# SPIN-ORBIT INTERACTION AND MAGNETIC PROPERTIES OF $d^1$-, $d^2$-, $d^8$-, AND $d^9$-SANDWICH COMPLEX COMPOUNDS

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$N$-electron wave functions for a strong ligand field of symmetry $D_{\infty h}$ were derived in the complex region, their transformation properties were studied and the particle-hole relation discussed. Further the matrix elements of the spin-orbit interaction operator and of the Zeeman magnetic interaction operator were calculated and on their basis formulas for the magnetic susceptibility or the effective magnetic moment were derived for $d^1$-, $d^2$-, $d^8$-, and $d^9$-sandwich complexes. Knowledge of the magnetic susceptibility at room temperature for $d^2$-electron systems with $kT/\zeta \approx 1\cdot3$ is not sufficient to make conclusions as to the orbital character of the ground state. Known values of effective magnetic moments of certain sandwich complexes were compared with theoretical ones and the spin-orbit interaction and magnetic susceptibility of nickelocene were calculated. The agreement between theory and experiments is very good in all cases.

Theoretical studies of optical and magnetic properties of complex compounds having an octahedral or tetrahedral symmetry, or an approximately cubic symmetry with components of a lower symmetry have been from the point of view of the method and formalism of the ligand field theory substantially completed[1−9]. Besides this type of complex compounds, which can be denoted as cubic complexes, there exist many complexes whose symmetry group is neither $O_h$ nor $T_d$ nor a subgroup $O_h(T_d)$. We have in mind mainly the so-called sandwich complex compounds, which can be classified according to their symmetry group $D_{\infty h}$ or its subgroups (the so-called axial model of sandwich complexes). The most well-known of them are the so-called metallocenes (and their carborane analogues) which were studied recently both experimentally and theoretically[10−17]. The application of the ligand field theory to the known sandwich complexes has been nearly as successful as in the case of cubic complexes, but the study of the former cannot be considered as finished. Krieger and Voitländer[18,19] attempted to elucidate unsuccessful EPR measurements of some metallocenes and to interpret others (manganocene, cobaltocene) on the basis of their molecular orbital calculations combined with the ligand field theory. Ammeter and Swalen[20] studied in detail the electron structure of cobaltocene, Thomas and Hayes[21] showed that dicyclooctatetraenyl vanadium(IV) and cyclooctatetraenyl (cyclopentadienyl) titanium(III) are also sandwich complexes, Pavlik and coworkers[22] studied the bonding in the carborane analogue of nickelocene, $Ni(B_9C_2H_{11})_2^{2-}$, Levenson and Dominguez[23] used the axial field formalism to study pentagonal bipyramidal complexes with the coordination number 7. Several authors were concerned with the ferricenium cation[24−28], the spectra of some $d^6$-sandwich complexes were studied with regard to the "complete" ligand field theory (neglecting the spin-orbit coupling)[29]. Veillard and coworkers[30] carried out an interesting *ab initio* molecular orbital calculation of the ferrocene molecule which is partially at variance with common concepts about the relative sequence of the highest occupied levels in metallocenes.

The ligand field theory has been very little employed in problems of spin-orbit interaction and magnetic properties of sandwich complexes. Only DeKock and Gruen[31] calculated the spin-orbit interaction for axial $d^2(d^8)$ electron systems in the weak ligand field approximation, which is not very suitable for metallocenes and other sandwich complexes since their ground state corresponds more to that corresponding to a strong ligand field. We therefore calculated the complete matrices of the spin-orbit interaction operator and magnetic operator $L + 2S$ for $d^1(d^9)$ and $d^2(d^8)$ electron systems in a strong ligand field, derived general relations valid for the application of the ligand field theory to noncubic complexes and formulas expressing the dependence of the magnetic susceptibility or effective magnetic moment on the temperature. These formulas and the magnetic susceptibility of nickelocene[11,12,32] are discussed from the point of view of the ligand field theory in the practical part (see Magnetic Susceptibility).

### THEORETICAL

The problem to be solved is the determination of the influence of an axial ligand field, $V_{AX}$, on a central $d^N$ ion[16]. If we take into account the spin-orbit coupling characterized by the operator

$$\mathscr{H}_{so} = \sum_{i=1}^{N} \xi(r_i)\,(l_i,\, s_i)\,, \tag{1}$$

the solution of this problem is given by the solution of the Schrödinger equation with the Hamiltonian

$$\mathscr{H}_0 = \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m}\, \nabla_i^2 - \frac{Z_{eff}e^2}{r_i} \right\} + \sum_{i<j}^{N} \frac{e^2}{r_{ij}} + V_{AX} + \mathscr{H}_{so}\,. \tag{2}$$

After applying a constant external magnetic field $H$, the following term is added to the Hamiltonian if we neglect a small diamagnetic contribution $(e^2/8mc^2)\sum_{i=1}^{N} \cdot |Hxr_i|^2$:

$$\mathscr{H}_1 = \beta(H,\, L + 2S)\,, \tag{3}$$

where $\beta$ denotes the Bohr magneton, and the eigen values of the operators $L$ and $S$ are expressed in $\hbar$ units.

The matrix elements of the operator $\mathscr{H}_0 - \mathscr{H}_{so}$ in the strong axial ligand field approximation can be obtained in several ways[1-7,33]. They are known for all values of $N$ (for $N = 2$ and 8 they are given in ref.[13,14], for $N = 3$ and 7 in ref.[16], for $N = 4$ and 6 in ref.[29], and for $N = 5$ they were calculated by the author[34]). To obtain the complete solution of our problem, it remains to determine the matrix elements of the operators (1) and (3).

*Wave functions.* Similarly as Griffith[2,3], we shall solve the given problem in a complex coordinate system. We define the complex one-electron wave function as follows (ref.[3], p. 31):

$$|e_{kg}\ 1\rangle = -\frac{i}{\sqrt{2}}|e_{kg}\ c\rangle + \frac{1}{\sqrt{2}}|e_{kg}\ s\rangle, \quad |a_{1g}\ 0\rangle = |a_{1g}\ \iota\rangle,$$

$$|e_{kg}\ -1\rangle = \frac{i}{\sqrt{2}}|e_{kg}\ c\rangle + \frac{1}{\sqrt{2}}|e_{kg}\ s\rangle, \tag{4}$$

where $k = 1$ or 2 and the meaning of symbols is given, *e.g.*, in ref.[16]

*N*-electron wave functions, $|a^N S\Gamma Mm\rangle$, where $a = e_{2g}$, $a_{1g}$ or $e_{1g}$, were composed from functions (4) according to the equations $(7,1)-(7,6)$ in ref.[3], p. $59-61$, and are given in Table I. From these it is possible to compose by the known procedure[2,3] the *N*-electron wave functions $|\omega S\Gamma Mm\rangle$, where $\omega = e_{2g}^{n2} a_{1g}^{n0} e_{1g}^{n1}$ and $N = n_2 + n_0 + + n_1$. The necessary coupling coefficients in the complex coordinate system, $\langle abij \mid ck\rangle$, are defined as

$$\langle abij \mid ck\rangle = \lambda^{1/2}(c)\ V\begin{pmatrix} a & b & c \\ -i & -j & k \end{pmatrix}. \tag{5}$$

The meaning of symbols and tables of the $V$ coefficients for the group $D_\infty$ are given in ref.[3], p. 124. The properties of the $V$ coefficients are chosen so as to preserve the invariance of the reduced matrix elements, $\langle a \parallel \mathbf{g}^c \parallel b\rangle$, of the operator $\mathbf{g}$ with respect to transformation from the real to the complex coordinate system (ref.[3], p. $19-21$ and 31). From the properties of the $V$ coefficients and Eq. (5) follows

$$\langle abij \mid ck\rangle = (-1)^{a+b+c}\langle baji \mid ck\rangle =$$

$$= \{-1\}^{a+b+c}\langle ab - i - j \mid c - k\rangle = \langle ab - i - j \mid c - k\rangle^* =$$

$$= (-1)^{a+b+c}\{-1\}^{a+b+c}\{\lambda(c)/\lambda(b)\}^{1/2}\langle ac - ik \mid bj\rangle = \ldots, \tag{6}$$

where the asterisk denotes complex conjugation, and

$(-1)^a = 1$   for   $a = A_1$   or   $E_n$   irreducible representation of group $D_\infty$,

$(-1)^a = -1$   for   $a = A_2$,   $\{-1\}^a = 1$   for   $a = A_1$,

$$\{-1\}^a = -1 \quad \text{for} \quad a = A_2 \quad \text{or} \quad E_n. \tag{7}$$

*Transformation properties.* *N*-electron wave functions, $|\omega S\Gamma Mm\rangle$, are trans-

formed according to the irreducible representations $\Gamma'$ of the double group* $D'_{\infty h}$; for $\Gamma' = E_{kg,u}$ (the subscripts $g$, $u$ will be ommitted in further text) or $E'_k$ ($k = 1, 2, \ldots$) is $m' = \pm 1$, for $\Gamma' = A_1$ or $A_2$ is $m' = 0$. To find the transformation properties of these functions, use can be made of the fact that only the following operators enter among the transformation operators $g$ of the group $D'_{\infty h}$:

$$C_\varphi(z), \ C'_2(\xi_\gamma), \ I, \ \sigma_h, \ \sigma_d(\xi_\gamma), \ S_\varphi(z), \ R \ . \tag{8}$$

