

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

## I. Semi-Empirical Analysis Including Axial Field Distortions\*

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The theory of magnetism at the  ${}^5T_2 - {}^1A_1$  crossover is developed including an axial distortion of the crystalline field, the covalency of the metal-ligand bond, and the amount of permanently paramagnetic "impurities". The results are applied to nineteen relevant iron(II) complexes and the energy separation,  $\varepsilon$ , between the original  ${}^5T_2$  and  ${}^1A_1$  states is calculated.

The compounds may be classified, according to the temperature dependence of  $\varepsilon$ , into three groups: (i) compounds which show a sharp change in  $\varepsilon$  at  $T_c$  of 200 to 600  $\text{cm}^{-1}$  due to a second-order phase transition between  ${}^5T_2(t_2^4 e^2)$  and  ${}^1A_1(t_2^6)$  ground state conformations; (ii) compounds which are characterized by a linear change of  $\varepsilon$  with  $T$  of up to 600  $\text{cm}^{-1}$  due to a thermal equilibrium between  ${}^5T_2$  and  ${}^1A_1$  ground states; (iii) compounds exhibiting a linear increase of  $\varepsilon$  with decreasing  $T$  followed by a maximum due to essentially the same reason as in group (ii) behaviour.

Previous erroneous treatments of the  $T$ -dependence of  $\varepsilon$  are pointed out and the inconsistency of an empirical adjustment of the vibrational partition function ratio,  $C$ , with the assumption of a  ${}^5T_2 - {}^1A_1$  transition is demonstrated.

Die Theorie des Magnetismus am  ${}^5T_2 - {}^1A_1$ -Überschnidungspunkt wird entwickelt unter Berücksichtigung einer axialen Verzerrung des Kristallfeldes, der Kovalenz der Metall-Ligand-Bindung sowie der Anteile permanent paramagnetischer „Verunreinigungen“. Die Ergebnisse werden auf neunzehn geeignete Eisen(II)-Komplexe angewendet und der Energieabstand  $\varepsilon$  zwischen den ursprünglichen Zuständen  ${}^5T_2$  und  ${}^1A_1$  wird berechnet.

Die Verbindungen können auf Grund der Temperaturabhängigkeit von  $\varepsilon$  in drei Gruppen eingeteilt werden: (i) Verbindungen, die bei  $T_c$  eine starke Änderung von  $\varepsilon$  von 200–600  $\text{cm}^{-1}$  erfahren. Diese ist auf eine Phasenänderung zweiter Ordnung zwischen den Konformationen der Grundzustände  ${}^5T_2(t_2^4 e^2)$  und  ${}^1A_1(t_2^6)$  zurückzuführen; (ii) Verbindungen, die durch eine lineare Änderung von  $\varepsilon$  in Abhängigkeit von  $T$  von bis zu 600  $\text{cm}^{-1}$  gekennzeichnet sind. Diese wird durch ein thermisches Gleichgewicht zwischen den Grundzuständen  ${}^5T_2$  und  ${}^1A_1$  hervorgerufen; (iii) Verbindungen, bei denen einer linearen Zunahme von  $\varepsilon$  bei fallendem  $T$  ein Maximum folgt. Die Ursache dieses Verhaltens ist praktisch identisch mit dem der Gruppe (ii).

Auf frühere unzutreffende Behandlungen der Temperaturabhängigkeit von  $\varepsilon$  wird hingewiesen. Der Widerspruch zwischen einer empirischen Festlegung des Verhältnisses  $C$  der Zustandssummen von Schwingungszuständen und der Annahme eines  ${}^5T_2 - {}^1A_1$ -Überganges wird aufgezeigt.

Développement de la théorie du magnétisme au croisement  ${}^5T_2 - {}^1A_1$  en y incluant une distorsion axiale du champ cristallin, la covalence de liaison entre le métal et le ligand, et la quantité « d'impuretés » à paramagnétisme permanent. Les résultats sont appliqués à dix-neuf complexes du fer (II), avec calcul de la séparation énergétique  $\varepsilon$  entre les états  ${}^5T_2$  et  ${}^1A_1$ . Selon la dépendance de  $\varepsilon$  à la température les composés peuvent être classés en trois groupes: (i) les composés qui présentent un brusque changement de  $\varepsilon$  de 200 à 600  $\text{cm}^{-1}$  pour une température  $T_c$  par suite d'une transition de phase du second ordre entre les conformations  ${}^5T_2(t_2^4 e^2)$  et  ${}^1A_1(t_2^6)$  de l'état fondamental; (ii) les composés qui présentent une variation linéaire de  $\varepsilon$  avec  $T$  jusqu'à 600  $\text{cm}^{-1}$ , ce qui est dû à un équilibre thermique entre les

\* This paper is dedicated to the memory of Professor Hans-Ludwig Schäfer.

états fondamentaux  $^5T_2$  et  $^1A_1$ ; (iii) les composés pour lesquels  $\varepsilon$  augmente linéairement lorsque  $T$  décroît jusqu'à un maximum, ce qui est dû essentiellement à la même raison que pour les composés du groupe (ii).

On souligne le côté erroné des précédentes études de la dépendance de  $\varepsilon$  à  $T$ , et l'on démontre l'inconsistance d'un ajustement empirique de la fraction de la fonction de partition vibrationnelle  $C$ , avec l'hypothèse d'une transition  $^5T_2 - ^1A_1$ .

### Introduction

Within the last few years, the interest in crossover situations of transition metal complexes has been rising continuously [1–3]. Regarding the subject matter which is going to concern us here, i.e. iron(II), the first example of a crossover has been encountered in *cis*-diisothiocyanato and *cis*-diisoselenocyanato-bis(1,10-phenanthroline) iron(II),  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$  and  $[\text{Fe}(\text{phen})_2(\text{NCSe})_2]$ . A definite evidence that, in fact, a crossover is present in these systems was presented by König and Madeja [4, 5] and was based essentially on magnetic and Mössbauer effect investigations.

The aforementioned compounds are typical in that a rather sharp change of the relevant physical (e.g. magnetic) properties occurs and that, therefore, a specific transition temperature  $T_c$  may be defined [5]. A similar situation is found in diisothiocyanato-bis(2,2'-bipyridyl) iron(II),  $[\text{Fe}(\text{bipy})_2(\text{NCS})_2]$  [6], in both the bromide and chloride of tris(2-aminomethylpyridine)iron(II),  $[\text{Fe}(\text{2-pic})_3]\text{X}_2$ ,  $\text{X} = \text{Cl}, \text{Br}$  [7], and in the perchlorate of tris(2-(2'-pyridyl)imidazoline)iron(II),  $[\text{Fe}(\text{pyim})_3](\text{ClO}_4)_2$  [8] (group I). In the Mössbauer effect, separate transitions within the  $^1A_1$  state and within components of the  $^5T_2$  state are observed, the relative intensities varying with temperature [5–8].

On the other hand, in some tris(2-methyl-1,10-phenanthroline)iron(II) complexes  $[\text{Fe}(\text{mphen})_3]\text{X}_2$ , where  $\text{X} = \text{ClO}_4, \text{BF}_4$ , and  $\text{PF}_6$  (group II), the change in e.g. the magnetic moment occurs over a more extended range of temperature and is therefore much less sharp than in the compounds showing group I properties [9]. The Mössbauer spectra are complicated by a pronounced temperature dependence of the quadrupole splitting and by considerable line broadening effects due to relaxation phenomena. The details of these findings will be reported separately [10].

The combination of a gradual change in the magnetic moment with separate  $^5T_2$  and  $^1A_1$  Mössbauer spectral transitions is also frequently encountered. This situation is consistent with slow relaxation between the different ground states. Relevant examples are provided by the poly(1-pyrazolyl)borate iron(II) termed "chelate I" [11] and by a series of iron(II) complexes  $[\text{Fe}(\text{pyi})_3]\text{X}_2$  of the ligand 2-(2'-pyridyl)imidazole (pyi) [12, 13].

