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Magnetic Susceptibility of d^4-Sandwich Complexes with Inclusion of Dynamic Jahn–Teller Effect

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The influence of the input parameters on the magnetic susceptibility of d^4-sandwich complexes has been studied in the vibronic interaction scheme. In this approximation, the magnetic moment of chromocene has been fitted and a reasonably good agreement between theory and experiment has been achieved by several sets of parameters.

Introduction

The problem of consistent interpretation of optical and magnetic properties of metallocenes on the basis of their electronic structure has been a challenging problem to theoretical chemists for many years. In spite of great progress in both the experimental and the theoretical methods used in the research of metallocenes during the last decade, there are still some problems which ought to be studied in more detail. One of them is the problem of the influence of the coupling between nuclear and electronic motion in metallocenes on their magnetic properties. The necessity of taking into account that kind of coupling in the cobaltocene molecule was pointed out by Ammeter and Swalen in their outstanding paper [1] nearly ten years ago. Later, a non-negligible manifestation of the dynamic Jahn–Teller effect was firmly established from the EPR experiments for other d^7- and d^5-metallocenes in a variety of host systems [2–4]. However, the first attempt of Ammeter's group to elucidate the other properties of metallocenes on the basis of dynamic Jahn–Teller effect was not fully successful in the case of magnetic susceptibility of cobaltocene [5]. The reason for this might be the necessity of taking into account two or more Jahn–Teller active modes in the vibronic coupling, instead of only one [6].

In the case of d^4-sandwich complexes no EPR signal was detected so that the information about details of the electronic structure must be taken from other experiments. König *et al.* [7] and Oswald [5] measured magnetic susceptibility of chromocene down to 1 K and 4 K respectively, but they did not make any attempt to fit their data with the inclusion of vibronic interaction explicitly. In spite of the above mentioned difficulties the following model calculations have been performed, as some quantitative information about the magnitude of Ham quenching in d^4-sandwich complexes can be obtained from the comparison of magnetic susceptibility measurements with the theory.

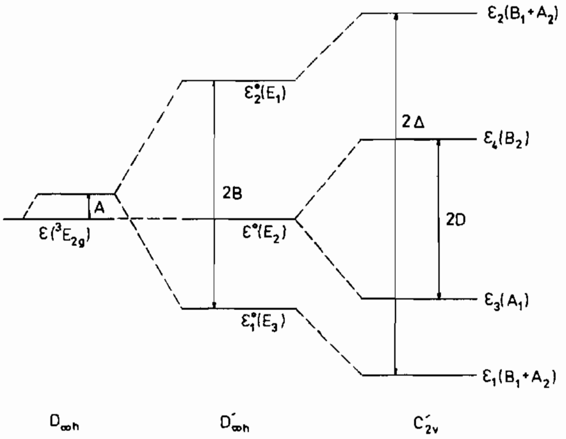

Fig. 1. Splitting pattern of a $^3E_{2g}$ pseudoaxial term due to both spin–orbit coupling (parameters A and B) and symmetry lowering (parameter D). $\Delta = (B^2 + D^2)^{1/2}$ and symbols in parentheses are the ones of irreducible representations of the double group $D'_{\infty h}$ or C'_{2v} (the x-axis being the main axis of symmetry).

Method of Calculation

The most general splitting of a $^3E_{2g}$ pseudoaxial term of d^4-sandwich complexes due to both spin–orbit coupling and symmetry lowering is discussed in a paper [8] from the point of view of the effective Hamiltonian (EH) method. When dropping out, for simplicity, the higher order EH terms depending on E, U, V and W [8], the set of two doubly degenerate (ϵ_1, ϵ_2) and two non-degenerate (ϵ_3, ϵ_4) energy levels is obtained (Fig. 1).