TABLE I

$N$-Electron Wave Functions $|a^N \ S\Gamma M \ m\rangle$ in Complex Region

| Configuration | Function |
|---|---|
| $e^1_{2g}$ | $|{}^2E_{2g} \tfrac{1}{2} \ \ 1\rangle = -i|2 \ 2^+\rangle \equiv |u^+\rangle$ |
| | $|{}^2E_{2g} \tfrac{1}{2} -1\rangle = \ \ i|2 -2^+\rangle \equiv |v^+\rangle$ |
| $e^2_{2g}$ | $|{}^3A_{2g} \ 1 \ \ \ 0\rangle = \ \ i|2^+ -2^+| \equiv i|u^+ \ v^+|$ |
| | $|{}^1A_{1g} \ 0 \ \ \ 0\rangle = \sqrt{(1/2)}\{|2^+ -2^-| - |2^- -2^+|\} \equiv \sqrt{(1/2)}\{|u^+ \ v^-| - |u^- \ v^+|\}$ |
| | $|{}^1E_{4g} \ 0 \ \ \ 1\rangle = -i|2^+ \ 2^-| \equiv i|u^+ \ u^-|$ |
| | $|{}^1E_{4g} \ 0 -1\rangle = \ \ i|-2^+ -2^-| \equiv -i|v^+ \ v^-|$ |
| $e^3_{2g}$ | $|{}^2E_{2g} \tfrac{1}{2} \ \ 1\rangle = \ \ i|2^+ \ 2^- -2^+| \equiv -|u^+ \ u^- \ v^+|$ |
| | $|{}^2E_{2g} \tfrac{1}{2} -1\rangle = -i|2^+ -2^+ -2^-| \equiv -|u^+ \ v^+ \ v^-|$ |
| $e^4_{2g}$ | $|{}^1A_{1g} \ 0 \ \ \ 0\rangle = -|2^+ \ 2^- -2^+ -2^-| \equiv -|u^+ \ u^- \ v^+ \ v^-|$ |
| $a^1_{1g}$ | $|{}^1A_{1g} \tfrac{1}{2} \ \ 0\rangle = \ \ \ |2 \ 0^+\rangle \equiv |a^+\rangle$ |
| $a^2_{1g}$ | $|{}^2A_{1g} \ 0 \ \ \ 0\rangle = \ \ \ |0^+ \ 0^-| \equiv |a^+ \ a^-|$ |
| $e^1_{1g}$ | $|{}^2E_{1g} \tfrac{1}{2} \ \ 1\rangle = \ \ i|2 \ 1^+\rangle \equiv |p^+\rangle$ |
| | $|{}^2E_{1g} \tfrac{1}{2} -1\rangle = \ \ i|2 -1^+\rangle \equiv |q^+\rangle$ |
| $e^2_{1g}$ | $|{}^3A_{2g} \ 1 \ \ \ 0\rangle = -i|1^+ -1^+| \equiv i|p^+ \ q^+|$ |
| | $|{}^1A_{1g} \ 0 \ \ \ 0\rangle = \sqrt{(1/2)}\{|1^- -1^+| - |1^+ -1^-|\} \equiv \sqrt{(1/2)}\{|p^+ \ q^-| - |p^- \ q^+|\}$ |
| | $|{}^1E_{2g} \ 0 \ \ \ 1\rangle = -i|1^+ \ 1^-| \equiv i|p^+ \ p^-|$ |
| | $|{}^1E_{2g} \ 0 -1\rangle = \ \ i|-1^+ -1^-| \equiv -i|q^+ \ q^-|$ |
| $e^3_{1g}$ | $|{}^2E_{1g} \tfrac{1}{2} \ \ 1\rangle = \ \ i|1^+ \ 1^- -1^+| \equiv -|p^+ \ p^- \ q^+|$ |
| | $|{}^2E_{1g} \tfrac{1}{2} -1\rangle = \ \ i|1^+ -1^+ -1^-| \equiv -|p^+ \ q^+ \ q^-|$ |
| $e^4_{1g}$ | $|{}^1A_{1g} \ 0 \ \ \ 0\rangle = -|1^+ \ 1^- -1^+ -1^-| \equiv -|p^+ \ p^- \ q^+ \ q^-|$ |

* Since characters of this group are not tabulated in the available literature, we calculated such a table (see Appendix).

Here $\gamma$ denotes the angle between the unit vector $\xi_\gamma$, through which the rotation axis $C_2'$ or plane $\sigma_d$ passes, and the $x$ axis. As a result of these operators acting on the position vector $\boldsymbol{r}$, its spherical coordinates $\Theta$ and $\Phi$ change according to the scheme given in Table II (second and third row). If the functions $I_\Phi(g)$, $I_\Theta(g)$, and $I_R(g)$ are defined according to Table II (4−6th row), the action of the operators (8) in the spin and coordinate spaces on the $N$-electron wave function $|\omega S\Gamma Mm\rangle$ can be expressed by the general formula (the argument $g$ is omitted for simplicity):

$$\boldsymbol{g}|\omega S\Gamma Mm\rangle = (I_R)^N (I_\Theta)^{M+k_\Gamma} \{I_\Phi\}^{N-S+M+\Gamma}.$$

$$\exp\left\{-i[I_\Phi(M + k_\Gamma m)]\,\Delta\Phi\right\}\big|\,\omega S\Gamma(I_\Phi M)(I_\Phi m)\rangle. \tag{9}$$

Here $\Delta\Phi = \Phi' - I_\Phi(g)\,\Phi$, $\Phi'$ is the spherical coordinate of the position vector $\boldsymbol{r}$ after transformation (Table II, second row), $k_\Gamma = 0$ for $\Gamma = A_1$ or $A_2$, and $k_\Gamma = k$ for $\Gamma = E_{kg}\,(k = 1, 2, \ldots)$. In the special case $\Gamma = A_{1g}\,(m = 0)$, Eq. (9) gives the transformation properties of pure spin functions. The transformation properties of functions in the coordinate space only are given by the equation

$$\boldsymbol{g}|\omega S\Gamma Mm\rangle = (I_\Theta)^{k_\Gamma} \{I_\Phi\}^\Gamma \exp\left\{-iI_\Phi(k_\Gamma m)\,\Delta\Phi\right\}|\omega S\Gamma M(I_\Phi m)\rangle. \tag{10}$$

In the derivation of Eqs (9) and (10), use was made of the properties (6) of the coupling coefficients. The number of electrons, $N$, does not occur explicitly in (10) since the functions (4) are even. In the explicit formulation, Eqs (9) and (10) would involve the factor $(I_\Theta)^{Nl}$, where $l$ is the azimuthal quantum number.

From the known transformation properties of the functions $|\omega S\Gamma Mm\rangle$ we can easily find their linear combinations that are transformed according to the standard representation of the group $D'_{\infty h}$ (see Appendix). From the comparison of the trans-

TABLE II

Definition of Functions $I_\Phi(g)$, $I_\Theta(g)$, $I_R(g)$ and Change of Spherical Coordinates $\Phi$ and $\Theta$ of the Position Vector $\boldsymbol{r}$

| | $R$ | $C_\varphi(z)$ | $C_2'(\xi_\gamma)$ | $I$ | $\sigma_h$ | $\sigma_d(\xi_\gamma)$ | $S_\varphi(z)$ |
|---|---|---|---|---|---|---|---|
| $\Phi \to \Phi' =$ | $\Phi$ | $\Phi + \varphi$ | $2\gamma - \Phi$ | $\Phi + \pi$ | $\Phi$ | $2\gamma - \Phi$ | $\Phi + \varphi$ |
| $\Theta \to \Theta' =$ | $\Theta$ | $\Theta$ | $\pi - \Theta$ | $\pi - \Theta$ | $\pi - \Theta$ | $\Theta$ | $\pi - \Theta$ |
| $I_\Phi \quad =$ | $1$ | $1$ | $-1$ | $1$ | $1$ | $-1$ | $1$ |
| $I_\Theta \quad =$ | $1$ | $1$ | $-1$ | $-1$ | $-1$ | $1$ | $-1$ |
| $I_R \quad =$ | $-1$ | $1$ | $1$ | $1$ | $-1$ | $1$ | $-1$ |

formed functions $|\Psi_1\rangle = |\omega SE_k Mm\rangle$ and $|\Psi_2\rangle = |\omega SE_k - M - m\rangle$ with the definition of the standard base of the group $D'_{\infty h}$ follows:

If $M$ is a whole number (*i.e.*, $N$ even) and $M + km > 0$, then the standard base of the irreducible representation $E_{1g}$ of the group $D'_{\infty h}$, where $l = M + km$, is formed by the functions $\Psi_1$ and $\Psi_2$ for $S - M$ even, and by $\Psi_1$ and $-\Psi_2$ for $S - M$ odd.

If $M$ is a whole number and $M + km = 0$, then the bases of the irreducible representation $A_{1g}$ and $A_{2g}$ of the group $D'_h$ are formed, respectively, by the functions

$$|A_{1g} 0\rangle = \frac{1}{\sqrt{2}}\left\{|\Psi_1\rangle + (-1)^{1-S-M}|\Psi_2\rangle\right\},$$

$$|A_{2g} 0\rangle = \frac{1}{\sqrt{2}}\left\{|\Psi_1\rangle - (-1)^{1-S-M}|\Psi_2\rangle\right\}.$$

If $M$ is a half integer (*i.e.*, $N$ odd) and $M + km > 0$, the standard base of the irreducible representation $E'_{1g}$ of the group $D'_{\infty h}$, where $1 = M + km + \frac{1}{2}$, is formed by the functions $\Psi_1$ and $\Psi_2$ for $S - M$ odd, and by $\Psi_1$ and $-\Psi_2$ for $S - M$ even.

Analogously, for the functions $|\Phi_0\rangle = |\omega SA_k 0\, 0\rangle$, $|\Phi_1\rangle = |\omega SA_k M\, 0\rangle$ and $|\Phi_2\rangle = |\omega SA_k - M\, 0\rangle$ $(k = 1, 2; M > 0)$ it follows:

If $M$ is a whole number, then the standard base $E_{1g}$, where $1 = M$, is formed by the functions $\Phi_1$ and $\Phi_2$ for $S - M$ even, and by $\Phi_1$ and $-\Phi_2$ for $S - M$ odd. $\Phi_0$ forms the base $A_{1g}$ if $k + 1 - S$ is even, and the base $A_{2g}$ if $k + 1 - S$ is odd.

If $M$ is a positive half integer, then the standard base $E'_{1g}$, where $1 = M + \frac{1}{2}$, is formed by the functions $\Phi_1$ and $\Phi_2$ for $S - M$ odd, and by $\Phi_1$ and $-\Phi_2$ for $S - M$ even.