Several additional compounds were claimed to exhibit  $^5T_2 - ^1A_1$  "equilibria", mostly on the basis of magnetic measurements alone. These include a series of iron(II) complexes  $[\text{Fe}(\text{paptH})_2]\text{X}_2$  with the ligand 2-(2-pyridylamino)-4-(2-pyridyl)thiazole (paptH) [14], the ferrous complex  $[\text{Fe}(\text{papt})_2]$  of the deprotonated ligand (papt) [15], and the iron(II) complexes  $[\text{Fe}(\text{pythiaz})_2]\text{X}_2$  with the ligand 2,4-bis(2-pyridyl) thiazole (pythiaz) [16]. The magnetism of these compounds is consistent with group II behaviour, although, in general, more detailed investigations are needed.

A simple theoretical treatment was suggested previously [4, 5] to provide a quantitative interpretation of the magnetism in systems which are close to the  ${}^5T_2 - {}^1A_1$  crossover. This approach is based on the two-level scheme and its results do not compare favourably with experiment [5, 13, 14], although some improvement was achieved recently by Harris and Sinn [17]. The inadequacy of the method is due, most likely, to the simplifying assumptions of (i) a strictly octahedral ligand field, (ii) a temperature-independent energy separation  $\varepsilon$  between the points of gravity of the  ${}^5T_2$  and  ${}^1A_1$  terms, (iii) no permanently paramagnetic impurities, and (iv) constant bond lengths and bond angles.

In the present paper, we will relax these assumptions as far as possible to see what improvements may thus be achieved. At first a conventional theory of magnetism at the  ${}^5T_2 - {}^1A_1$  is presented which includes axial (i.e. tetragonal or trigonal) field distortions. Secondly, the resulting expressions are applied to the experimental data of relevant iron(II) complexes and the temperature dependence of  $\varepsilon$  is calculated. Finally, consequences with regard to the physical processes involved are discussed.

In a subsequent paper [18], the effect of the full configuration interaction and spin-orbit coupling on the magnetic properties at the  ${}^5T_2 - {}^1A_1$  crossover will be examined.

### Fine Structure and Zeeman Energy Levels

The energy levels which we are going to consider are those generated by application of the axial field, spin-orbit, and Zeeman operators on the cubic  ${}^5T_2$  and  ${}^1A_1$  terms. If the symmetry is strictly  $O_h$ , spin-orbit interaction partly lifts the degeneracy of the  ${}^5T_2$  state separating it into three levels, *viz.*  $\Gamma_5, \Gamma_3 + \Gamma_4$ ,

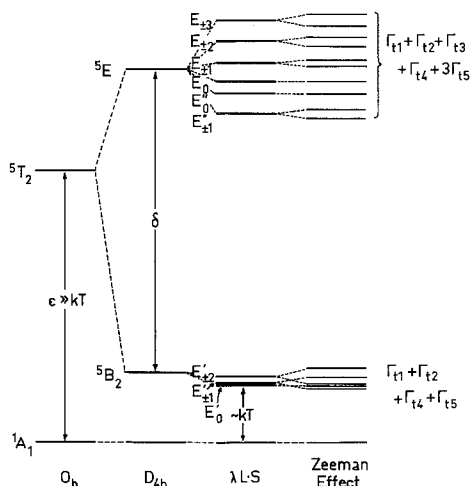


Fig. 1. Disposition of energy levels close to the  ${}^5T_2 - {}^1A_1$  crossover ( $\lambda = -80 \text{ cm}^{-1}$ ,  $\delta = -1000 \text{ cm}^{-1}$ ,  $\varepsilon = 900 \text{ cm}^{-1}$ ). The notation of spin-orbit energies is that used in Ref. [21]

and  $\Gamma_1 + \Gamma_4 + \Gamma_5$  with relative energies of  $3\lambda$ ,  $\lambda$ , and  $-2\lambda$ , respectively. Here,  $\lambda$  is the spin-orbit coupling parameter,  $\lambda = -\zeta/4$ . The  ${}^1A_1$  state is changed over into  $\Gamma_1$ . Spin-orbit mixing does not occur, the matrix element between  $\Gamma_1({}^5T_2)$  and  $\Gamma_1({}^1A_1)$  being zero.

If, in addition, an axial field is taken into account, the splitting of the  ${}^5T_2$  term is according to Fig. 1, where the actual disposition of levels for the situation characterized by  $\varepsilon = 900 \text{ cm}^{-1}$ ,  $\delta = -1000 \text{ cm}^{-1}$ , and  $\lambda = -80 \text{ cm}^{-1}$  is shown ( $\delta$  is the axial field splitting and positive, whenever the  ${}^5E$  is lowest). On the basis of group theory, the resulting components are, in tetragonal ( $D_{4h}$ ) symmetry,

$$\begin{aligned} {}^5B_2 &\rightarrow \Gamma_{t11} + \Gamma_{t12} + \Gamma_{t14} + \Gamma_{t15} \\ {}^5E &\rightarrow \Gamma_{t11} + \Gamma_{t12} + \Gamma_{t13} + \Gamma_{t14} + 3\Gamma_{t15} \end{aligned} \quad (1)$$

whereas in trigonal ( $D_{3d}$ ) symmetry, one obtains

$$\begin{aligned} {}^5A_1 &\rightarrow \Gamma_1^T + 2\Gamma_3^T \\ {}^5E &\rightarrow 2\Gamma_1^T + 2\Gamma_2^T + 3\Gamma_3^T \end{aligned} \quad (2)$$

( $t =$  tetragonal,  $T =$  trigonal [19]). Again, there is no spin-orbit interaction between the  $\Gamma_{t11}$  levels of (1) and  $\Gamma_{t11}({}^1A_1)$  and, likewise not, between the  $\Gamma_1^T$  levels of (2) and  $\Gamma_1^T({}^1A_1)$ .

### The Magnetic Moment at the ${}^5T_2$ — ${}^1A_1$ Crossover

Starting from the spin-orbit levels listed above, the effective magnetic moment,  $\mu_{\text{eff}}$ , may be obtained via the Van Vleck formalism [20]. It has been shown previously [5, 6] that, within octahedral symmetry,  $\mu_{\text{eff}}$  at the  ${}^5T_2$ — ${}^1A_1$  crossover is simply determined according to

$$\mu_{\text{eff}}^2 = \frac{3[(28x + \frac{28}{3})e^{2x} + (\frac{45}{2}x + \frac{25}{6})e^{-x} + (\frac{49}{2}x - \frac{27}{2})e^{-3x}]}{x(e^{x/kT} + 7e^{2x} + 5e^{-x} + 3e^{-3x})} \quad (3)$$

where  $x = \lambda/kT$ .

If the predominant field is axially symmetric, the expression corresponding to Eq. (3) may be set up starting from the magnetism of a *pure*  ${}^5T_2$  term. The theory for this case was recently developed [21] and will be directly referred to<sup>1</sup>. For the present purpose, the corresponding expressions relating to  $\delta > 0$  and  $\delta < 0$  may be combined by a suitable multiplication of Eq. (11) through Eq. (18) of [21] by factors  $e^{-E_1/kT}$  and  $e^{-E_0/kT}$ . The  ${}^1A_1$  term is being incorporated by a modification of the denominator,  $Z$  or  $Z'$ , and by taking care of the change in the energy zero, *viz.* Fig. 1. Thus, within an axially distorted field,  $\mu_{\text{eff}}$  at the

<sup>1</sup> There are several obvious misprints in [21] which should be observed:

Eq. (16): the curled bracket should be placed in front of  $G_{22}^{E_0}$ ;

Eq. (I-1): in the off-diagonal matrix elements, square roots should not extend above  $\lambda_{\perp}$ ;

Eq. (II-1): in  $G_{22}^{E_0}$ , the factor of 2 should be dropped;

in  $G_{22}^{E_0}$ , both factors of 2 should be dropped;

in  $G_{22}^{E_1}$ , the sign of the second expression should be positive;

in  $G_{22}^{E_0}$ , the factor of 2 should be dropped.