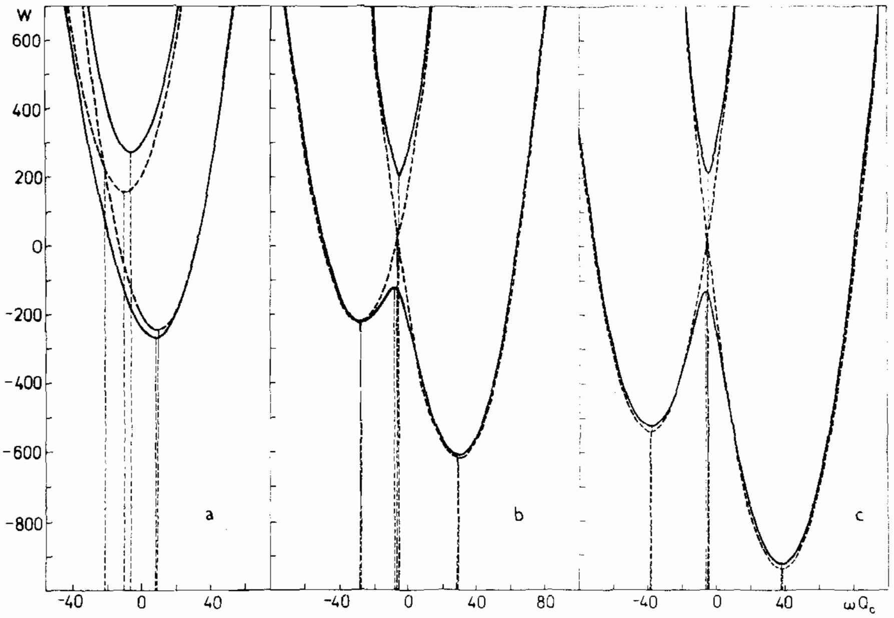

Fig. 2. Cross-sections through the potential surfaces of the term $^3E_{2g}$ in the plane $Q_s = 0$. Full lines: cross-sections corresponding to the doubly degenerate levels ϵ_1 and ϵ_2 of Fig. 1; broken lines: the ones corresponding to the non-degenerate levels ϵ_3 and ϵ_4. A = 25 cm^{-1}, B = −175 cm^{-1}, D = 200 cm^{-1}, $\hbar\omega$ = 370 cm^{-1}, (a) $k_{JT} = 0.5$, (b) $k_{JT} = 1.5$, (c) $k_{JT} = 2$.

The EH eigenfunctions $|1E_2Mj\rangle$, $M = \pm1, 0$, $j = \pm1$, are in fact N-electron (N = 4) eigenfunctions of the ligand field Hamiltonian when both the potential of axial symmetry and the spin–orbit interaction are taken fully into account. They consist of the linear combinations of $|(e_{2g}^{N_2}a_{1g}^{N_o}e_{1g}^{N_1})S\Gamma M_S m_\Gamma\rangle$ functions, $N_2 + N_o + N_1 = 4$, having in the double group $D'_{\infty h}$ the same transformation properties as $|1E_2Mj\rangle$ [9]. A possible non-zero value of the EH parameter A is a consequence of differences in both the number of interacting spin–orbit levels E_1, E_2 or E_3, and the form of interaction within them. For the same reason, there is a difference in the value of the 'first order' spin–orbit parameter ζ (controlling the splitting of the $^3E_{2g}$ term in the first order approximation [10]) and the EH parameter B (see [8] for the discussion of the meaning of all parameters in question).

Matrix elements of the EH, $\mathcal{H}_o$, of axial symmetry are given in [8] as well as the ones of low symmetry EH, $\hat{\mathcal{H}}_{l.s.}$. Jahn–Teller active mode of vibration in the case of orbitally double degenerate $^3E_{2g}$ pseudo-axial ground state is the E_{4g} (E_{1g} in D_{5d} point group) mode. The solution of zero-order vibronic problems with Hamiltonian consisting of both the $\hat{\mathcal{H}}_o$ and the unperturbed vibrational Hamiltonian, $\mathcal{H}_Q$, in the absence of Jahn–Teller coupling [11] gives the 2n-times degenerate zero-order energy levels

$$E^{(o)}_{Mj;n} = (MA + jB)M + n\hbar\omega \qquad (1)$$

$M = \pm1, 0$, $j = \pm1$, $n = 1, 2, 3, \ldots$. The corresponding vibronic functions $|Mj; nm\rangle = |1E_2Mj\rangle|\chi_{nm}\rangle$, $m = -n + 1, -n + 3, \ldots, n - 1$, where χ_{nm} are Pauling and Wilson's functions [12], are zero-order functions for calculation when both the interaction Hamiltonian* [11, 13],

$$\hat{\mathcal{H}}_{JT} = \frac{i\rho}{\sqrt{2}}\,[\hat{V}_1(E_4)e^{-i\theta} - \hat{V}_{-1}(E_4)e^{i\theta}], \qquad (2)$$

and the low symmetry EH, $\hat{\mathcal{H}}_{l.s.}$, are taken into account. Details of the calculation can be found elsewhere [14], as well as the resulting formulas for the components of magnetic moment μ_α, $\alpha = x, y, z$, which were obtained by employing Zeeman magnetic interaction in the form given in [8].