*Kramers conjugation.* A special and important case of the transformation of the functions $|\omega S\Gamma Mm\rangle$ is the transformation at the Kramers' (complex) conjugation. From the properties (6) of the coupling coefficients $\langle abij \mid ck\rangle$ and the properties of the Wigner (Clebsch–Gordan) coefficients $\langle S_1 S_2 M_1 M_2 \mid SM\rangle$ it is possible to derive the following equations for the functions $|\omega S\Gamma Mm\rangle$:

$$|\omega S\Gamma Mm\rangle^* = (-1)^{1/2N-S+M}|\omega S\Gamma - M - m\rangle,$$

$$\langle\omega S\Gamma Mm|^* = (-1)^{1/2N-S-M}\langle\omega S\Gamma - M - m|. \tag{11}$$

*Particles and holes.* For the particular calculations it is advantageous to know how the expressions for the matrix elements of the one-electron operators and of the electron repulsion operator change on passing from the $d^N$ to the $d^{10-N}$ electron system. According to ref.[2], p. 245–256, we can generalize the formulas derived for the coupling of two configurations ($t_2^n$ and $e^m$ configurations) to obtain formulas for the coupling of three configurations ($e_2^{n_2}$, $a_1^{n_0}$, and $e_1^{n_1}$ configurations).

The relations between the wave functions in the $R$ and $L$ states can be expressed with the aid of the functions $\mu_1(n_1 S_1 \Gamma_1)$ and $\mu_2(n_2 S_2 \Gamma_2)$ as follows:

$$\left| e_2^{n_2}(S_2\Gamma_2)\, a_1^{n_0}(S_0\Gamma_0)\, e_1^{n_1}(S_1\Gamma_1)\, S\Gamma Mm \right\rangle_R = (-1)^{n_2 n_0 + n_2 n_1 + n_0 n_1}\, \mu_2(n_2 S_2 \Gamma_2)$$

$$\mu_1(n_1 S_1 \Gamma_1)\, \left| e_2^{n_2}(S_2\Gamma_2)\, a_1^{n_0}(S_0\Gamma_0)\, e_1^{n_1}(S_1\Gamma_1)\, S\Gamma Mm \right\rangle_L . \tag{12}$$

Here $\mu_i(n_i S_i \Gamma_i) = -1$ for $S_i \Gamma_i = {}^3A_2, {}^1E_2;$ and $n_i = 2$, otherwise $\mu_i = 1$ $(i = 1, 2)$.

For the matrix elements of the one-electron Hermitean operators **U**, formulas can be derived which bind the matrix elements corresponding to $N$-electron wave functions in $L$ states with those corresponding to $(10\text{-}N)$-electron wave functions in $R$ states. Since the wave functions in Table I. and the general wave functions formed from them are $L$ functions, we rewrite the corresponding formulas using Eq. $(12)$ directly for $L$ states:

$$\left\langle n_2 n_0 n_1 \right| \mathbf{U} \left| n_2' n_0' n_1' \right\rangle = -\eta(-1)^{n_2 n_0 + n_2 n_1 + n_0 n_1 + n'_2 n'_0 + n'_2 n'_1 + n'_0 n'_1}\, \mu_2(n_2 S_2 \Gamma_2)$$

$$\mu_2(n_2' S_2' \Gamma_2')\, \mu_1(n_1 S_1 \Gamma_1)\, \mu_1(n_1' S_1' \Gamma_1') .$$

$$. \left\langle 4 - n_2,\, 2 - n_0,\, 4 - n_1 \right| \mathbf{U} \left| 4 - n_2',\, 2 - n_0',\, 4 - n_1' \right\rangle \tag{13}$$

for nondiagonal elements, and

$$\left\langle n_2 n_0 n_1 \right| \mathbf{U} \left| n_2 n_0 n_1 \right\rangle = C - \eta \left\langle 4 - n_2,\, 2 - n_0,\, 4 - n_1 \right| \mathbf{U} \left| 4 - n_2, \right.$$

$$\left. 2 - n_0,\, 4 - n_1 \right\rangle \tag{14}$$

for diagonal elements. Here

$$\left| xyz \right\rangle = \left| e_2^x(S_2\Gamma_2)\, a_1^y(S_0\Gamma_0)\, e_1^z(S_1\Gamma_1)\, S\Gamma Mm \right\rangle_L \tag{15}$$

and analogously for the primed functions; $\eta = \pm 1$ according to whether the Hermitean operator **U** changes its sign in the complex conjugation

$$\mathbf{U}\dagger = \mathbf{U} = \eta \mathbf{U}^* . \tag{16}$$

Hence $\eta = 1$ for $\mathbf{U} = \mathbf{V}_{AX}$ and $\mathbf{U} = \mathscr{H}_{so}$, $\eta = -1$ for the operator **L** and **S**. $C$ is a constant independent of the functions $\left| n_2 n_0 n_1 \right\rangle$. For $\mathbf{U} = \mathscr{H}_{so}$ is $C = 0$ so that the diagonal matrix elements of the spin–orbit interaction are zero among the wave functions corresponding to the configuration $(e_2^2 a_1^1 e_1^2)$.

It was proved by Griffith[2] (p. 256) for the electron repulsion matrix elements that

a) the nondiagonal matrix elements of a $(10\text{-}N)$ electron system in the $R$ state

are equal to the corresponding nondiagonal matrix elements of an $N$-electron system in the $L$ state,

*b*) the diagonal matrix elements in these states can differ only by a constant which is in the approximation of "pure" d functions the same for all configurations in the given $N$-electron system.

These conclusions remain valid also in the case of axial symmetry; the passage from the matrix elements in the $R$ state to those in the $L$ state can be easily performed according to Eq. *(12)*.

It should be noted that the above conclusions as to the relations between the particles and holes are valid both for the complex and real coordinate systems, *i.e.*, for $m = \pm 1$, 0 and for $m = c$, $s$, $\iota$ independent of the way of coupling of the quantum states $S_2 \Gamma_2$, $S_0 \Gamma_0$ and $S_1 \Gamma_1$.

MATRIX ELEMENTS

The application of the Wigner–Eckart theoreme[5,35–39] to the operators $\mathscr{H}_{so}$ and $\mathscr{H}_1$ requires that the operators of which they are composed have the correct transformation properties. It follows from the transformation properties of the operator of the angular momentum, $\mathbf{l}$, that the following operators are transformed according to the standard representation of the group $D'_{\infty h}$:

$$\mathbf{l}_1^{E_1} = -\frac{1}{\sqrt{2}}\,\mathbf{l}^+\,, \quad \mathbf{l}_{-1}^{E_1} = -\frac{1}{\sqrt{2}}\,\mathbf{l}^-\,, \quad \mathbf{l}_0^{A_2} = i\mathbf{l}_z\,. \tag{17}$$

These can be treated by the formalism using the Wigner–Eckart theoreme generalized for point group[2,3,5,7]. As far as the spin operator $\mathbf{s}$ is concerned, it is preferable to make use of its properties as of an irreducible tensor operator of the order one[3,5,35–39] rather than to define the operator $\mathbf{s}_i^{\Gamma}$:

$$\mathbf{s}_1^{(1)} = -\frac{1}{\sqrt{2}}\,\mathbf{s}^+\,, \quad \mathbf{s}_{-1}^{(1)} = \frac{1}{\sqrt{2}}\,\mathbf{s}^-\,, \quad \mathbf{s}_0^{(1)} = \mathbf{s}_z\,. \tag{18}$$

We shall further define the operators $\mathbf{V}$ as*

$$\mathbf{V}_{00}(1A_2) \;\; = \sum_{i=1}^{N} \xi(r_i)\,\mathbf{s}_0^{(1)}(i)\,\mathbf{l}_0^{A_2}(i)\,,$$

$$\mathbf{V}_{1\,-1}(1E_1) = \sum_{i=1}^{N} \xi(r_i)\,\mathbf{s}_1^{(1)}(i)\,\mathbf{l}_{-1}^{E_1}(i)\,,$$

$$\mathbf{V}_{-1\,1}(1E_1) = \sum_{i=1}^{N} \xi(r_i)\,\mathbf{s}_{-1}^{(1)}(i)\,\mathbf{l}_1^{E_1}(i)\,, \tag{19}$$

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*      In the case $N = 1$ the symbol $\mathbf{V}$ will be replaced by $\mathbf{v}$.

so that

$$\mathscr{H}_{s0} = (-i)\,\mathbf{V}_{00}(1A_2) - \mathbf{V}_{-1\,1}(1E_1) + \mathbf{V}_{1\,-1}(1E_1)\,. \qquad (20)$$

From this and the condition of invariance of the reduced matrix elements follows the expression for the matrix elements of the operator $\mathscr{H}_{s0}$:

$$\langle\omega S\Gamma M i|\,\mathscr{H}_{s0}|\omega' S'\Gamma' M'j\rangle = (-1)^{S-M}\left\{(-i)\begin{pmatrix} S & 1 & S' \\ -M & 0 & M' \end{pmatrix} V\begin{pmatrix} \Gamma & \Gamma' & A_2 \\ -i & j & 0 \end{pmatrix}\cdot\right.$$

$$\langle\omega S\Gamma \parallel \mathbf{V}(1A_2) \parallel \omega' S'\Gamma'\rangle + \langle\omega S\Gamma \parallel \mathbf{V}(1E_1) \parallel \omega' S'\Gamma'\rangle\,.$$

$$\left[-\begin{pmatrix} S & 1 & S' \\ -M & -1 & M' \end{pmatrix}\mathbf{V}\begin{pmatrix} \Gamma & \Gamma' & E_1 \\ -i & j & 1 \end{pmatrix} + \begin{pmatrix} S & 1 & S' \\ -M & 1 & M' \end{pmatrix}V\begin{pmatrix} \Gamma & \Gamma' & E_1 \\ -i & j & -1 \end{pmatrix}\right]\right\}\,. \qquad (21)$$

With the aid of Eq. $(11)$ we obtain

$$\langle\omega' S'\Gamma' \parallel \mathbf{V}(1\bar\Gamma) \parallel \omega S\Gamma\rangle = (-1)^{S'-S+1+\Gamma+\Gamma'+\bar\Gamma}\,\langle\omega S\Gamma \parallel \mathbf{V}(1\bar\Gamma) \parallel \omega' S'\Gamma'\rangle\,, \qquad (22)$$

where $\bar\Gamma = A_2, E_1$. The calculated nonzero reduced matrix elements of the operators $(19)$ for $N = 1$ and 2 are given in Tables III and IV; the remaining ones are calculated according to Eq. $(22)$.