The numerical results listed in [21] are not affected.

${}^5T_2 - {}^1A_1$  crossover may be written

$$\mu_{\text{eff}}^2 = \frac{a}{e^{\varepsilon/kT} + b}, \quad (4)$$

where

$$\begin{aligned} a = & 2kT(G_{2z}^{E_0} + 2G_{2x}^{E_0}) e^{-E_0/kT} + 2kT(G_{2z}^{E_0} + 2G_{2x}^{E_0}) e^{-E_0/kT} \\ & + 2kT(G_{2z}^{E_0} + 2G_{2x}^{E_0}) e^{-E_0/kT} + (G_{1z}^{E_1} + 2kT G_{2z}^{E_1} + 4kT G_{2x}^{E_1}) e^{-E_1/kT} \\ & + (G_{1z}^{E_1} + 2kT G_{2z}^{E_1} + 4kT G_{2x}^{E_1}) e^{-E_1/kT} \\ & + (G_{1z}^{E_1} + 2kT G_{2z}^{E_1} + 4kT G_{2x}^{E_1}) e^{-E_1/kT} \end{aligned} \quad (5)$$

$$\begin{aligned} & + (G_{1z}^{E_2} + 2kT G_{2z}^{E_2} + 4kT G_{2x}^{E_2}) e^{-E_2/kT} \\ & + (G_{1z}^{E_2} + 2kT G_{2z}^{E_2} + 4kT G_{2x}^{E_2}) e^{-E_2/kT} + (G_{1z}^{E_3} + 4kT G_{2x}^{E_3}) e^{-E_3/kT} \\ b = & e^{-E_0/kT} + e^{-E_0/kT} + e^{-E_0/kT} + 2e^{-E_1/kT} + 2e^{-E_1/kT} \\ & + 2e^{-E_1/kT} + 2e^{-E_2/kT} + 2e^{-E_2/kT} + 2e^{-E_3/kT} \end{aligned} \quad (6)$$

and where all the quantities involved in (5) and (6) were defined previously [21].

### Permanently Paramagnetic Material and Molecular Vibrational Partition Functions

On the basis of magnetic and Mössbauer effect investigations, one of the authors has shown [5, 6] that, in some of the compounds, the transition from the  ${}^5T_2$  to the  ${}^1A_1$  ground state is incomplete. The same was assumed by Harris and Sinn [17] in order to obtain a successful fit of the magnetic data in a group of complexes displaying similar behaviour. There has to be accepted, therefore, a certain proportion of permanently paramagnetic material,  $\alpha$ , having essentially the same chemical composition as the major part of the sample under study. The magnetism of this paramagnetic "impurity" should then equal that of a  ${}^5T_2$  ground state system, the temperature dependence thereof following the theory quoted above [21]. Thus  $\mu_{\text{eff}}$  may be obtained, in terms of the usage introduced in Eq. (4), according to

$$(\mu_{\text{eff}}^{\text{pure}})^2 = \frac{a}{b}. \quad (7)$$

The total magnetic moment,  $\mu_{\text{eff}}^{\text{tot}}$ , which should compare to the experimentally determined value,  $\mu_{\text{eff}}^{\text{exp}}$ , will be, in general, the averaged sum of the contributions corresponding to Eq. (4) and Eq. (7) above, thus

$$(\mu_{\text{eff}}^{\text{exp}})^2 \approx (\mu_{\text{eff}}^{\text{tot}})^2 = (1 - \alpha) \frac{a}{C e^{\varepsilon/kT} + b} + \alpha (\mu_{\text{eff}}^{\text{pure}})^2 \quad (8)$$

where  $C$  will be discussed below.

If  $\mu_{\text{eff}}^{\text{exp}}$  is known, the energy separation,  $\varepsilon$ , may be calculated directly from Eq. (8), viz.

$$\varepsilon = kT \left\{ \ln \frac{(\mu_{\text{eff}}^{\text{pure}})^2 - (\mu_{\text{eff}}^{\text{exp}})^2}{(\mu_{\text{eff}}^{\text{exp}})^2 - \alpha (\mu_{\text{eff}}^{\text{pure}})^2} + \ln b - \ln C \right\}. \quad (9)$$

The quantity  $C$  denotes the ratio of the molecular vibrational partition functions,  $C = Q_A/Q_T$ ,  $Q_A$  referring to the  ${}^1A_1$  and  $Q_T$  to the  ${}^5T_2$  ground state. The corresponding ratio with respect to the  ${}^6A_1$  and  ${}^2T_2$  states was introduced by Ewald *et al.* [22] in a study of certain iron(III) tris(dialkyldithiocarbamate) complexes. The expected decrease of the Fe–S distance at the  ${}^6A_1 - {}^2T_2$  transition should affect the vibrational partition function and, indeed, such change was inferred from the pressure dependence of magnetism [22, 23]. At the  ${}^5T_2 - {}^1A_1$  crossover of *cis*-[Fe(bipy)<sub>2</sub>(NCS)<sub>2</sub>], the different Fe–N(bipy) distances were demonstrated *directly* employing single crystal x-ray methods [24]. Although thus the change in vibrational frequencies is well established [25], it will be shown below that a treatment of  $C$  as an adjustable parameter [17] is a questionable procedure.

### Numerical Procedures and Results

Preliminary calculations showed clearly that, in most compounds, an accurate numerical fit of the experimentally determined moments would be unsuccessful on the basis of constant values of  $\varepsilon$ . Therefore,  $\varepsilon$  was evaluated directly according to Eq. (9) at each temperature at which values of  $\mu_{\text{eff}}^{\text{exp}}$  are available. The general result may be summarized as follows: in practically all compounds studied,  $\varepsilon$  is temperature dependent, showing either a sharp increase in the region of decreasing  $\mu_{\text{eff}}^{\text{exp}}$  or a slight maximum at some intermediate temperature; finally, an almost linear increase in  $\varepsilon$  with decreasing temperature may be found.

If a fixed temperature is considered, both  $\mu_{\text{eff}}$  and  $\varepsilon$  are functions of the parameters  $\lambda$ ,  $\delta$ ,  $\kappa$ ,  $\alpha$ , and  $C$ , where  $\kappa$  is the Stevens' orbital reduction factor and where the other quantities were defined above. With respect to these parameters, two approaches were followed: (i) the effect on  $\varepsilon(T)$  of a variation in the parameter values was investigated; (ii) where possible, a set of reasonable values of the parameters was derived from the experimental  $\mu_{\text{eff}}(T)$  curves or from the  $\Delta E_Q$ -values in the  ${}^{57}\text{Fe}$  Mössbauer effect (*vide infra*).

The influence of a variation in  $\delta$ ,  $\kappa$ , and  $\alpha$  is illustrated in Fig. 2. According to these plots, a change in  $\delta$  shifts the  $\varepsilon(T)$  curve along the vertical axis by an amount corresponding approximately to the energy separation between the lowest component of the  ${}^5T_2$  and the  ${}^1A_1$  state (cf. Fig. 1). Although absolute values of  $\varepsilon$  may be influenced considerably, the overall shape of the curves remains essentially unchanged. The effect of a variation in  $\kappa$  and  $\alpha$  is almost negligible at low and high temperatures, respectively, and is not very significant at the other extreme. The shape of  $\varepsilon(T)$  is not markedly affected (cf. Fig. 2). The variation of  $\lambda$  was studied on [Fe(bipy)<sub>2</sub>(NCS)<sub>2</sub>], polymorph II, assuming  $\delta = 0$ ,  $\kappa = 0.80$ , and  $\alpha = 0.028$ . Again, the  $\varepsilon(T)$  curve is shifted slightly along the  $\varepsilon$ -axis. Thus, e.g., if  $\lambda = -102.5$ ,  $-90$ ,  $-80$ , and  $-70 \text{ cm}^{-1}$ , the maximum of  $\varepsilon$  obtains at  $173^\circ \text{K}$  and  $\varepsilon_{\text{max}} = 793$ ,  $762$ ,  $739$ , and  $716 \text{ cm}^{-1}$ , respectively.