Results and Discussion

Jahn–Teller active modes for the $^3E_{2g}$ ground term of d^4-sandwich complexes are the ones of E_{1g} symmetry in D_{5d} point group. From them, the symmetry ring tilt mode ν_{16} of the Raman shift at 370 cm^{-1} [15] was employed in the present calculations. Their results can be summarized as follows.

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*The form of $\hat{\mathcal{H}}_{JT}$ in (2) was obtained by the transformation of its more familiar form in real coordination system (with components $Q_c = \rho\cos\theta$ and $Q_s = \rho\sin\theta$) to the one in complex coordination system [9].

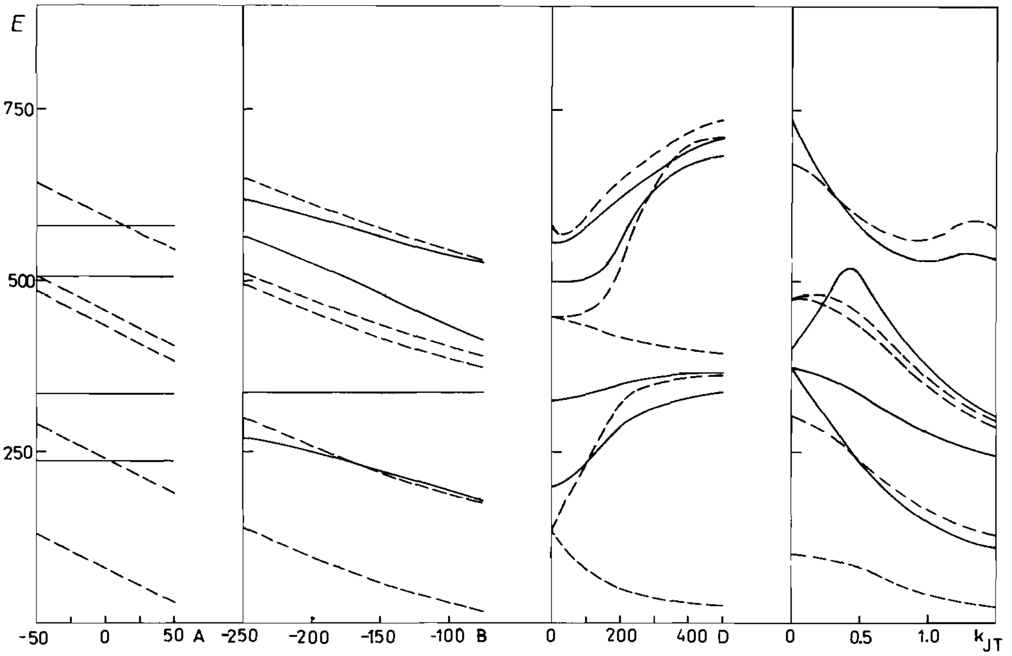

Fig. 3. The dependence of the lowest energy levels on the effective Hamiltonian parameters A, B, D and the Jahn–Teller parameter k_{JT}. $\zeta_0 = \{A = 0,\ B = -175\ \mathrm{cm}^{-1},\ D = 100\ \mathrm{cm}^{-1},\ N = 20, \hbar\omega = 370\ \mathrm{cm}^{-1},\ k_{JT} = 0.5\}$ represents the starting set of parameters. The energy levels are referred to the doubly degenerate ground state level which is taken to be zero. Full lines: doubly degenerate energy levels; broken lines: nondegenerate ones.