Analogously, the operator $\mathscr{H}_1$ can be rewritten as

$$\mathscr{H}_1 = \beta\left\{2H_z\mathbf{S}_z + H^+\mathbf{S}^- + H^-\mathbf{S}^+ - \left[iH_z\mathbf{L}_0^{A_2} + \frac{1}{\sqrt{2}}\left(H^+\mathbf{L}_{-1}^{E_1} + H^-\mathbf{L}_1^{E_1}\right)\right]\right\}\,. \qquad (23)$$

For the reduced matrix elements of the operator $\mathbf{l}_i^\Gamma$ we have

$$\langle a \parallel \mathbf{l}^\Gamma \parallel b\rangle = \sqrt{2/3}\,k_{ab}\zeta_{ab}^{-1}\,\langle\tfrac{1}{2}a \parallel \mathbf{v}(1\Gamma) \parallel \tfrac{1}{2}b\rangle\,, \qquad (24)$$

where $k_{ab}$ are the so-called reduction factors $(\text{ref.}^2, \text{p. 284})$ corresponding to the configuration $ab$, and $\zeta_{ab}$ is given in Table III. The reduced matrix elements of the operator of the total angular momentum, $\mathbf{L}_i^\Gamma$, for $N = 2$ are given in Table V. The remaining nonzero reduced elements are calculated as

$$\langle\omega' S'\Gamma' \parallel \mathbf{L}^\Gamma \parallel \omega S\Gamma\rangle = (-1)^{\Gamma+\Gamma'+\bar\Gamma+1}\,\langle\omega S\Gamma \parallel \mathbf{L}^\Gamma \parallel \omega' S'\Gamma'\rangle\,. \qquad (25)$$

TABLE III

Reduced Matrix Elements[a] $\left\langle \tfrac{1}{2}a \,\|\, \mathbf{v}(1\varGamma) \,\|\, \tfrac{1}{2}b \right\rangle$

$$\left\langle \tfrac{1}{2}e_2 \,\|\, \mathbf{v}(1A_2) \,\|\, \tfrac{1}{2}e_2 \right\rangle = 2\sqrt{3}\,\zeta_{22}, \quad \left\langle \tfrac{1}{2}e_1 \,\|\, \mathbf{v}(1A_2) \,\|\, \tfrac{1}{2}e_1 \right\rangle = \sqrt{3}\,\zeta_{11}$$

$$\left\langle \tfrac{1}{2}e_1 \,\|\, \mathbf{v}(1E_1) \,\|\, \tfrac{1}{2}e_2 \right\rangle = -\mathrm{i}\sqrt{6}\,\zeta_{12}, \quad \left\langle \tfrac{1}{2}e_1 \,\|\, \mathbf{v}(1E_1) \,\|\, \tfrac{1}{2}a_1 \right\rangle = 3\mathrm{i}\,\zeta_{10}$$

[a] $\zeta_{ab}$ represents the integral of the radial parts of the functions $|a\,m_a\rangle$, $|b\,m_b\rangle$ and function $\xi(r)\,h^2$ .
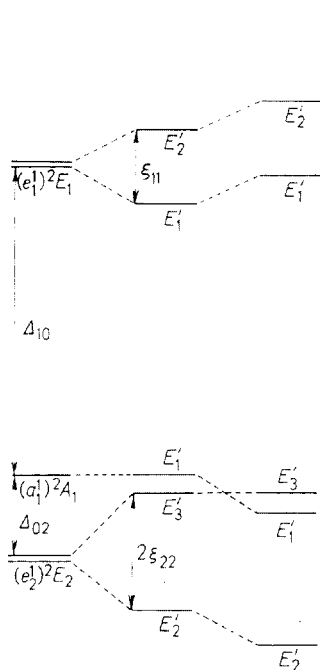


FIG. 1

Energy Levels of a $d^1$-Electron System in the Field $D_{\infty h}$
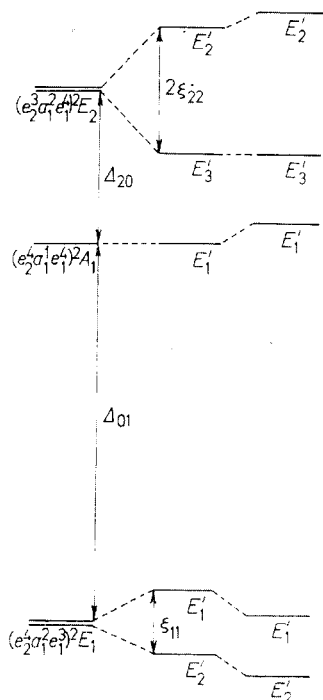
FIG. 2

Energy Levels of a $d^9$-Electron System in the Field $D_{\infty h}$

The matrix elements of the operators $\mathscr{H}_0$ and $\mathscr{H}_1$ for $N = 1$ and 2 were calculated according to Eq. $(21)$ and an analogous one for $\mathscr{H}_1$ with the use of Tables III – V, tabulated 3-$j$ coefficients[40] and $V$ coefficients[3]. For $N = 8$ and 9, the matrix elements

* The matrix elements of the electron repulsion operator are for $N = 8$ given in ref.[14]. To avoid a discrepancy in phases, the sign of the matrix element $(3\mid 6) = (4\mid 5)$ was changed.

were obtained from Eqs $(13)$ and $(14)^*$. The results of the calculations with the operator $\mathcal{H}_0$ are shown schematically in Figs 1–4; in Figs 3 and 4 only several lowest energy levels are indicated. In the left part of these figures, the influence of the ligand field without the spin–orbit interaction is visualized, in the center and in the right part with consideration of this interaction in the first and higher-order terms of the perturbation theory. The energy levels are indicated only schematically, without a scale, and the index $g$ with the level symbols was omitted. In the first approximation of the perturbation theory, we have $\Delta_{02} = \Delta_{20} = 4Ds - 5Dt$, $\Delta_{10} = \Delta_{01} = = -Ds + 10Dt$, $\Delta = -\Delta_{02} + 12B$, $\delta = 4C$, and $d = 6B + 2C$.

### MAGNETIC SUSCEPTIBILITY

To determine the relative order of the energy levels, it is necessary to know all parameter values on which this energy depends. Usually the general parameters of the electron repulsion[2,5] are reduced to three Racah parameters $A$, $B$, $C$, and the general parameters of the spin–orbit interaction[2,3,5] to one, $\zeta$. Their values (except for those expressing a part of the energy level shift that is for all levels the same) are deter-
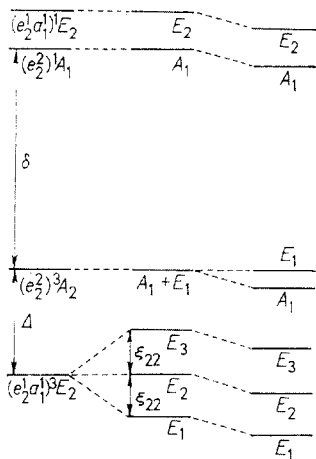


FIG. 3

Energy Levels of a $d^2$-Electron System in the Field $D_{\infty h}$
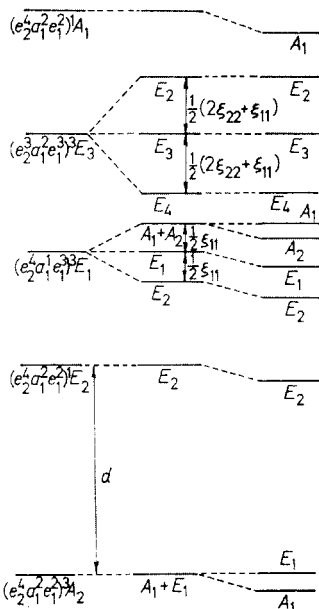Only several lowest levels are shown.

FIG. 4

Energy Levels of a $d^8$-Electron System in the Field $D_{\infty h}$
Only several lowest levels are shown.

mined together with the ligand field parameters from the absorption spectra of the corresponding compounds.

An independent criterion for the correctness of the chosen assignment and certain calculated parameter values is the measurement of the magnetic susceptibility and comparison of the experimental curve of the effective magnetic moment with the theoretical one. Expressions for the magnetic susceptibility for individual $N$ values can be obtained from the knowledge of the matrix elements of the operators $\mathscr{H}_0$ and $\mathscr{H}_1$ by the known procedure[1,2,4].*

$N = 1$. According to Fig. 1, the ground level of $d^1$ sandwich complexes is the $^2E_{2g}$ level, closely above which is the $^2A_{1g}$ level. If the interaction of the spin–orbit $E'_2$ levels corresponding to the $^2E_{2g}$ and $^1E_{1g}$ terms is neglected, the following formulas are obtained for the $\mu_{\parallel}^2$ and $\mu_{\perp}^2$ components of the effective magnetic moment $\mu_{\text{eff}}^2 = = (\mu_{\parallel}^2 + 2\mu_{\perp}^2)/3$ of the ground level $^2E_{2g}$ :

$$\mu_{\parallel}^2 = 3(e^x + 9e^{-x})/(e^x + e^{-x}), \quad \mu_{\perp}^2 = 3(e^x - e^{-x})/(xe^x + xe^{-x}), \qquad (26)$$

where $x = \zeta_{22}/kT$. Assuming that the near levels $^2E_{2g}$ and $^2A_{1g}$ contribute to the magnetic susceptibility, we can write

$$\mu_{\parallel}^2 = 3(e^x + 9e^{-x} + e^{-Cx})/(e^x + e^{-x} + e^{-Cx}),$$

$$\mu_{\perp}^2 = 3(e^x - e^{-x})/x(e^x + e^{-x} + e^{-Cx}), \qquad (27)$$

where $C = \Delta_{02}/\zeta_{22}$ and $\Delta_{02} = E(a_{1g}) - E(e_{2g})$. From these equations it follows that $\mu_{\parallel}^2$ and $\mu_{\perp}^2$ increase with increasing $C$ and approach the values from Eqs (26).