The value of  $C$  enters Eq. (9) through the additive term  $-kT \ln C$  only. Thus a *linear* increase in  $\varepsilon$  with decreasing  $T$  may be counterbalanced by a suitable choice of  $C$  thus producing  $\varepsilon = \text{const}$ . However, due to the functional dependence between  $\varepsilon$  and  $C$ , there is no way to compensate, by a variation of  $C$ , for a pronounced maximum in  $\varepsilon(T)$ .

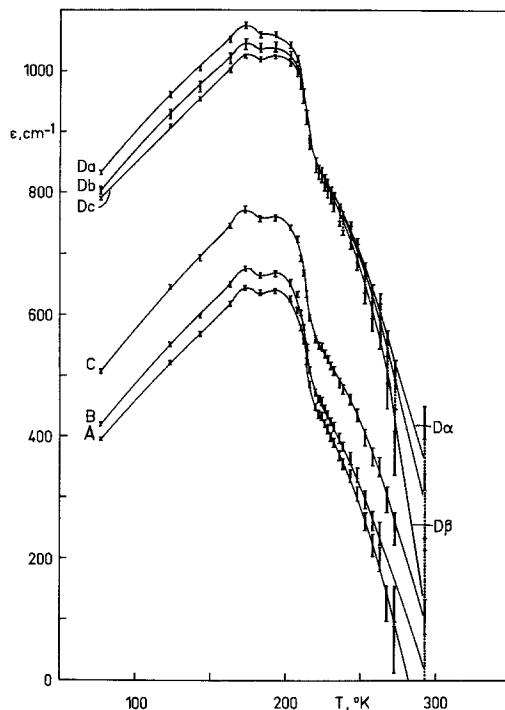


Fig. 2. Effect of parameter variation on the temperature dependence of  $\varepsilon$  in  $[\text{Fe}(\text{bipy})_2(\text{NCS})_2]$ , polymorph II. The parameter values employed are  $\lambda = -80 \text{ cm}^{-1}$ ,  $\kappa = 0.90$ , (A)  $\delta = 1000 \text{ cm}^{-1}$ ,  $\alpha = 0.026$ ; (B)  $\delta = 500 \text{ cm}^{-1}$ ,  $\alpha = 0.034$ ; (C)  $\delta = 0$ ,  $\alpha = 0.042$ ; (D)  $\delta = -500 \text{ cm}^{-1}$  ((a)  $\alpha = 0.042$ ; (b)  $\alpha = 0.021$ ; (c)  $\alpha = 0.0105$ ). In addition,  $\lambda = -80 \text{ cm}^{-1}$ ,  $\delta = -500 \text{ cm}^{-1}$ , (D $\alpha$ )  $\kappa = 1.00$ ,  $\alpha = 0.026$ ; (D $\beta$ )  $\kappa = 0.80$ ,  $\alpha = 0.028$ . The error bars correspond to an assumed experimental uncertainty of  $\pm 1\%$  in  $\mu_{\text{eff}}^{\text{exp}}$ . Dotted lines are used where error bars overlap

In order to investigate, in a semi-quantitative way, the function  $\varepsilon(T)$ , considerable simplifications may be introduced on the basis of the results quoted above. Thus we fix  $\lambda = -80 \text{ cm}^{-1}$  and treat  $\kappa$ , within the range  $\kappa = 1.0$  to  $\kappa = 0.80$ , as an adjustable parameter. Whenever possible, we will estimate values of  $\delta$  from  $\mu_{\text{eff}}^{\text{exp}}$  at temperatures sufficiently high *above* the temperature at which the crossover behaviour sets in [26]. In compounds where results of  ${}^{57}\text{Fe}$  Mössbauer effect studies are available, the theory of Golding [27] is applied to estimate  $\delta$  from the observed quadrupole splitting,  $\Delta E_Q$ .

The parameter  $\alpha$  is estimated from  $\mu_{\text{eff}}^{\text{exp}}$ -values *below* the temperature of the crossover. To this end, the moment values are extrapolated linearly to temperatures between  $150^\circ$  and  $1^\circ \text{ K}$ , depending on the range covered experimentally. It is assumed that, at the lower limit of extrapolation, the first term of Eq. (8) is determined by the temperature-independent paramagnetism (TIP) corresponding to  $\sim 0.10 \text{ BM}$  (for a different choice of TIP, *vide infra*). The effect on the results of small changes in the TIP amount is negligible.

In all compounds showing a sharp increase and/or a pronounced maximum in  $\varepsilon(T)$ , we fix  $C = 1.0$ . In compounds characterized by a linearly increasing  $\varepsilon$

with decreasing  $T$  or by a slight maximum in  $\varepsilon(T)$  we take, at first,  $C = 1.0$  and fit  $\varepsilon$ , by the method of least squares, to the linear relation

$$\varepsilon = A = mT + c. \quad (10)$$

Here we denote the first two terms of Eq. (9) as  $A$ . Secondly, we try to compensate for slope and curvature by relaxing the assumption  $C = 1.0$  and requesting that

$$\varepsilon = A - kT \ln C = c. \quad (11)$$

Thus from Eq. (10) and Eq. (11),

$$C = e^{m/k}. \quad (12)$$

The precision of each numerical fit is estimated on the basis of the sum of the squared deviations,

$$D = \sum_{i=1}^n (\mu_{\text{eff},i}^{\text{exp}} - \mu_{\text{eff},i}^{\text{calcd}})^2 \quad (13)$$

the sum being extended over all experimentally available temperatures. Obviously,  $D$  is equal for both procedures outlined, viz. Eq. (10) and Eq. (11) above.

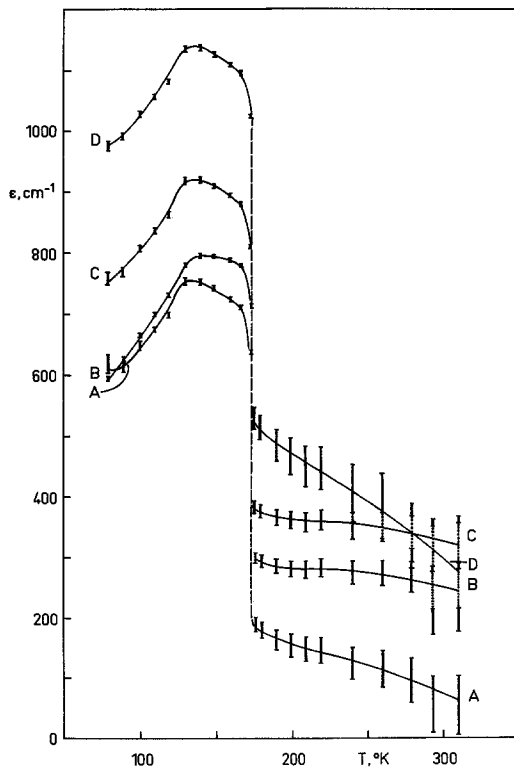


Fig. 3. Temperature dependence of  $\varepsilon$  in  $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ , polymorph (a). Parameter values employed are: (A)  $\delta = 500 \text{ cm}^{-1}$ ,  $\kappa = 0.90$ ,  $\alpha = 0.013$ ; (B)  $\delta = 0$ ,  $\kappa = 1.00$ ,  $\alpha = 0.008$ ; (C)  $\delta = -200 \text{ cm}^{-1}$ ,  $\kappa = 1.00$ ,  $\alpha = 0.012$ ; (D)  $\delta = -500 \text{ cm}^{-1}$ ,  $\kappa = 0.80$ ,  $\alpha = 0.013$  and always  $\lambda = -80 \text{ cm}^{-1}$ . For the significance of error bars, cf. Fig. 2



Specific results for the various compounds which were studied in detail, are presented below.