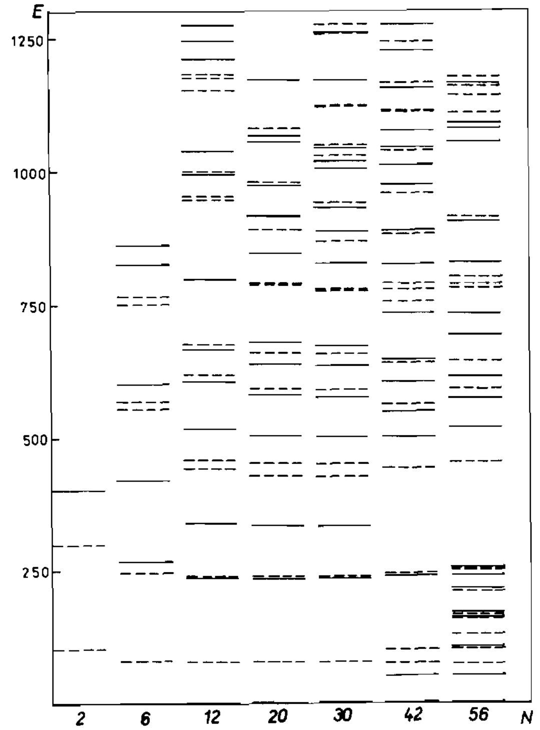

Fig. 4. The lowest energy levels for the particular numbers of dimensions, N's, of the virbonic matrix, calculated with the starting set ζ_0 of Fig. 3. Full lines: doubly degenerate energy levels; broken lines: nondegenerate ones.

Energy Levels and Potential Surfaces

In the approximation of linear harmonic oscillator for the Jahn–Teller active mode of vibration, the potential surfaces corresponding to the energy levels $\epsilon_1 - \epsilon_4$ (Fig. 1) are given by

$$W_\pm = A + \tfrac{1}{2}\omega^2(Q_c^2 + Q_s^2) \pm$$

$$\pm \left[B^2 + (D + k_{JT}\sqrt{\hbar\omega}\,\omega Q_c)^2 + k_{JT}^2(\hbar\omega)\omega^2 Q_s^2\right]^{1/2} \tag{3}$$

in the case of double degenerate levels ϵ_1 and ϵ_2 or by the analogous expression with A = B = 0 in the case of nondegenerate levels ϵ_3 and ϵ_4*.

When $D \neq 0$, the extreme points of surfaces (3) can be found only in the plane $Q_s = 0$ (see Fig. 2). In Fig. 2a the lowering of symmetry clearly prevails over the Jahn–Teller coupling and there is only one local minimum on the potential surface W_-. By increasing the Jahn–Teller parameter k_{JT} over the value $\sqrt{(|D|/\hbar\omega)}$, two local minima occur on the spin orbital surface corresponding to ϵ_3. The same should be true, within reliable values of parameters,

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*Jahn–Teller parameter k_{JT} was defined by the relation
$k_{JT} = -\langle 1E_2M \| \hat{V}(E_4) \| 1E_2M\rangle / 2\omega\sqrt{\hbar\omega}$
in such a manner as to give expressions like $k_{JT}\hbar\omega\sqrt{k}$, k = 1, 2, ..., for off-diagonal matrix elements of the $\hat{\mathcal{H}}_{JT}$, eqn. (2), in $|Mj; nm\rangle$ vibronic basis.

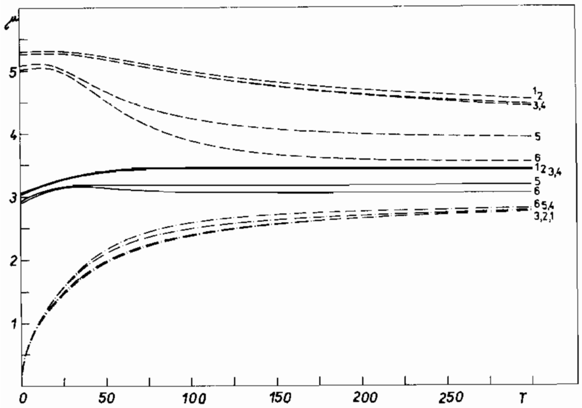

Fig. 5. The dependence of μ_z (– – –), $\mu_x = \mu_y$ (–·–·–) components and magnetic moment μ (———) on the number of dimensions, N, of the vibronic matrix, calculated with the starting set $\zeta = \{\zeta_o, g_\parallel = 2.0, g'_\parallel = 1.4, g_\perp = 2, 0, g_p = 0\}$. 1. N = 6, 2. N = 12, 3. N = 20, 4. N = 30, 5. N = 42, 6. N = 56.