The dependence of $\mu_{\parallel}$, $\mu_{\perp}$, and $\mu_{\text{eff}}$ on $1/x = kT/\zeta_{22}$ is shown in Fig. 5. The case $C = 0$ corresponds to degeneration of the $^2A_{1g}$ and $^2E_{2g}$ levels. According to a rough estimate based on the values of $Ds$ and $Dt$ found for nickelocene[14], vanadocene[16], and ferrocene[29], and on the spin-orbital parameter $\zeta$ for Ni(II), V(II), and Fe(II) (ref.[2], p. 437), the parameter $C$ should be in the interval $(5,50)$. However, as can be seen from Fig. 5, the curves calculated from Eqs (26) and (27) in the interval $0 \leqq \leqq 1/x \leqq 3$ for $C$ as small as 5 practically coincide, so that the contribution of the $^2A_{1g}$ level to the total susceptibility for $C \geqq 5$ is in this interval very small.

According to Wilkinson and Birmingham[41], the cations $Ti(C_5H_5)_2^+$ and $V(C_5H_5)^{2+}$ belong to $d^1$ metallocenes. The measurement of the magnetic susceptibility of the former in the form of picrate yields[41] the value of 2·30 BM for its effective magnetic moment at 298 K, and in the case of $[V(C_5H_5)_2]Cl_2$ 1·85 BM. For the $Ti^{3+}$ and $V^{4+}$

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*      In all cases discussed below, it was assumed that the influence of the Jahn–Teller effect on the orbitally degenerated ground states is negligibly small, and the reduction factors $k_{ab}$ were set equal to one.

ions, the values of $\zeta$ are given[2] as 150 and 250 cm$^{-1}$, respectively. The decreasing of $\zeta$-value by complex formation suggests rough estimates of $\zeta(Ti^{3+}) \approx 100$ cm$^{-1}$ and $\zeta(V^{4+}) \approx 200$ cm$^{-1}$ leading to $x \approx 0.5$ and $x \approx 1$. Introducing these values in Eqs (26) we obtain $\mu_{eff} = 2.24$ BM and $1.86$ BM, respectively. Although the agreement with the experimental values is good, it would be necessary to compare
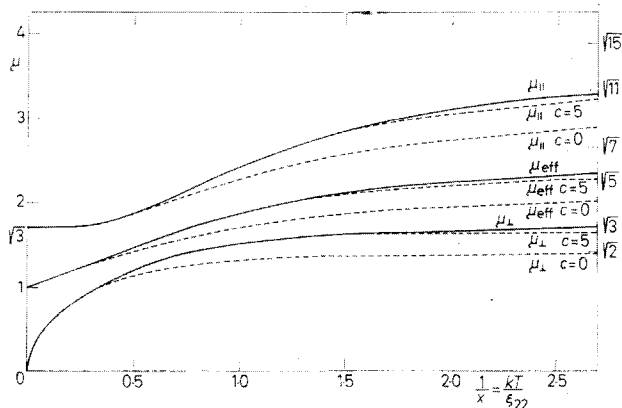


FIG. 5

Dependence of Magnetic Moment $\mu_{eff}$, $\mu_{\parallel}$ and $\mu_{\perp}$ for a $d^1$-Electron System in the Field $D_{\infty h}$ on $1/x = kT/\zeta_{22}$ and $C = \Delta_{02}/\zeta_{22}$
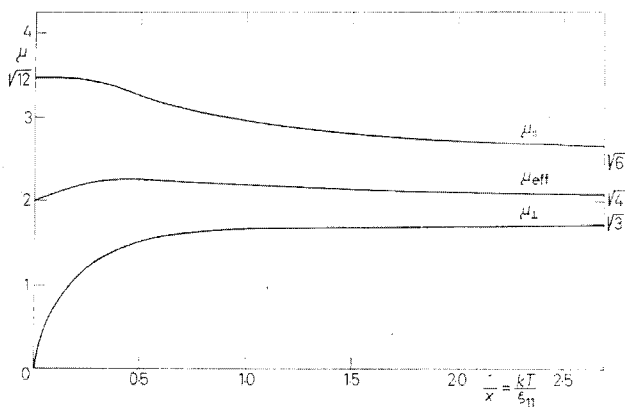Limiting values for different $\mu$ are given on ordinates.



FIG. 6

Dependence of Magnetic Moment $\mu_{eff}$, $\mu_{\parallel}$ and $\mu_{\perp}$ for a $d^9$-Electron System in the Field $D_{\infty h}$ on $1/x = kT/\zeta_{11}$

TABLE IV

Nonzero Reduced Matrix Elements of the Operator $\mathbf{V}$ for a $d^2$-Electron System[a]

$$\langle (e_2^2)\,^3A_2 \| \mathbf{V}(1A_2)\| (e_2^2)\,^1A_1 \rangle \quad = v_{22}$$

$$\langle (e_1^2)\,^3A_2 \| \mathbf{V}(1A_2)\| (e_1^2)\,^1A_1 \rangle \quad = v_{11}$$

$$\langle (e_2 e_1)\,^3E_1 \| \mathbf{V}(1A_2)\| (e_2 e_1)\,^3E_1 \rangle = v_{22} - v_{11}$$

$$\langle (e_2 e_1)\,^3E_1 \| \mathbf{V}(1A_2)\| (e_2 e_1)\,^1E_1 \rangle = (v_{22} + v_{11})/\sqrt{2}$$

$$\langle (e_2 e_1)\,^3E_3 \| \mathbf{V}(1A_2)\| (e_2 e_1)\,^3E_3 \rangle = v_{22} + v_{11}$$

$$\langle (e_2 e_1)\,^3E_3 \| \mathbf{V}(1A_2)\| (e_2 e_1)\,^1E_3 \rangle = (v_{22} - v_{11})/\sqrt{2}$$

$$\langle (e_2 a_1)\,^3E_2 \| \mathbf{V}(1A_2)\| (e_2 a_1)\,^3E_2 \rangle = v_{22}$$

$$\langle (e_2 a_1)\,^3E_2 \| \mathbf{V}(1A_2)\| (e_2 a_1)\,^1E_2 \rangle = v_{22}/\sqrt{2}$$

$$\langle (a_1 e_1)\,^3E_1 \| \mathbf{V}(1A_2)\| (a_1 e_1)\,^3E_1 \rangle = v_{11}$$

$$\langle (a_1 e_1)\,^3E_1 \| \mathbf{V}(1A_2)\| (a_1 e_1)\,^1E_1 \rangle = -v_{11}/\sqrt{2}$$

$$\langle (e_2 a_1)\,^1E_2 \| \mathbf{V}(1E_1)\| (a_1 e_1)\,^3E_1 \rangle = v_{21}/\sqrt{2}$$

$$\langle (e_2 a_1)\,^3E_2 \| \mathbf{V}(1E_1)\| (a_1 e_1)\,^1E_1 \rangle = v_{21}/\sqrt{2}$$

$$\langle (e_2 a_1)\,^3E_2 \| \mathbf{V}(1E_1)\| (a_1 e_1)\,^3E_1 \rangle = -v_{21}$$

$$\langle (e_2^2)\,^3A_2 \| \mathbf{V}(1E_1)\| (e_2 e_1)\,^1E_1 \rangle \quad = -v_{21}/\sqrt{2}$$

$$\langle (e_2^2)\,^3A_2 \| \mathbf{V}(1E_1)\| (e_2 e_1)\,^3E_1 \rangle \quad = v_{21}$$

$$\langle (e_2^2)\,^1A_1 \| \mathbf{V}(1E_1)\| (e_2 e_1)\,^3E_1 \rangle \quad = v_{21}/\sqrt{2}$$

$$\langle (e_2^2)\,^1E_4 \| \mathbf{V}(1E_1)\| (e_2 e_1)\,^3E_3 \rangle \quad = v_{21}$$

$$\langle (e_2 e_1)\,^1E_1 \| \mathbf{V}(1E_1)\| (e_1^2)\,^3A_2 \rangle \quad = v_{21}/\sqrt{2}$$

$$\langle (e_2 e_1)\,^3E_1 \| \mathbf{V}(1E_1)\| (e_1^2)\,^3A_2 \rangle \quad = -v_{21}$$

$$\langle (e_2 e_1)\,^3E_1 \| \mathbf{V}(1E_1)\| (e_1^2)\,^1A_1 \rangle \quad = v_{21}/\sqrt{2}$$

$$\langle (e_2 e_1)\,^3E_3 \| \mathbf{V}(1E_1)\| (e_1^2)\,^1E_2 \rangle \quad = v_{21}$$

$$\langle (a_1 e_1)\,^3E_1 \| \mathbf{V}(1E_1)\| (a_1^2)\,^1A_1 \rangle \quad = -v_{10}$$

$$\langle (e_1^2)\,^3A_2 \| \mathbf{V}(1E_1)\| (a_1 e_1)\,^1E_1 \rangle \quad = -v_{10}/\sqrt{2}$$

$$\langle (e_1^2)\,^3A_2 \| \mathbf{V}(1E_1)\| (a_1 e_1)\,^3E_1 \rangle \quad = -v_{10}$$

$$\langle (e_1^2)\,^1A_1 \| \mathbf{V}(1E_1)\| (a_1 e_1)\,^3E_1 \rangle \quad = -v_{10}/\sqrt{2}$$

$$\langle (e_1^2)\,^1E_2 \| \mathbf{V}(1E_1)\| (a_1 e_1)\,^3E_1 \rangle \quad = -v_{10}$$

$$\langle (e_2 e_1)\,^1E_1 \| \mathbf{V}(1E_1)\| (e_2 a_1)\,^3E_2 \rangle = v_{10}/\sqrt{2}$$

$$\langle (e_2 e_1)\,^3E_1 \| \mathbf{V}(1E_1)\| (e_2 a_1)\,^1E_2 \rangle = -v_{10}/\sqrt{2}$$

$$\langle (e_2 e_1)\,^3E_1 \| \mathbf{V}(1E_1)\| (e_2 a_1)\,^3E_2 \rangle = v_{10}$$

$$\langle (e_2 e_1)\,^1E_3 \| \mathbf{V}(1E_1)\| (e_2 a_1)\,^3E_2 \rangle = v_{10}/\sqrt{2}$$

$$\langle (e_2 e_1)\,^3E_3 \| \mathbf{V}(1E_1)\| (e_2 a_1)\,^1E_2 \rangle = -v_{10}/\sqrt{2}$$

$$\langle (e_2 e_1)\,^3E_3 \| \mathbf{V}(1E_1)\| (e_2 e_1)\,^3E_2 \rangle = v_{10}$$