**[Fe(phen) $_2$ (NCS) $_2$ ], polymorph (a).** From the temperature dependence of  $\mu_{\text{eff}}^{\text{exp}}$  between 290° and 430° K, the estimates  $\delta = -880 \text{ cm}^{-1}$  and  $\kappa = 0.80$  were obtained. On the other hand,  $\Delta E_Q = 2.67 \text{ mm/sec}$  at 293° K [5] gives  $\delta$  between  $-450$  and  $-500 \text{ cm}^{-1}$ . Curves  $\varepsilon(T)$  were calculated using  $\delta$  between  $-500$  and  $+500 \text{ cm}^{-1}$  with  $\kappa = 1.00$  to  $\kappa = 0.80$ . According to Fig. 3 there is a sudden increase in  $\varepsilon$  at  $T_c = 174^\circ \text{ K}$  from, e.g.,  $\varepsilon = 530$  to  $\varepsilon = 1024 \text{ cm}^{-1}$  if  $\delta = -500 \text{ cm}^{-1}$  and  $\kappa = 0.80$  are assumed.

**[Fe(phen) $_2$ (NCS) $_2$ ], polymorph (b).** The same experimental parameters as for polymorph (a) apply here. Curves  $\varepsilon(T)$  were obtained using  $\delta$  between  $-500$  and  $+1000 \text{ cm}^{-1}$  with  $\kappa = 1.00$  to  $\kappa = 0.80$ . A TIP contribution of 0.64 BM was assumed on the basis of data from (a) [5, 6]. The general appearance is that of Fig. 3 with a somewhat less sharp rise in  $\varepsilon$  at  $T_c = 182^\circ \text{ K}$ . Thus, e.g.,  $\varepsilon$  increases from 655 to  $863 \text{ cm}^{-1}$  if  $\delta = -500 \text{ cm}^{-1}$  and  $\kappa = 0.80$  are assumed.

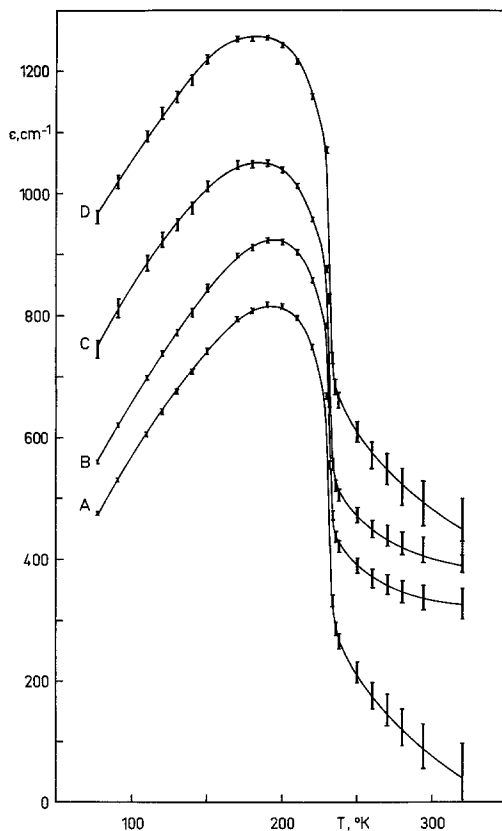


Fig. 4. Temperature dependence of  $\varepsilon$  in  $[\text{Fe}(\text{phen})_2(\text{NCSe})_2]$ , polymorph (a). Parameter values employed are: (A)  $\delta = 1000 \text{ cm}^{-1}$ ,  $\kappa = 0.80$ ,  $\alpha = 0.015$ ; (B)  $\delta = 0$ ,  $\kappa = 1.00$ ,  $\alpha = 0.014$ ; (C)  $\delta = -200 \text{ cm}^{-1}$ ,  $\kappa = 1.00$ ,  $\alpha = 0.021$ ; (D)  $\delta = -500 \text{ cm}^{-1}$ ,  $\kappa = 0.80$ ,  $\alpha = 0.023$  and always  $\lambda = -80 \text{ cm}^{-1}$ . For the significance of error bars, cf. Fig. 2

**[Fe(phen)<sub>2</sub>(NCSe)<sub>2</sub>], polymorph (a).** From the temperature dependence of  $\mu_{\text{eff}}^{\text{exp}}$  between 330° and 440° K,  $\delta = -1400 \text{ cm}^{-1}$  and  $\kappa = 0.80$  was previously derived [5]. With these parameter values, however, we were unable to reasonably fit the experimental data. On the other hand,  $\Delta E_Q = 2.52 \text{ mm/sec}$  at 293° K [5] provides the estimate of  $\delta = -400$  to  $-430 \text{ cm}^{-1}$ . Thus  $\varepsilon(T)$  was calculated employing values of  $\delta$  between  $-500$  and  $+1000 \text{ cm}^{-1}$  and  $\kappa = 1.00$  to  $\kappa = 0.80$ . A few examples are plotted in Fig. 4. There is again a sharp rise in  $\varepsilon$  at  $T_c = 232^\circ \text{ K}$  starting, e.g., at  $\varepsilon = 730$  and ending above  $\varepsilon = 1073 \text{ cm}^{-1}$  if  $\delta = -500 \text{ cm}^{-1}$  and  $\kappa = 0.80$  are used.

**[Fe(phen)<sub>2</sub>(NCSe)<sub>2</sub>], polymorph (b).** The same experimental values of  $\delta$  and  $\kappa$  and the same assumptions as for polymorph (a) apply here, except that a TIP contribution of 0.84 BM was taken into account (cf. polymorph (a) [5]). The results are similar to those of Fig. 4, although the rise in  $\varepsilon$  is less sharp covering the region 242° to 230° K ( $\varepsilon = 790$  to  $1042 \text{ cm}^{-1}$  if  $\delta = -500 \text{ cm}^{-1}$  and  $\kappa = 0.90$ ).

**[Fe(bipy)<sub>2</sub>(NCS)<sub>2</sub>], polymorph I.** Experimental magnetic data indicate  $\delta < 0$  [6] and, from  $\Delta E_Q$  at 293° K,  $\delta \sim -350 \text{ cm}^{-1}$  may be estimated. The general form of  $\varepsilon(T)$  is similar as above with a sharp increase in  $\varepsilon$  from 354 to  $976 \text{ cm}^{-1}$  at  $T_c = 216^\circ \text{ K}$  if  $\delta = -200 \text{ cm}^{-1}$  and  $\kappa = 1.00$ .

**[Fe(bipy)<sub>2</sub>(NCS)<sub>2</sub>], polymorph II.** Again  $\delta$  between  $-350$  and  $-400 \text{ cm}^{-1}$  is expected [6]. On the basis of the data from polymorph I, a TIP contribution of 0.93 BM was taken into account. Calculated  $\varepsilon(T)$  was obtained for a large range of the parameters  $\lambda$ ,  $\delta$ , and  $\kappa$ , viz. Fig. 2. There is a moderate rise in  $\varepsilon$ , e.g., from  $\sim 156 \text{ cm}^{-1}$  at 293° K to  $\varepsilon = 840 \text{ cm}^{-1}$  at 220° K followed by a sharp increase to  $1005 \text{ cm}^{-1}$  at 208° K if  $\delta = -500 \text{ cm}^{-1}$  and  $\kappa = 0.80$ .