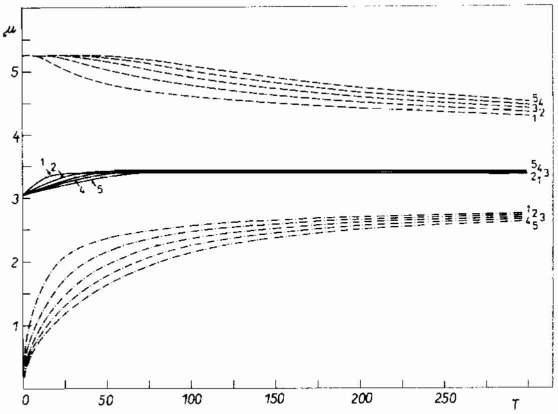

Fig. 6. The dependence of μ_z (– – –), $\mu_x = \mu_y$ (–·–·–) and μ (———) on the effective Hamiltonian parameter A. 1. A = –50 cm^{-1}, 2. A = –25 cm^{-1}, 3. A = 0 cm^{-1}, 4. A = 25 cm^{-1}, 5. A = 50 cm^{-1}. See Fig. 5 for the initial set, ζ, of the parameters.

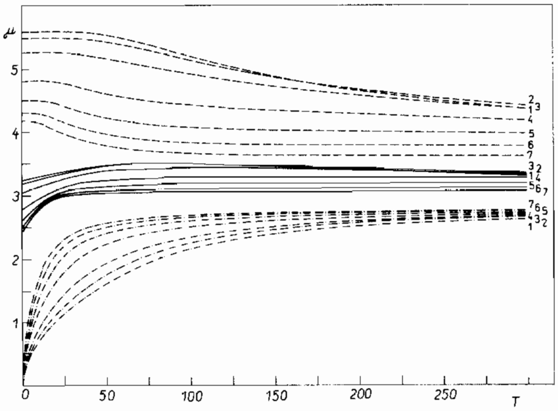

Fig. 7. The dependence of μ_z (– – –), $\mu_x = \mu_y$ (–·–·–) and μ (———) on the effective Hamiltonian parameter D. 1. D = 0 cm^{-1}, 2. D = 50 cm^{-1}, 3. D = 100 cm^{-1}, 4. D = 200 cm^{-1}, 5. D = 300 cm^{-1}, 6. D = 400 cm^{-1}, 7. D = 500 cm^{-1}. See Fig. 5 for the initial set, ζ, of the parameters.

also for W_-. The former surface turned into the lowest one for particular values of A (A > 0) and k_{JT}, in spite of the inverse order of the corresponding levels ϵ_1 and ϵ_3.

The dependence of the lowest vibronic levels on the EH parameters A, B, D and the Jahn–Teller parameter k_{JT} is depicted in Fig. 3. The convergence of the differences between lowest energy levels in relation to the increasing number of dimensions, N = n(n + 1), of the vibronic matrix was also studied and the result is given in Fig. 4. As can be seen, the apparent stability of the lowest levels for N = 12, 20 and 30 breaks up when N = 42 or 56, having as a consequence a pronounced decrease of the μ_z component of magnetic moment μ (Fig. 5). The reason has not been fully understood and the decrease ought to be studied in more detail. It might be related to the approximation of the linear harmonic oscillator for ν_{16} mode of vibration, leading to a parabolic shape of the potential surfaces (see marginal parts of the curves in Fig. 2) while, *e..g*, the Morse potential [16] gives more reliable expressions for both the vibrational energy levels and the wave functions in the case of higher vibrational states. Further on, the interaction Hamiltonian $\hat{\mathcal{H}}_{JT}$ in its linear form (2) does not consider quadratic and higher order terms which are responsible for the warping of potential surfaces, not only near the minimum points but also in the part corresponding to the states with a high quantum number n. Finally, the energies of those states can be closer to the low lying vibronic states of the excited term $^3A_{2g}$* than to the ground vibronic state, thus demanding the additional interaction between the two sets of vibronic states to be taken into account. Therefore, the present calculations were confined to the number of dimensions, N, to be less than or equal to 30.