[a] $v_{22} = \langle \tfrac{1}{2}e_2 \| \mathbf{v}(1A_2)\| \tfrac{1}{2}e_2 \rangle, \quad v_{11} = \langle \tfrac{1}{2}e_1 \| \mathbf{v}(1A_2)\| \tfrac{1}{2}e_1 \rangle$

$v_{21} = \langle \tfrac{1}{2}e_2 \| \mathbf{v}(1E_1)\| \tfrac{1}{2}e_1 \rangle, \quad v_{10} = \langle \tfrac{1}{2}e_1 \| \mathbf{v}(1E_1)\| \tfrac{1}{2}a_1 \rangle$

the dependence of the magnetic susceptibility on temperature with the functions (26) or (27) before a final judgement could be made.

$N = 9$. The distance of the ground level $^2E_{1g}$ (Fig. 2) from the $^2A_{1g}$ and $^2E_{2g}$ levels enables to arrive at the following simple equations for the magnetic moment components:

$$\mu_\parallel^2 = 12/(1 + e^{-x}), \quad \mu_\perp^2 = 6(1 - e^x)/x(1 + e^{-x}), \qquad (28)$$

where $x = \zeta_{11}/kT$. The dependence of $\mu_\parallel$, $\mu_\perp$, and $\mu_{\mathrm{eff}}$ on temperature is shown in Fig. 6. It is interesting that the magnetic moment is almost independent of tempera-

TABLE V

Nonzero Reduced Matrix Elements of the Operator **L** for a $d^2$-Electron System[a]

$$\langle (e_2^2) E_4 \| \mathbf{L}^{A_2} \| (e_2^2) E_4 \rangle = 2\lambda_{22} = 4\sqrt{2}k_{22}$$
$$\langle (e_1^2) E_2 \| \mathbf{L}^{A_2} \| (e_1^2) E_2 \rangle = 2\lambda_{11} = 2\sqrt{2}k_{11}$$
$$\langle (e_2 e_1) E_1 \| \mathbf{L}^{A_2} \| (e_2 e_1) E_1 \rangle = \lambda_{22} - \lambda_{11}$$
$$\langle (e_2 e_1) E_3 \| \mathbf{L}^{A_2} \| (e_2 e_1) E_3 \rangle = \lambda_{22} + \lambda_{11}$$
$$\langle (e_2 e_1) E_2 \| \mathbf{L}^{A_2} \| (e_2 a_1) E_2 \rangle = \lambda_{22}$$
$$\langle (a_1 e_1) E_1 \| \mathbf{L}^{A_2} \| (a_1 e_1) E_1 \rangle = \lambda_{11}$$

$$\langle (e_2^2) A_1 \| \mathbf{L}^{E_1} \| (e_2 e_1) E_1 \rangle = \lambda_{21} = 2ik_{21}$$
$$\langle (e_2^2) A_2 \| \mathbf{L}^{E_1} \| (e_2 e_1) E_1 \rangle = \lambda_{21}$$
$$\langle (e_2^2) E_4 \| \mathbf{L}^{E_1} \| (e_2 e_1) E_3 \rangle = \sqrt{2}\lambda_{21}$$

$$\langle (e_1^2) A_1 \| \mathbf{L}^{E_1} \| (e_2 e_1) E_1 \rangle = -\lambda_{21}$$
$$\langle (e_1^2) A_2 \| \mathbf{L}^{E_1} \| (e_2 e_1) E_1 \rangle = -\lambda_{21}$$
$$\langle (e_1^2) E_2 \| \mathbf{L}^{E_1} \| (e_2 e_1) E_3 \rangle = -\sqrt{2}\lambda_{21}$$

$$\langle (e_2 a_1) E_2 \| \mathbf{L}^{E_1} \| (a_1 e_1) E_1 \rangle = -\lambda_{21}$$

$$\langle (a_1 e_1) E_1 \| \mathbf{L}^{E_1} \| (e_1^2) A_1 \rangle = \lambda_{01} = -i\sqrt{6}k_{01}$$
$$\langle (a_1 e_1) E_1 \| \mathbf{L}^{E_1} \| (e_1^2) A_2 \rangle = \lambda_{01}$$
$$\langle (a_1 e_1) E_1 \| \mathbf{L}^{E_1} \| (e_1^2) E_2 \rangle = \sqrt{2}\lambda_{01}$$

$$\langle (a_1^2) A_1 \| \mathbf{L}^{E_1} \| (a_1 e_1) E_1 \rangle = \sqrt{2}\lambda_{01}$$

$$\langle (e_2 a_1) E_2 \| \mathbf{L}^{E_1} \| (e_2 e_1) E_1 \rangle = \lambda_{01}$$
$$\langle (e_2 a_1) E_2 \| \mathbf{L}^{E_1} \| (e_2 e_1) E_3 \rangle = \lambda_{01}$$

[a] $\lambda_{22} = \langle e_2 \| \mathbf{I}^{A_2} \| e_2 \rangle$, $\quad \lambda_{11} = \langle e_1 \| \mathbf{I}^{A_2} \| e_1 \rangle$,
$\lambda_{21} = \langle e_2 \| \mathbf{I}^{E_1} \| e_1 \rangle$, $\quad \lambda_{01} = \langle a_1 \| \mathbf{I}^{E_1} \| e_1 \rangle$.

ture range, its value $(\approx 2\ \text{BM})$ exceeding somewhat the pure spin value $(1\cdot73\ \text{BM})$. $N = 2$. The situation is more complicated with $d^2$ sandwich complexes, for which the Tanabe–Sugano's diagrams[13] indicate that the ground level of these compounds is according to the values of $Ds/B$ and $Dt/B$ either the $^3E_{2g}$ or $^3A_{2g}$ level. If the lowest one is $^3A_{2g}$, then the magnetic susceptibility is in the given approximation expressed by the "spin only" formula. In the case of the $^3E_{2g}$ ground term the components of the magnetic moment are given by the equations

$$\mu_\parallel^2 = 12(1 + 4e^{-x})/(1 + e^x + e^{-x}), \quad \mu_\perp^2 = 12(e^x - e^{-x})/x(1 + e^x + e^{-x}),$$
$$(29)$$

where $x = \zeta_{22}/kT$. If both $^3A_{2g}$ and $^3E_{2g}$ levels contribute to the magnetic moment, Eq. $(29)$ takes the form

$$\mu_\parallel^2 = 12(1 + 4e^{-x} + e^{-Cx})/(1 + e^x + e^{-x} + \tfrac{3}{2}e^{-Cx}),$$
$$\mu_\perp^2 = 12(e^x - e^{-x} + xe^{-Cx})/x(1 + e^x + e^{-x} + \tfrac{3}{2}e^{-Cx}), \quad (30)$$

where $C = \Delta/\zeta_{22}$ $(\Delta = E(^3A_{2g}) - E(^3E_{2g}))$. In the approximation neglecting the interaction of two $^3A_{2g}$ terms we have $\Delta = -\Delta_{02} + 12B$. If this interaction is taken into account then the function of the ground state is given as $|^3A_{2g}Mm\rangle = a|(e_2^2)$. $.^3A_{2g}Mm\rangle + b|(e_1^2)\,^3A_{2g}Mm\rangle$, where $a^2 + b^2 = 1$. From Tables IV and V and from the exclusion principles for **S** then follows that the matrix elements of the
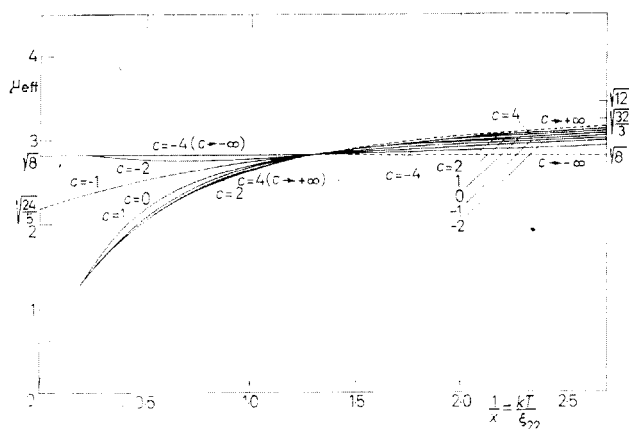


FIG. 7

Dependence of Effective Magnetic Moment $\mu_{\text{eff}}$ for a $d^2$-Electron System in the Field $D_{\infty h}$ on $1/x = kT/\zeta_{22}$ and $C = \Delta/\zeta_{22}$

operators $\mathscr{H}_{s0}$ and $\mathscr{H}_1$ between the functions $|^3A_{2g}Mm\rangle$ and $|^3A_{2g}M'm'\rangle$, and between the functions $|^3A_{2g}Mm\rangle$ and $|(e_2a_1)\,^3E_{2g}M'm'\rangle$ do not change. Therefore, also in this case Eqs (30) remain valid, but $\Delta$ is different. However, for a rough estimate of the parameter $C$ with the use of $\zeta$, $Ds$, $Dt$, and $B$ the original $\Delta$ value is sufficient and leads to the conclusion that $C$ is in the interval $(-5, +5)$.