**[Fe(bipy)<sub>2</sub>(NCS)<sub>2</sub>], polymorph III.** For the same reason as above, again  $\delta \sim -350 \text{ cm}^{-1}$  is expected and TIP of 0.93 BM is assumed [6]. The appearance of calculated  $\varepsilon(T)$ -curves is similar to polymorph I with a sharp rise of  $\varepsilon$  from  $390 \text{ cm}^{-1}$  to  $\sim 840 \text{ cm}^{-1}$  at  $T_c = 216^\circ \text{ K}$  ( $\delta = -200 \text{ cm}^{-1}$ ,  $\kappa = 1.0$ ).

**Iron(II) poly(1-pyrazolyl)borate I.** Employing the experimental data of Jesson *et al.* [11] and taking  $\lambda = -82 \text{ cm}^{-1}$ ,  $\delta = -1000 \text{ cm}^{-1}$ , and  $\kappa = 0.80$ ,  $\varepsilon$  is found to increase from  $657 \text{ cm}^{-1}$  at 300° K to  $1582 \text{ cm}^{-1}$  at 143° K, whereupon a decrease to  $\varepsilon = 1068 \text{ cm}^{-1}$  at 5.7° K is observed. Thus there is a very pronounced maximum of  $\varepsilon(T)$  at 143° K. This result is in sharp contrast to the claim of Jesson *et al.* [11] that the complete temperature variation can be reproduced by a linear relationship,  $\varepsilon = mT + c$ , where  $m = -1270$  and  $c = 5.25$ . At most, the increase between 300° and 143° K may be approximately fitted to the above relation with  $m = -7.267$  and  $c = 2786.7$  ( $D = 0.226$ ).

**[Fe(py)<sub>3</sub>]<sub>3</sub> Cl<sub>2</sub> · 2½ H<sub>2</sub>O.** It was realized previously by Dosser *et al.* [12] that values of  $\mu_{\text{eff}}^{\text{exp}}$  may be well reproduced by Eq. (3), provided a temperature dependent  $\varepsilon$  is assumed. This inference was verified ( $\delta = 0$ ,  $\kappa = 1.0$ ), the result being that  $\varepsilon$  rises from  $857 \text{ cm}^{-1}$  at 293° K to  $919 \text{ cm}^{-1}$  at 233° K and then decreases from 173° to 113° K where  $\varepsilon = 797 \text{ cm}^{-1}$ . However, based on  $\Delta E_Q = 2.30 \text{ mm/sec}$  at 293° K [12], a value of  $\delta$  between  $-350$  and  $-400 \text{ cm}^{-1}$  may be estimated. Using  $\delta = -400 \text{ cm}^{-1}$ ,  $\kappa = 0.80$ , and  $\alpha = 0.033$ ,  $\varepsilon$  increases from  $1046 \text{ cm}^{-1}$  at 293° K to  $1132 \text{ cm}^{-1}$  at 193° and then decreases to  $1006 \text{ cm}^{-1}$  at 113° K.

**[Fe(py)<sub>3</sub>]<sub>3</sub> (ClO<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>O.** Goodgame and Machado [13] reported recently that no reasonable fit of  $\mu_{\text{eff}}^{\text{exp}}$  between 341.7° and 85.7° K could be achieved on

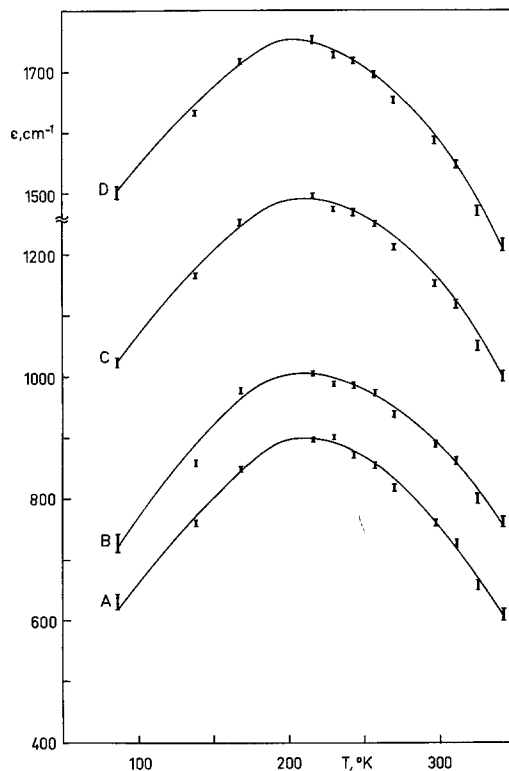


Fig. 5. Temperature dependence of  $\varepsilon$  in  $[\text{Fe}(\text{py})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ . Parameter values employed are: (A)  $\delta = 1000 \text{ cm}^{-1}$ ,  $\kappa = 0.80$ ,  $\alpha = 0.012$ ; (B)  $\delta = 0$ ,  $\kappa = 1.00$ ,  $\alpha = 0.011$ ; (C)  $\delta = -500 \text{ cm}^{-1}$ ,  $\kappa = 0.80$ ,  $\alpha = 0.012$ ; (D)  $\delta = -1000 \text{ cm}^{-1}$ ,  $\kappa = 0.80$ ,  $\alpha = 0.013$  and always  $\lambda = -80 \text{ cm}^{-1}$ ,  $C = 1.00$ . For the significance of error bars, cf. Fig. 2

the basis of Eq. (3) in conjunction with a constant value of  $\varepsilon$  between 800 and  $1000 \text{ cm}^{-1}$ . Indeed, according to Fig. 5,  $\varepsilon$  is strongly temperature dependent showing a pronounced maximum at  $210^\circ \text{ K}$ . Since  $\Delta E_Q \sim 2.0 \text{ mm/sec}$ ,  $\delta = -350 \text{ cm}^{-1}$  may be estimated. For comparison, if  $\delta = -500 \text{ cm}^{-1}$ ,  $\varepsilon$  rises from  $1000 \text{ cm}^{-1}$  at  $342^\circ \text{ K}$  to  $1300 \text{ cm}^{-1}$  at  $217^\circ$  and then decreases to  $\varepsilon = 1023 \text{ cm}^{-1}$  at  $85.7^\circ \text{ K}$ .

**$[\text{Fe}(\text{mphen})_3](\text{ClO}_4)_2$ .** Unfortunately, magnetic data on this and the following compounds do not extend to sufficiently high temperatures to obtain estimates of  $\delta$  and  $\kappa$  therefrom. On the basis of  $\Delta E_Q = 1.02 \text{ mm/sec}$  at  $298^\circ \text{ K}$  [10], it should be either  $\delta = -200 \text{ cm}^{-1}$  or  $\delta = +250 \text{ cm}^{-1}$ . In addition, the Mössbauer spectrum suggests a high portion of permanently paramagnetic material, *viz.*  $\alpha = 0.273$ . With this value of  $\alpha$ ,  $\delta = 0$ , and  $\kappa = 1.00$ ,  $\varepsilon$  is an almost linear function of temperature,  $\varepsilon = mT + c$  where  $m = -2.263$  and  $c = 810.9$  ( $D = 0.033$ ). In this case,  $C$  may be computed according to Eq. (12) as  $C = 0.0386$  to yield a good fit with the constant value of  $\varepsilon = 810.9 \text{ cm}^{-1}$ , cf. Fig. 6. Similar results are obtained if different estimates of  $\delta$  and  $\kappa$  are introduced.