Dependence of Magnetic Moment on Parameters

Changes of the EH parameters A, B, and D as well as of the Jahn–Teller parameter k_{JT} result in the changes of both the shape and the magnitude of magnetic moment μ(T). Two typical examples are presented in Figs. 6 and 7, where μ_z(T), μ_x(T) = μ_y(T) and μ(T) are given for several values of the EH parameters A and D. The increase of the latter parameter results in the decrease of the difference between the first excited level and the ground level

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*König *et al.* [7] calculated the energy of this term to be about 7000 cm^{-1} while the value of 1000–2000 cm^{-1} can be assessed by using the data given by Warren [17].

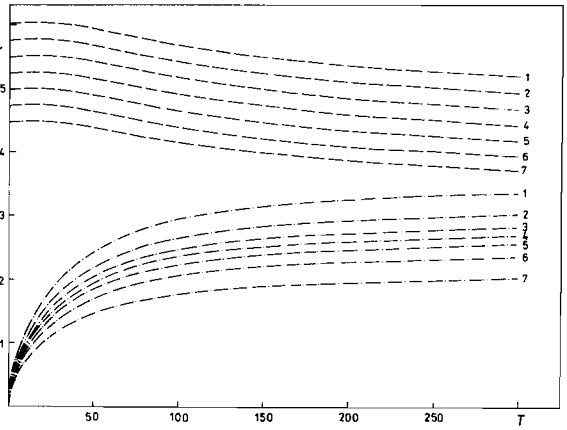

Fig. 8. The dependence of μ_z (– – –, a) and $\mu_x = \mu_y$ (–·–·–), b) components of magnetic moment on the effective Hamiltonian parameters $g'_\parallel$ and $g_\perp$, respectively. a: 1. $g'_\parallel = 2.0$, 2. $g'_\parallel = 1.8$, 3. $g'_\parallel = 1.6$, 4. $g'_\parallel = 1.4$, 5. $g'_\parallel = 1.2$, 6. $g'_\parallel = 1.0$, 7. $g'_\parallel = 0.8$. b: 1. $g_\perp = 2.5$, 2. $g_\perp = 2.25$, 3. $g_\perp = 2.1$, 4. $g_\perp = 2.0$, 5. $g_\perp = 1.9$, 6. $g_\perp = 1.75$, 7. $g_\perp = 1.5$, See Fig. 5 for the initial set, ζ, of parameters.

Fig. 3) having, as a consequence, the decrease of the value of $\mu(T)$ and the increase of its curvature at a very low temperature. Nearly the same alteration of magnetic moment can also be revealed by the increase of parameters B ($B < 0$) and k_{JT}, in spite of the remarkable difference in the course of the corresponding second and higher vibronic levels in comparison to their course in the case of parameter D (Fig. 3). From this and further analyses we suggest that it is the difference between the first excited level and the ground vibronic level which is the leading factor in determining the shape of magnetic moment. Some 'empirical' rules concerning the magnitude of this difference will be formulated in the discussion concerning the fitting of the magnetic moment of chromocene (*vide infra*).

The magnitude of magnetic moment $\mu(T)$ can also be influenced by the values of g-parameters (see Fig. 8 and Fig. 3 in [8]). It ought to be borne in the mind, however, that the second order effects in the ligand field calculations will modify their values only to a lesser extent [18], contrary to the EH calculations [8] where they are modified to a far greater extent due to (implicit) embracement of the dynamic Jahn–Teller effect.

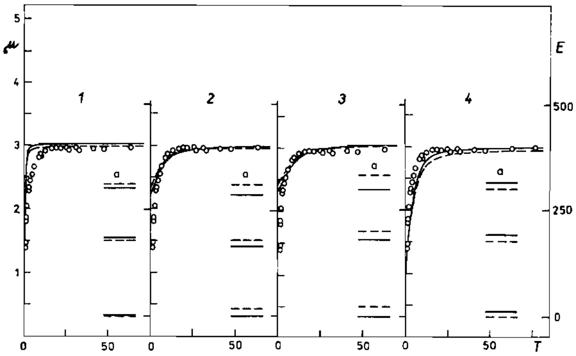

Fig. 9. The fitting of the magnetic moment, μ, of chromocene in the temperature range 0–70 K. Full lines: calculated using the sets ζ_i, i = 1, 2, 3, 4; broken lines: $g_\parallel = 2.0$, $g_\perp = 2.0$; circles: experimental points (reference [7]).