The analysis of Eqs (29) and (30) yields certain general results. In accord with the physical concept, Eq. (30) with increasing $C$ takes the form of (29), and with $C$ decreasing to $-\infty$ it gives $\mu_2^{\|} = \mu_{\perp}^2 = \mu_{\mathrm{eff}}^2 = 8$, a pure spin value. In the point $T = 0$, the quantities $\mu_{\|}^2, \mu_{\perp}^2$, and $\mu_{\mathrm{eff}}^2$ attain the value: 8 for $C < 1$, 24/5 for $C = -1$, and 0 for $C > -1$. At very high temperatures, $\mu_{\|}^2$ approaches 16, $\mu_{\perp}^2$ 8, hence $\mu_{\mathrm{eff}}^2$ 32/3 regardless of $C$, but for $\mu$ determined by the formulas (29) $\mu_{\|}^2$ approaches 20, $\mu_{\perp}^2$ 8, hence $\mu_{\mathrm{eff}}^2$ 12. However, for large $T$ values the given approximation is not justified since the occupation of different energy levels with electrons becomes equally probable for all levels; moreover most compounds decompose at elevated temperatures. For this reason we shall consider such an interval of temperatures where the highest value of $1/x$ is $5-6$. In Fig. 7 is shown the dependence of $\mu_{\mathrm{eff}}$ on $1/x$ for $C = \pm 4, \pm 2, \pm 1$, and 0, and the dependence calculated from Eq. (29). From this and the above statements it follows that it is not possible to decide from the course of $\mu_{\mathrm{eff}}$ at higher temperatures whether the ground state is the term $^3A_{2g}$ or $^3E_{2g}$, neither their mutual distance can be estimated. This information can be obtained only from the course of $\mu_{\mathrm{eff}}$ at temperatures close to the absolute zero.
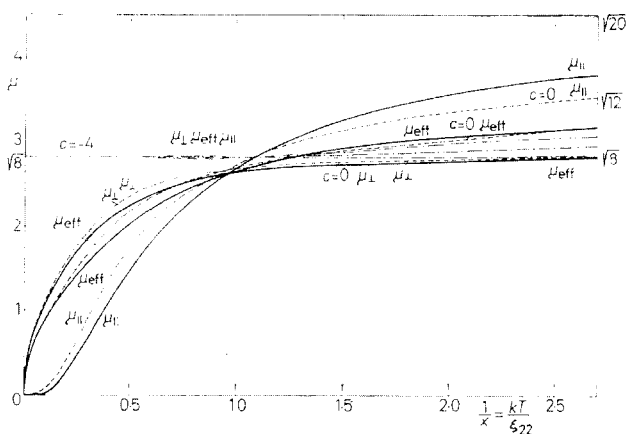


FIG. 8

Dependence of Magnetic Moment $\mu_{\mathrm{eff}}$, $\mu_{\|}$ and $\mu_{\perp}$ for a $d^2$-Electron System in the Field $D_{\infty h}$ on $kT/\zeta_{22}$ and $C = \Delta/\zeta_{22}$

$----$ $C = 0$; $-\cdot-\cdot-\cdot-$ $C = -4$; ——— pure ground term $^3E_{2g}$.

It is interesting that the crossing point of the effective magnetic moments with different $C$ values is independent of $C$ and is given by

$$x = 4 \sinh x / (1 + 4 \sinh x) . \tag{31}$$

If the value of $x$ calculated from this equation is introduced in the expression for $\mu_{\text{eff}}^2$, the effective magnetic moment is equal to the pure spin value, $2\sqrt{2}$, independent of $C$.

An example of $d^2$ sandwich complexes is $V(C_5H_5)_2^+$ whose measured magnetic moment is $2 \cdot 86 \pm 0 \cdot 06$ BM (ref.[42]). An estimate of the parameter $\zeta$ for this ion leads to $kT/\zeta = 1 \cdot 1 - 1 \cdot 4$ at room temperature, *i.e.*, close to the crossing point given by Eq. *(31)*. Therefore, it is not possible to make conclusions[13] from the experimental $\mu_{\text{eff}}$ value at room temperature as to whether the ground state of the $V(C_5H_5)_2^+$ ion is the $^3A_{2g}$ or $^3E_{2g}$ state. To get the answer, the knowledge of the whole dependence of $\mu_{\text{eff}}$ on temperature would be necessary.

TABLE VI

Energy Levels in $Ni(C_5H_5)_2$ for $\zeta = 350$ cm$^{-1}$ and 600 cm$^{-1}$

In each case was $B = 580$ cm$^{-1}$, $C = 3975$ cm$^{-1}$, $Ds = 3290$ cm$^{-1}$ and $Dt = 1695$ cm$^{-1}$.

| Term | Level | Calculated, cm$^{-1}$ | | Experiment[14] |
|------|-------|------|------|------|
| | | $\zeta = 350$ cm$^{-1}$ | $\zeta = 600$ cm$^{-1}$ | |
| $^3A_{2g}$ | $A_{1g}$ | 0 | 0 | |
| | $E_{1g}$ | 9·0 | 25·7 | |
| $^1E_{2g}$ | $E_{2g}$ | 11 535 | 11 445 | 11 720 |
| $^3E_{1g}$ | $E_{2g}$ | 14 285 | 14 280 | |
| | $E_{1g}$ | 14 419 | 14 460 | |
| | $A_{2g}$ | 14 600 | 14 775 | 14 400 |
| | $A_{1g}$ | 14 605 | 14 780 | |
| $^3E_{3g}$ | $E_{4g}$ | 16 395 | 16 065 | |
| | $E_{3g}$ | 16 915 | 16·950 | 16 900 |
| | $E_{2g}$ | 17 465 | 17 910 | |
| $^1A_{1g}$ | $A_{1g}$ | 19 160 | 19 170 | 19 150 |
| $^3E_{1g}$ | $E_{2g}$ | 23 250 | 23 170 | |
| | $E_{1g}$ | 23 370 | 23 315 | 23 450 |
| | $A_{2g}$ | 23 605 | 23 780 | |
| | $A_{1g}$ | 23 625 | 23 830 | |

In addition, in Fig. 8 is shown the dependence of $\mu_{\parallel}$, $\mu_{\perp}$, and $\mu_{\mathrm{eff}}$ on temperature for $C = 0$ (degeneration of $^3E_{2g}$ and $^3A_{2g}$), $C = -4$ (practically pure ground term $^3A_{2g}$), and $C \to \infty$ (term $^3E_{2g}$). Also here the crossing point of the components $\mu_{\parallel}$ and $\mu_{\perp}$ for different $C$ values is independent of $C$ and given by the equation $x(1 + 4e^{-x}) = 2 \sinh x$.

$N = 8$. It has been stated unambiguously[13,14] that the ground state of $d^8$ sandwich complexes is the $^3A_{2g}$ state and that for real values of the parameters $B$, $C$, $Ds$, and $Dt$ this state is sufficiently far apart from the nearest higher excited states so that the magnetic susceptibility is as a good approximation given by the "spin only" formula. Similarly as with $d^2$ sandwich complexes, this fact is not altered even by a mutual interaction of two $^3A_{2g}$ terms.

The $d^8$ sandwich complexes are theoretically interesting since their representative is nickelocene whose absorption spectra[11-14] and magnetic susceptibility[11,12,32] are known and have been studied theoretically. For this reason we calculated the spin–orbit interaction and magnetic susceptibility for nickelocene and compared the results with experiments.

The calculations were based on the assignment in ref.[14], whence the parameters $B$, $C$, $Ds$, and $Dt$ were taken. The parameters $\zeta_{01}$, $\zeta_{21}$, $\zeta_{22}$, and $\zeta_{11}$ were reduced to one parameter $\zeta$ and the secular determinants corresponding to the matrices $A_1$, $E_1$, $E_2$, $E_3$, $E_4$, and $A_2$ of ranks 7, 7, 6, 3, 2, and 2 were solved with the given $B$, $C$, $Ds$, and $Dt$ for $\zeta = 325$, 350, 375, 400, 450, 500, 550, and 600 cm$^{-1}$. The results for $\zeta = 350$ and 600 cm$^{-1}$ are given in Table VI; it is seen that $\zeta$ has only a very small influence on the position of the levels and that an increase in $\zeta$ causes a larger difference between the highest and lowest levels originating in a common term $^{2s+1}\Gamma$.

Since in the envisaged approximation the expressions for the magnetic susceptibility lead to the "spin only" formula, which is for $Ni(C_5H_5)_2$ a good approximation up to about 70 K[11], to describe the whole dependence of the magnetic susceptibility on temperature it is necessary to consider also the contributions from the excited levels by diagonalization of the complete spin-orbit matrices. This was achieved by the previously described method[43]. The calculations were performed for $\zeta = 350$, 500, 550, and 600 cm$^{-1}$ and for $k_{11} = k_{22} = k_{01} = k_{21} = k = 0.5$, 0.6, 0.7, 0.8, 0.9, and 1. From the obtained matrices of the rank 45 it is always possible to separate a $3 \times 3$ matrix corresponding to the lowest levels $A_1$ and $E_1$:

$$
\begin{vmatrix}
0 & \beta B H^+ & \beta B H^- \\
\beta B H^- & D + \beta A H_z & 0 \\
\beta B H^+ & 0 & D - \beta A H_z
\end{vmatrix}
\begin{vmatrix}
|A_1\ 0\rangle \\
|E_1\ 1\rangle \\
|E_1\ -1\rangle
\end{vmatrix}. \tag{32}
$$

where $A$ and $B$ are linear combinations of coefficients $a_i$ corresponding to the spin-orbit function $|A_1\ 0\rangle$ and $b_i$ corresponding to the functions $|E_1\ 1\rangle$ and $|E_1\ -1\rangle$, and $D$ is the distance between the levels $A_1$ and $E_1$. Although the susceptibility was calculated

with regard to contributions from other levels, it turned out that they are negligible regardless of the values of $\zeta$ and $k$ (at temperatures close to normal, the values of $\mu_{eff}$ involving the mentioned contributions differred from those calculated only from the matrices $(32)$ by not more than 0·03 BM). This result corresponds fully to the fact that the ground term $^3A_{2g}$ is enough far apart from the nearest higher terms $^1E_{2g}$ and $^3E_{1g}$. A comparison of the matrix $(32)$ with that corresponding to the spin Hamiltonian

$$\mathscr{H}_s = g_{\|}\beta H_z \mathbf{S}_z + \tfrac{1}{2}g_{\perp}\beta(H^+\mathbf{S}^- + H^-\mathbf{S}^+) + D[\mathbf{S}_2^2 - \tfrac{1}{3}S(S+1)] \qquad (33)$$

enables to calculate the parameters* $g_{\|}$, $g_{\perp}$, and $D$:

$$\text{for} \quad \zeta = 600 \text{ cm}^{-1} \quad \text{and} \quad k = 1 \quad \text{is} \quad g_{\|} = 1·999, \quad g_{\perp} = 2·208$$
$$\text{and} \quad D = 25·72 \text{ cm}^{-1},$$

$$\text{for} \quad \zeta = 350 \text{ cm}^{-1} \quad \text{and} \quad k = 1 \quad \text{is} \quad g_{\|} = 2·001, \quad g_{\perp} = 2·124$$
$$\text{and} \quad D = 9·04 \text{ cm}^{-1}.$$