**$[\text{Fe}(\text{mphen})_3](\text{BF}_4)_2$ .** With  $\Delta E_Q = 1.02 \text{ mm/sec}$  at  $298^\circ \text{ K}$  [10], the situation is similar to that in the previous compound. Assuming  $\delta = 0$ ,  $\kappa = 1.00$ , and taking,

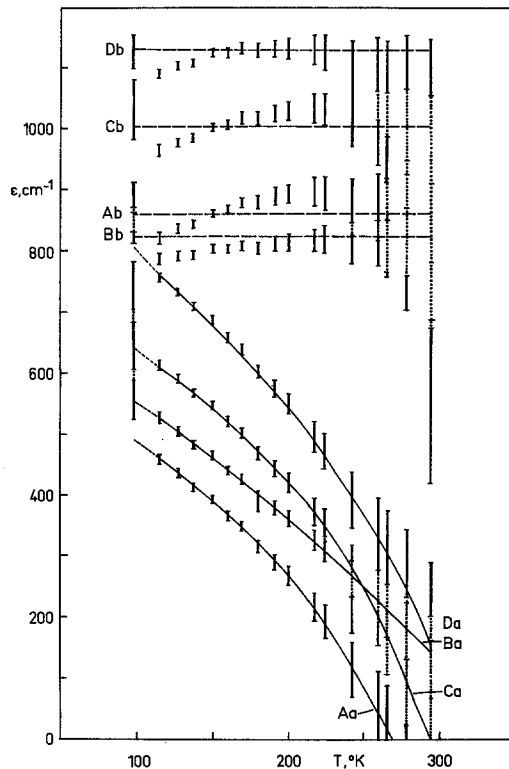


Fig. 6. Temperature dependence of  $\varepsilon$  in  $[\text{Fe}(\text{mphen})_3](\text{ClO}_4)_2$ . Parameter values employed are: (Aa)  $\delta = 300 \text{ cm}^{-1}$ ,  $\kappa = 0.90$ ,  $\alpha = 0.284$ ,  $C = 1.00$ ; (Ab) same but  $C = 0.0110$ ; (Ba)  $\delta = 0$ ,  $\kappa = 1.00$ ,  $\alpha = 0.273$ ,  $C = 1.00$ ; (Bb) same but  $C = 0.0386$ ; (Ca)  $\delta = -200 \text{ cm}^{-1}$ ,  $\kappa = 0.90$ ,  $\alpha = 0.287$ ,  $C = 1.00$ ; (Cb) same but  $C = 0.0125$ ; (Da)  $\delta = -400 \text{ cm}^{-1}$ ,  $\kappa = 1.00$ ,  $\alpha = 0.289$ ,  $C = 1.00$ ; (Db) same but  $C = 0.0150$  and always  $\lambda = -80 \text{ cm}^{-1}$ . For the significance of error bars, cf. Fig. 2

in agreement with Mössbauer spectra,  $\alpha = 0.320$ , an almost linear dependence of  $\varepsilon$  on  $T$  results. Again, calculated  $C = 0.0319$  produces a good fit of the data with constant  $\varepsilon = 762.2 \text{ cm}^{-1}$  ( $D = 0.028$ ).

**$[\text{Fe}(\text{mphen})_3](\text{PF}_6)_2$  (I) and  $[\text{Fe}(\text{mphen})_3]\text{I}_2$  (II).** Only slight curvature of  $\varepsilon(T)$  again is observed and thus  $C$  may be obtained to yield the best fit with  $\varepsilon = \text{const}$ . In I, e.g.,  $\delta = 500 \text{ cm}^{-1}$ ,  $\kappa = 0.90$ ,  $\alpha = 0.491$ , and  $C = 0.0613$  produces  $\varepsilon = 616.1 \text{ cm}^{-1}$  ( $D = 0.045$ ), whereas in II,  $\delta = 500 \text{ cm}^{-1}$ ,  $\kappa = 0.90$ ,  $\alpha = 0.474$ , and  $C = 0.5392$  give constant  $\varepsilon = 418.1 \text{ cm}^{-1}$  ( $D = 0.008$ ).

**$[\text{Fe}(\text{pythiaz})_2](\text{ClO}_4)_2$ .** There is the beginning of a curvature in  $\varepsilon(T)$  at the lowest temperatures investigated. However,  $\varepsilon = mT + c$  is again a good approximation. The best fit is achieved if  $\delta = 0$ ,  $\kappa = 0.90$ , and  $\alpha = 0.376$  is used, whereupon  $m = -2.092$  and  $c = 758.9$  are obtained. Adjusting to  $C = 0.0493$  produces a fit with constant  $\varepsilon = 758.9 \text{ cm}^{-1}$  ( $D = 0.005$ ).

**$[\text{Fe}(\text{papt})_2]$ .** In this compound, a pronounced curvature in  $\varepsilon(T)$  is observed. Thus if  $\delta = -500 \text{ cm}^{-1}$ ,  $\kappa = 0.80$ , and  $\alpha = 0.079$ ,  $\varepsilon$  increases from  $430 \text{ cm}^{-1}$  at  $340^\circ \text{ K}$  to  $892 \text{ cm}^{-1}$  at  $171^\circ$  and then stays almost constant down to  $94^\circ \text{ K}$ .

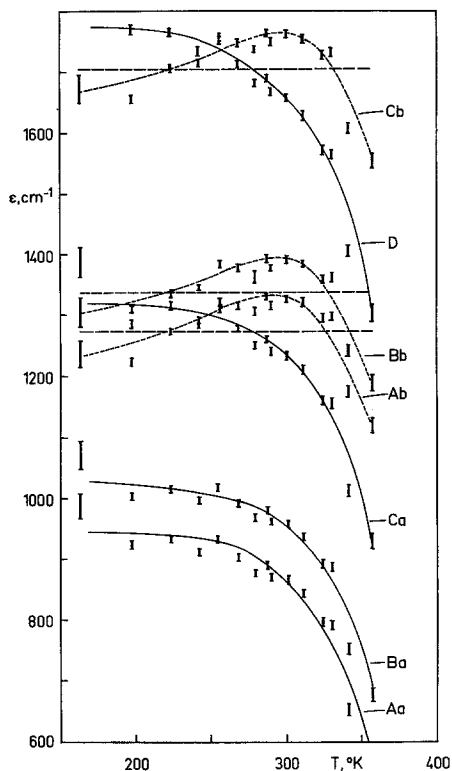


Fig. 7. Temperature dependence of  $\epsilon$  in  $[\text{Fe}(\text{paptH})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ . Parameter values employed are: (Aa)  $\delta = 500 \text{ cm}^{-1}$ ,  $\kappa = 1.00$ ,  $\alpha = 0.027$ ,  $C = 1.00$ ; (Ab) same but  $C = 0.1098$ ; (Ba)  $\delta = 0$ ,  $\kappa = 1.00$ ,  $\alpha = 0.026$ ,  $C = 1.00$ ; (Bb) same but  $C = 0.1266$ ; (Ca)  $\delta = -500 \text{ cm}^{-1}$ ,  $\kappa = 1.00$ ,  $\alpha = 0.029$ ,  $C = 1.00$ ; (Cb) same but  $C = 0.0807$ ; (D)  $\delta = -1000 \text{ cm}^{-1}$ ,  $\kappa = 0.80$ ,  $\alpha = 0.033$ ,  $C = 1.00$  and always  $\lambda = -80 \text{ cm}^{-1}$ . For the significance of error bars, cf. Fig. 2

Fitting to a linear relationship gives unsatisfactory results and the same applies, *a fortiori*, to a variation of  $C$ . Similar results are obtained if different parameter values are chosen.

**$[\text{Fe}(\text{paptH})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ .** The  $\mu_{\text{eff}}^{\text{exp}}$  values of this and the following compounds were previously fitted by Harris and Sinn [17] to an expression similar to Eq. (3) using a trial and error procedure. Specifically it was claimed that, in  $[\text{Fe}(\text{paptH})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , the parameter values  $\delta = 0$ ,  $\kappa = 1.0$ ,  $\alpha = 0.0297$ ,  $C = 0.07$ , and  $\epsilon = 1500 \text{ cm}^{-1}$ <sup>2</sup> should provide a reasonable agreement with experiment. However, inspection of Fig. 7 reveals a considerable temperature dependence of  $\epsilon$  which is increasing from, e.g.,  $678 \text{ cm}^{-1}$  at  $357^\circ$  to  $1072 \text{ cm}^{-1}$  at  $163^\circ \text{ K}$  if  $\delta = 0$ ,  $\kappa = 1.00$ ,  $\alpha = 0.026$ , and  $C = 1.00$  are assumed. If the computed value  $C = 0.1266$  is applied,  $\epsilon$  still varies between  $1190 \text{ cm}^{-1}$  at  $357^\circ$  and  $1393 \text{ cm}^{-1}$  at  $287^\circ \text{ K}$ .