$\zeta_1 = \{A = 25\ \text{cm}^{-1}, B = -175\ \text{cm}^{-1}, k_{JT} = 1.25\}$

$\zeta_2 = \{A = 0\ \text{cm}^{-1}, B = -175\ \text{cm}^{-1}, k_{JT} = 1.5\}$

$\zeta_3 = \{A = 0\ \text{cm}^{-1}, B = -175\ \text{cm}^{-1}, k_{JT} = 1.25\}$

$\zeta_4 = \{A = 25\ \text{cm}^{-1}, B = -125\ \text{cm}^{-1}, k_{JT} = 1.25\}$

The other parameters ($D = 200\ \text{cm}^{-1}$, $\hbar\omega = 370\ \text{cm}^{-1}$, $N = 30$, $g_\parallel = 1.9$, $g'_\parallel = 1.4$, $g_\perp = 2.1$, $g_p = 0$) have the same values in all sets ζ_i.

a: The lowest energy levels for the given sets ζ_i. Full lines: doubly degenerate energy levels, broken lines: non-degenerate ones. The energy difference, ΔE_{low}, between the two lowest energy levels for the given sets ζ_i: 1. $\Delta E_{low} = 1.7\ \text{cm}^{-1}$, 2. $\Delta E_{low} = 17.6\ \text{cm}^{-1}$, 3. $\Delta E_{low} = 22.3\ \text{cm}^{-1}$, 4. $\Delta E_{low} = 13.1\ \text{cm}^{-1}$.

Fitting of Magnetic Moment of Chromocene

The course of the magnetic moment of the chromocene molecule was simulated with the aid of the above analysis. The EH parameters were varied within limits which were given by the expected values of the ligand field calculations, and the Jahn–Teller parameter k_{JT} took on the values from the interval 0.5–2.0. The experimental values were taken from [7].

It follows from the limiting properties of formulas for the components of the magnetic moment [14] that in the case of (i) doubly degenerate ground state

$$\lim_{T \to 0} \mu(T) = \left| g_\parallel + \left[\sum_{n,m} (\beta^N_{nm})^2 - \sum_{n,m} (\alpha^N_{nm})^2 \right] g'_\parallel \right| , \quad (4)$$

i.e. $\lim_{T \to 0} [1/\chi(T)] = 0$, while in the case of (ii) non-degenerate ground state $\lim_{T \to 0} \mu(T) = 0$, *i.e.* $\lim_{T \to 0} [1/\chi(T)] \neq 0$. In (4), α^N_{nm}, resp. β^N_{nm} are coefficients of the linear combination with zero-order vibronic functions $|1{-}1; nm\rangle$, resp. $|11, nm\rangle$, in an expansion of the eigenfunction corresponding to the lowest double degenerate energy level E_N [14]. Because of orthonormalization relations of the coefficients, the value in square brackets in (4) can be assessed to be within the interval (–0.5, 0.5) for $\Sigma(\alpha^N_{nm})^2$ from the interval (0.75, 0.25). For $g_\parallel$ and $g'_\parallel$, being near to the values given by the ground-state approximation [10, 8], *i.e.* $g_\parallel \cong 2.0$, $g'_\parallel = 2k' \cong 1.4$, it leads to the limiting values of $\mu(T)$, $T \to 0$, spreading from 1.3 to 2.7. In the case (i), it is therefore in principle impossible to fit experimental values of the magnetic moment

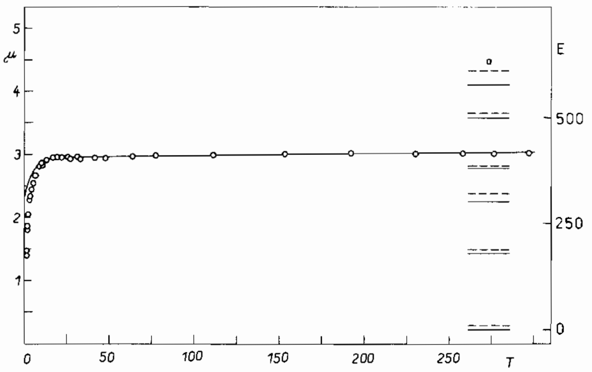

Fig. 10. The fitting of the magnetic moment, μ, of chromocene in the temperature range 0–300 K. Full line: calculated with A = 0 cm^{-1}, B = –125 cm^{-1}, D = 200 cm^{-1}, N = 30, $\hbar\omega$ = 370 cm^{-1}, k_{JT} = 1.25, $g_{\parallel}$ = 2.0, $g'_{\parallel}$ = 1.4, $g_{\perp}$ = 2.0, g_p = 0. Circles: experimental points [7].

