}$Fe Mössbauer spectra [5]. Additional results on systems of related interest will be published separately [6].

In the present study, the magnetic properties of a $d^6$ electron system will be calculated by means of ligand field theory. We are interested particularly in the region close to the $^5T_2 - ^1A_1$ crossover, in the mixing effects of excited terms on the magnetic susceptibility and in the temperature dependence of the ligand field splitting parameter $10Dq$ and of the $^5T_2 - ^1A_1$ energy separation $\varepsilon$. Therefore, full configuration and spin-orbit interaction will be included. Since, in this investigation, accurate reproduction of experimental data is considered only on a second priority basis, we will disregard axial and lower symmetry distortions and assume, in what follows, a cubic field to be present.

Octahedral Ligand Field and Interelectronic Repulsion Matrices and Resulting Eigenvectors

The combined ligand field and interelectronic repulsion matrices for a $d^6$ transition metal ion in a field of octahedral symmetry were derived by Tanabe and Sugano [7, 8]. These authors also performed detailed numerical calculations on the $d^6$ Co$^{3+}$ ion. In Fig. 1 we present the results of similar calculations on the low lying excited states of the Fe$^{2+}$ ion. In analogy to the Tanabe-Sugano diagrams [7, 8], $E/B$ is plotted versus $A/B$ where $E$ is the energy relative to the ground state and $A = 10Dq$ the octahedral ligand field splitting parameter. Free ion values of the Racah interelectronic repulsion parameters (viz. $B = 917$ cm$^{-1}$, $C = 4040$ cm$^{-1}$) were used. The crossover between the groundstates $^5T_2$ and $^1A_1$ occurs, within this approximation, at $10Dq = \Pi \sim 17,006.8$ cm$^{-1}$. Without configuration interaction, the $^5T_2 - ^1A_1$ energy separation is determined according to

$$\varepsilon = 20Dq - 5B - 8C$$

(1)

whereas if non-diagonal matrix elements are approximately accounted for [9],

$$\varepsilon = 20Dq - 5B - 8C + \frac{120B^2}{10Dq}.$$  

(2)

It should be observed that the value of $\Pi$ at the crossover as determined from Eq. (1) or Eq. (2) with $\varepsilon = 0$ is largely in error. Thus using the values of $B$ and $C$ listed above, Eq. (1) results in $\Pi = 18,452.5$ cm$^{-1}$, whereas the quadratic Eq. (2) gives the value $\Pi = 15,114.4$ cm$^{-1}$ which is no better. Both equations provide, therefore, only very crude estimates of the crossover energy $\Pi$. 