**$[\text{Fe}(\text{paptH})_2](\text{NCS})_2 \cdot \text{H}_2\text{O}$ .** In close analogy to the above compound, there is a pronounced temperature dependence of  $\epsilon$  which is monotonically increasing

<sup>2</sup> It should be observed that there are serious misprints in Table II of [17] which should read in the last column marked  $C$  (from top to bottom): 0.02; 0.024; 0.07; 0.08; 0.07; 0.15 [28].

with lowering of  $T$  from, e.g.,  $545\text{ cm}^{-1}$  at  $370^\circ$  to  $1143\text{ cm}^{-1}$  at  $136^\circ\text{ K}$  if  $\delta = -500\text{ cm}^{-1}$ ,  $\kappa = 0.80$ ,  $\alpha = 0.173$ , and  $C = 1.00$  are assumed. If the computed  $C = 0.0332$  is used,  $\varepsilon$  varies between  $1425$  and  $1532\text{ cm}^{-1}$ . Similar results obtain if different values of the parameters are used. This behaviour is again in contrast to the claimed [17] fit using  $\delta = 0$ ,  $\kappa = 1.00$ ,  $\alpha = 0.165$ ,  $C = 0.07$ , and a constant  $\varepsilon = 1100\text{ cm}^{-1}$ .

**[Fe(paptH)<sub>2</sub>]Br<sub>2</sub>·2H<sub>2</sub>O.** In this compound, there exists an almost linear increase of  $\varepsilon$  with decreasing  $T$ . Thus, if, e.g.,  $\delta = -500\text{ cm}^{-1}$ ,  $\kappa = 0.80$ ,  $\alpha = 0.026$ , and  $C = 1.00$ , a fit to  $\varepsilon = mT + c$  yields  $m = -4.610$  and  $c = 3002.1$ . The computation gives  $C = 0.0013$ , and thus a constant  $\varepsilon = 3002.1\text{ cm}^{-1}$  obtains ( $D = 0.039$ ). The result for  $\delta = 0$ , i.e.  $\kappa = 0.80$ ,  $\alpha = 0.025$ ,  $C = 0.0018$ ,  $\varepsilon = 2657.5\text{ cm}^{-1}$  is in fair agreement with Harris and Sinn [17] who report  $\kappa = 1.00$ ,  $\alpha = 0$ ,  $C = 0.02$ , and  $\varepsilon = 2010\text{ cm}^{-1}$ . However, a recalculation with the accurate values of the parameters from [17] yields  $D = 0.419$  which is rather discouraging. In addition, it is more accurately  $\varepsilon = 1821.3\text{ cm}^{-1}$ . As for an appraisal of the adjustment of  $C$ , *vide infra*.

### General Results and Conclusions

In most compounds where  $\varepsilon$  is fitted to a linear relationship, there is one set of parameter values which affords the minimum value of  $D$ . These values are, in general, those which are listed above. However, the accuracy of these parameters is suspect, since often there are several other parameter sets providing adequate agreement between theory and experiment with insignificantly larger  $D$ . The uncertainty involved is the amount of the experimental error which, rarely listed in the original papers, was assumed here rather optimistically to be  $\pm 1\%$ . The error bars drawn in Fig. 2 to 7 are based on this assumption.

Thus, in general, the attempt at determination of *unique* values of the parameters involved seems to be successful only with recourse to methods other than magnetism, *viz.*, e.g., the Mössbauer effect. Another limitation of this approach is the assumption of temperature-independent values of  $\delta$  and  $\kappa$ .

In a qualitative way, the most useful result of the present study seems to be that of the temperature dependence of  $\varepsilon$ . With respect to the latter, the compounds may be divided into several groups:

i) In bis(diimine) complexes such as [Fe(phen)<sub>2</sub>(NCS)<sub>2</sub>], there is a sharp increase of  $\varepsilon$  at the temperature  $T_c$ . Generalizing x-ray structure results which were obtained [24] on [Fe(bipy)<sub>2</sub>(NCS)<sub>2</sub>], polymorph II, and applying the consequences of calculated ionic radii [29], it is expected that, in each one of these compounds, the metal-ligand separation (and thus, to some extent, the molecular geometry) will be different in the  $^5T_2(t_2^4 e^2)$  and  $^1A_1(t_2^6)$  ground states. Consequently, each of the ground states is characterized by a separate value of  $\varepsilon$ . The change of  $\varepsilon$  at  $T_c$  is *sharp*, since the transition is occurring within the narrow range of  $3^\circ$  to  $13^\circ\text{ K}$ . A crystallographic phase change was ruled out [24] and thus the transition may be considered as a *second-order phase transition*.

ii) In the complexes [Fe(mphen)<sub>3</sub>]X<sub>2</sub>, where X = ClO<sub>4</sub>, BF<sub>4</sub>, and PF<sub>6</sub>, in [Fe(pythiaz)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub>, and in [Fe(paptH)<sub>2</sub>]Br<sub>2</sub>·2H<sub>2</sub>O, there is an almost linear increase of  $\varepsilon$  with decreasing temperature. The nature of the change is

clearly established as a  ${}^5T_2 - {}^1A_1$  transition. Consequently, it is to be assumed that metal-ligand separations in the two states will be different (cf. (i) above) and, therefore, an increase in  $\varepsilon$  is expected. The change in  $\varepsilon$  is *gradual*, since the transition is taking place over an extended range of temperature. The situation may thus be considered as a *spin-state equilibrium*.

It was demonstrated above that, by an adjustment of  $C$  according to Eq. (12), the linear increase of  $\varepsilon$  with decreasing temperature may be changed into a behaviour characterized by  $\varepsilon = \text{const}$ . Although, in actual fact,  $C$  may be different from 1.00, the treatment of  $C$  as an adjustable parameter which was applied to several compounds by Harris and Sinn [17] seems to be of questionable physical value. Such a procedure contradicts the expected change of, e.g., the metal-ligand distances within the complex which affects  $\varepsilon$  directly and which cannot, in other compounds (*viz.* (i) above), be compensated by adjustment of  $C$ .

iii) This final group collects examples of intermediate or, in some respect, incompletely characterized behaviour. Thus in the hydrotris (pyrazol-1-yl)borate iron(II) complex, there is a pronounced maximum in  $\varepsilon(T)$ , although the increase in  $\varepsilon$  is gradual. A similar behaviour is encountered in  $[\text{Fe}(\text{pyi})_3]\text{Cl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$  and  $[\text{Fe}(\text{pyi})_3](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ , whereas in  $[\text{Fe}(\text{papt})_2]$ ,  $[\text{Fe}(\text{paptH})_2](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$  and  $[\text{Fe}(\text{paptH})_2](\text{NCS})_2 \cdot \text{H}_2\text{O}$  the maximum occurs at the lower end of the experimentally studied temperature range. In these compounds, the dependence of  $\varepsilon$  on  $T$  has been often not or incorrectly recognized [11, 13, 17]. However, the behaviour is essentially that of group (ii), since, at higher temperatures, an almost linearly increasing  $\varepsilon$  precedes the observed maximum and since, in group (ii) compounds at low temperature, it may be expected that the slope of  $\varepsilon(T)$  will change in sign producing a maximum. The definite clarification of these more subtle points would be considerable eased by an extension of the magnetic measurements to higher and/or lower temperatures.

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