The course of the obtained magnetic susceptibility (or effective magnetic moment) is shown in Figs 9 and 10 for the case $\zeta = 350, 550,$ and $600$ cm$^{-1}$ at $k = 1$. In Fig. 11 is shown the influence of the parameter $k$ on the magnetic susceptibility at low temperatures for $\zeta = 600$ cm$^{-1}$. It is seen from our results that the experimental values of the magnetic susceptibility[11,32] are well approached at the given $B$, $C$, $Ds$, and $Dt$
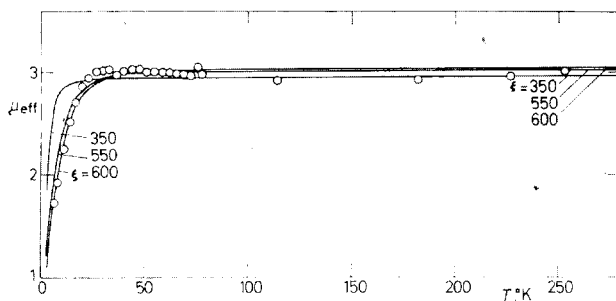


FIG. 9

Dependence of Calculated Effective Magnetic Moment $\mu_{eff}$ on $T$ for Different $\zeta$ Values
   Curves calculated for nickelocene; ○ experimental values[11].

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* Prins[11,12] gives the following experimental values: $g_{\|} = 2·0023$, $g_{\perp} = 2·06 \pm 0·10$, and $D = 25·6 \pm 3·0$ cm$^{-1}$.

values for $\zeta \approx 550 - 600\ cm^{-1}$ at low temperatures and for $\zeta \approx 350\ cm^{-1}$ above 70 K.

We shall not discuss the obtained results since such a discussion would have to involve an analysis of such problems as the influence of a change of the parameters* $B$, $C$, $Ds$, and $Dt$ on the magnetic susceptibility, correlation between the orbital reduction factor $k$ with the value of $\zeta(Ni(C_5H_5)_2)$, admissibility of the reduction of four spin-orbit parameters $\zeta_{ij}$ and four orbital reduction factors $k_{ij}$ to one parameter $\zeta$ and $k$, *etc.* Our aim was only to show on the example of nickelocene to what extent can the consequently applied ligand field theory explain the experimental data even in the case of noncubic, sandwich complexes.

After the present work has been completed, the author became acquainted with the recent paper of Warren[44] dealing with the spin-orbit interaction of certain sandwich complexes. Since Warren in his paper did not indicate explicitly the matrix elements of the spin-orbit interaction (we do not have the Appendix) and since he probably did not distinguish in the Appendix the individual parameters $\zeta_{ij}$, the Tables III and IV in the present work were not deleted. Warren's discussion concerning the assignment
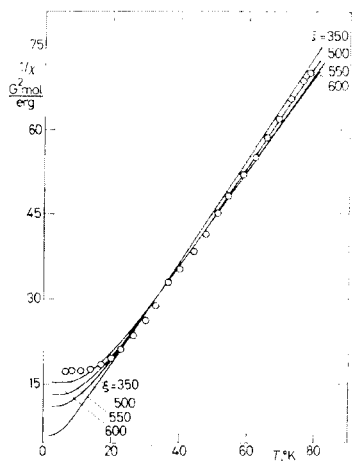


FIG. 10

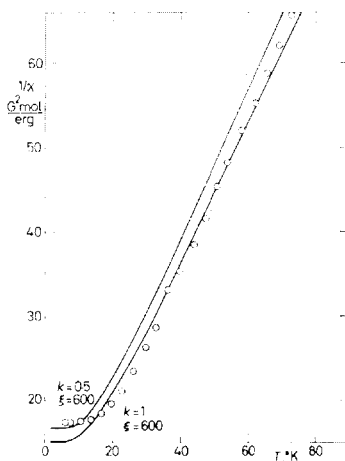Dependence of Reciprocal Value of Calculated Magnetic Susceptibility of Nickelocene, $1/\chi$, on $T$ for Different $\zeta$ Values

FIG. 11

Change of the Dependence of $1/\chi$ for Nickelocene ($\zeta = 600\ cm^{-1}$) on $T$ for two Values of the Orbital Reduction Factor $k$

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*    It should be noted that these parameters were obtained by analysis of the absorption spectra at room temperature and their dependence on temperature was not investigated. In addition, the position of the bands $^3E_{1g} \rightarrow\,^3A_{2g}$, $^3E_{3g} \rightarrow\,^3A_{2g}$, and $^1A_{1g} \rightarrow\,^3A_{2g}$ was determined only by gaussian analysis.

proposed in ref.[14] is studied by the author from the point of view of the magnetic susceptibility of nickelocene.

**APPENDIX**

Table of two-valued representations of the double group $D'_{\infty h}$:

| $D'_{\infty h}$ | $E$ | $R$ | $2C_\varphi$ | $2RC_\varphi$ |
|---|---|---|---|---|
| $E'_{kg}$ | 2 | $-2$ | $2\cos(2k-1)\frac{1}{2}\varphi$ | $-2\cos(2k-1)\frac{1}{2}\varphi$ |
| $E'_{ku}$ | 2 | $-2$ | $2\cos(2k-1)\frac{1}{2}\varphi$ | $-2\cos(2k-1)\frac{1}{2}\varphi$ |

| $C'_2$ | $I$ | $RI$ | $2IC_\varphi$ | $2RIC_\varphi$ | $\sigma_d$ |
|---|---|---|---|---|---|
| 0 | 2 | $-2$ | $2\cos(2k-1)\frac{1}{2}\varphi$ | $-2\cos(2k-1)\frac{1}{2}\varphi$ | 0 |
| 0 | $-2$ | 2 | $-2\cos(2k-1)\frac{1}{2}\varphi$ | $2\cos(2k-1)\frac{1}{2}\varphi$ | 0 |

Here $k = 1, 2, 3, \ldots$, and the symbols have their usual significance. The transformation formulas (9) are compatible to one another for $S_\varphi = IC_{\varphi+\pi}$ and $\sigma_d(\xi_\gamma) = IC'_2(\xi_{\gamma+(3/2)\pi})$.

The decomposition of the direct product of irreducible representation of the double group $D'_{\infty h}$ to the direct sum of representations is given by the following rules:

$$A_i \times E_k = E_k, \quad A_i \times E'_k = E'_k, \quad E_k \times E_1 = E_{k+1} + E_{k-1}, \quad E'_k \times E_1 =$$

$$= E'_{k+1} + E'_{k-1} \quad \text{for} \quad k > 1, \quad E'_k \times E_1 = E'_{k+1} + E'_{1-k+1} \quad \text{for} \quad k \leqq 1, \quad E'_k \times E'_1 =$$

$$= E_{k+1-1} + E_{|k-1|}, \quad E_k \times E_k = A_1 + A_2 + E_{2k}, \quad E'_k \times E'_k = A_1 + A_2 + E_{2k-1},$$

where $i = 1$ or 2, $k = 1, 2, \ldots, l = 1, 2, \ldots$ The subscripts $g$ and $u$ are supplemented according to the known rules $g \times g = u \times u = g, g \times u = u \times g = u$.

The standard base of the double group $D'_{\infty h}$ was defined as follows:

$$C_\varphi|A_{jg,u}\, 0\rangle = |A_{jg,u}\, 0\rangle, \quad C_\varphi|E_{kg,u} \pm 1\rangle = \exp\{\mp ik\varphi\}\,|E_{kg,u} \pm 1\rangle,$$

$$C_\varphi|E'_{1g,u} \pm 1\rangle = \exp\{\pm i(1-\tfrac{1}{2})\,\varphi\}\,|E'_{1g,u} \pm 1\rangle, C'_2(\xi_\gamma)|A_{jg,u}\, 0\rangle =$$

$$= (-1)^{j+1}|\,A_{jg,u}\, 0\rangle, \quad C'_2(\xi_\gamma)|E_{kg,u} \pm 1\rangle =$$

$$= (-1)^{k+1}\exp\{\pm 2ik\gamma\}\,|E_{kg,u} \pm 1\rangle, C'_2(\xi_\gamma)|E'_{1g,u} \pm 1\rangle =$$

$$= (-1)^{1+1/2}\exp\{\pm i(2l-1)\,\gamma\}|E'_{1g,u} \pm 1\rangle, I|\Gamma_g\, m\rangle = |\Gamma_g\, m\rangle, \quad I|\Gamma_u\, m\rangle = -|\Gamma_u\, m\rangle,$$

$$R|A_{jg,u}\, 0\rangle = |A_{jg,u}\, 0\rangle, \quad R|E_{kg,u} \pm 1\rangle = |E_{kg,u} \pm 1\rangle, \quad R|E'_{1g,u} \pm 1\rangle = -|E'_{1g,u} \pm 1\rangle.$$

Here $j = 1$ or 2, $k = 1, 2, \ldots, l = 1, 2, \ldots, \Gamma = A_1, A_2, E_k, E'_1$ and $m = \pm 1$ or 0.

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