a: the lowest vibronic levels calculated with the given set of parameters. The energy difference, ΔE_{low}, between the two lowest vibronic levels equals 11.9 cm^{-1}.

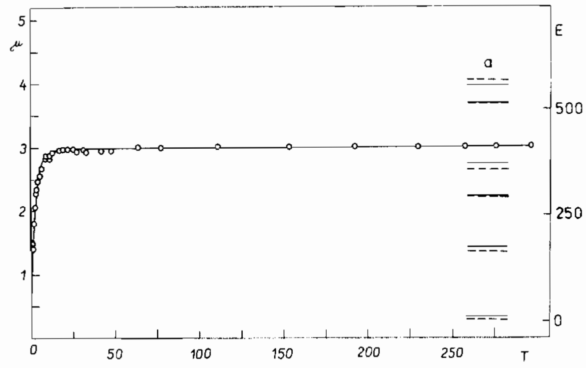

Fig. 11. The fitting of the magnetic moment, μ, of chromocene in the temperature range 0–300 K. Full line: calculated with A = 25 cm^{-1}, B = –175 cm^{-1}, D = 200 cm^{-1}, N = 30, $\hbar\omega$ = 370 cm^{-1}, k_{JT} = 1.5, $g_{\parallel}$ = 1.9, $g'_{\parallel}$ = 1.4, $g_{\perp}$ = 2.1, g_p = 0. Circles: experimental points [7]

a: the lowest vibronic levels calculated with the given set of parameters, ΔE_{low} = 7.4 cm^{-1}.

of chromocene near the zero temperature (see Figs. 9 and 10) even by inclusion of the dynamic Jahn–Teller effect. Hence, in accordance with the results of work [15], it seems inevitable to suppose the further splitting of the ground level ϵ_1 (Fig. 1) due to low symmetry effects (EH parameters V, W and E [8]). There is, however, one more possibility of obtaining the agreement between theory and experiment, which follows from the limiting properties of μ(T) in the case (ii). As a result of unequal stabilization of the energy levels $\epsilon_1 - \epsilon_4$ of Fig. 1 due to dynamic Jahn–Teller effect, the lowest nondegenerate vibronic level could turn into the ground state level for the realistic values of both the EH parameters A (A > 0), B, D and the Jahn–Teller parameter k_{JT} (see Figs. 2, 9 and 11). The magnetic moment can be in this latter case fitted up to the very low temperature (Fig. 11), contrary to the former case (i).

In fitting the magnetic moment of chromocene, the difference between the lowest nondegenerate level and the lowest doubly degenerate one appeared to be the factor controlling the shape of the magnetic moment near the zero temperature. In the case (i), this difference must be about 12 cm^{-1} (Figs. 9 and 10) while in the case (ii) it should be only about 7 cm^{-1} (Figs. 9 and 11) so that a good agreement between theory and experiment could be obtained. Anticipating the results of our EH-analysis of the fitting of the magnetic moment in the case of (iii) splitting the doubly degenerate level ϵ_1, the difference in the range from 5 to 10 cm^{-1} between the ground level and the first excited one must be used so that the calculation could reproduce the experimental curve in this case too. The decision as to which of the two cases, (ii) and (iii), corresponds to the real situation in the chromocene molecule cannot be made on the ground of the knowledge of the temperature dependence of magnetic moment only, as there are so many degrees of freedom in the parameters in question that it is always possible to find a number of sets of parameters reproducing the experimental curve. An example of the three sets was given in [14] where the same fitting was obtained by changing the two parameters, D an k_{JT}. However, when performing complete ligand field calculations, a set of the EH parameters A, B, D (eventually V, W, E and U) as well as g-parameters can be obtained and the only parameter which is to be fitted is the Jahn–Teller parameter k_{JT}.

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