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Elastic interaction of high-spin and low-spin complex molecules in spin-crossover compounds: II

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Abstract. Several transition-metal compounds show a transition from the low-spin to the high-spin electronic state with increasing temperature. The cooperative nature of the transition in the solid state is attributed to the elastic interaction between the spin-changing ions as a result of the deformation of the crystal accompanying the transition. In a previous work the long range part of the elastic interaction due to the image pressure on a spherical surface was treated. In this work the elastic energy originating from the direct elastic interaction between the high-spin and low-spin complex molecules randomly distributed over the lattice sites is computed. The crystal is considered as an isotropic homogeneous elastic medium with the spin-changing ions as point defects described by elastic dipole tensors $\mathbf{P}^{HS}$ and $\mathbf{P}^{LS}$, respectively. The interaction depends on the components of the tensor difference $\mathbf{P}^{HL} = \mathbf{P}^{HS} - \mathbf{P}^{LS}$ which are unequivocally determined based on the x-ray data of the compounds $[Fe(2\text{-pic})_3]\ Cl_2 \cdot Sol$ (2-pic = 2-aminomethylpyridine, Sol = MeOH, EtOH). Collecting both contributions (the image and the direct part) the value of the interaction constant Γ can be explained in a consistent way for both compounds.

1. Introduction

The phenomenon of thermally induced high spin (HS) low $\rightleftharpoons$ spin (LS) transition in transition-metal compounds, particularly iron (II) complexes, is still the object of various experimental and theoretical investigations. The transition is usually described by the fraction γ of molecules in the HS state. The fraction γ is a function of temperature T. A large variety of transition curves $\gamma(T)$ have been observed (Ewald *et al* 1969, Haddad *et al* 1981, Gütlich 1981, 1984, König 1987). The $\gamma(T)$ curves measured in crystalline solids deviate from a Boltzmann population of the HS and LS energy levels of the spin-changing ions. The intensive studies on mixed-crystal systems, especially on the compounds $[Fe_xM_{1-x}(2\text{-pic})_3]X_2 \cdot Sol$ (M = Co, Zn; X = Cl, Br; Sol = MeOH, EtOH) (Adler *et al* 1987, Sanner *et al* 1984, Köppen *et al* 1982) and the corresponding deuterated compounds (Jakobi *et al* 1988, Meissner 1984) have been very successful in discovering the interaction mechanism responsible for the HS $\rightleftharpoons$ LS transition. In these systems the distances between the interacting spin-changing ions have been varied by replacing part of them by other transition-metal ions M without changing the structure of the crystal.

The main features of the spin-transition behaviour in solid compounds are well described by a Gibbs free energy $G(\gamma, p, T)$ which is a sum of two parts, the free energy $G_0(\gamma, p, T)$ of the isolated non-interacting ions ($x \rightarrow 0$) and an interaction part G_{int}

which has been parametrised as

$$G_{\text{int}} = \gamma\Delta(x) - \gamma^2\Gamma(x). \tag{1.1}$$

In order to relate the parameters Δ and Γ to the crystal properties, Spiering *et al* (1982) and Willenbacher and Spiering (1988) in more detail have discussed the elastic interaction between the HS and the LS ions via the image pressure (Eshelby 1954, 1956). The starting point of all considerations is the observed volume change and deformation of the lattice accompanying the transition of the ions from the LS to the HS state. Microscopically, an increase of the Fe–N bond lengths of about 10% is observed by x-ray studies (Mikami 1980, Wiehl 1986) on going from the LS state to the HS state. This situation has been approximated by point defects representing the spin-changing ions which are embedded in an isotropic homogeneous elastic medium characterised by elastic moduli K and σ representing the lattice.

In our previous work (Willenbacher *et al* 1988) we have treated the interaction of three tyes of point defects with dipole tensors $\mathbf{P}^{\text{M}}$, $\mathbf{P}^{\text{HS}}$ and $\mathbf{P}^{\text{LS}}$ randomly distributed over a sphere. All complexes (HS, LS and other metal complexes M) are taken as defects even in the case of a lattice of only one species. The shape of a fictitious complex with vanishing tensor-$\mathbf{P}$ leading to the minimum elastic energy of the lattice is introduced to simplify the description of the system. The measured quantities as the deformtion tensor $\boldsymbol{\varepsilon}_{\text{c}}$ of the crystal and the interaction constant Γ depend on differences of the tensors $\mathbf{P}^{\nu}$ so that the fictitious reference system drops out of the relevant equations. The deformation tensor differences $\boldsymbol{\varepsilon}_{\text{c}}^{\text{HL}} = \boldsymbol{\varepsilon}_{\text{c}}^{\text{HS}} - \boldsymbol{\varepsilon}_{\text{c}}^{\text{LS}}$, $\boldsymbol{\varepsilon}_{\text{c}}^{\text{ML}} = \boldsymbol{\varepsilon}_{\text{c}}^{\text{M}} - \boldsymbol{\varepsilon}_{\text{c}}^{\text{LS}}$ and $\boldsymbol{\varepsilon}_{\text{c}}^{\text{MH}} = \boldsymbol{\varepsilon}_{\text{c}}^{\text{M}} - \boldsymbol{\varepsilon}_{\text{c}}^{\text{LH}}$ are obtained from x-ray measurements (Wiehl *et al* 1986). The relation between the lattice deformation tensor $\boldsymbol{\varepsilon}_{\text{c}}^{\nu}$ and the dipole tensor $\mathbf{P}^{\nu}$ of N defects homogeneously distributed over a crystal with volume V_{a} is given by

$$\varepsilon_{\text{c,s}}^{\nu} = 3NV_{\text{a}}^{-1}(3\lambda + 2\mu)^{-1}P_{\text{s}}^{\nu} \qquad \varepsilon_{\text{c},M}^{\nu} = NV_{\text{a}}^{-1}(2\mu)^{-1}P_{M}^{\nu} \tag{1.2}$$

where $\varepsilon_{\text{c,s}} = \varepsilon_{\text{c},xx} + \varepsilon_{\text{c},yy} + \varepsilon_{\text{c},zz}$ (the superscript ν is dropped) is the trace of the Cartesian tensor $\varepsilon_{\text{c},ik}$; $i, k = x, y, z$ and $\varepsilon_{\text{c},M}$ are the spherical components of the traceless part $\boldsymbol{\varepsilon}_{\text{c,d}}$

$$\begin{aligned} &\varepsilon_{\text{c},0} = (1/\sqrt{6})(2\varepsilon_{\text{c},zz} - \varepsilon_{\text{c},xx} - \varepsilon_{\text{c},yy}) \qquad \varepsilon_{\text{c},\pm1} = \mp(\varepsilon_{\text{c},xz} \pm \text{i}\varepsilon_{\text{c},yz}) \\ &\varepsilon_{\text{c},\pm2} = \tfrac{1}{2}(\varepsilon_{\text{c},xx} - \varepsilon_{\text{c},yy}) \pm \text{i}\varepsilon_{\text{c},xy}. \end{aligned} \tag{1.3}$$

The Lamé coefficients λ and μ are related to the bulk modulus K and Poisson ratio σ by $K = \frac{1}{3}(3\lambda + 2\mu)$ and $\sigma = \frac{1}{2}\lambda/(\lambda + \mu)$. The strength of an elastic dipole is therefore characterised by six parameters: P_{s} and P_M ($M = -2, -1, 0, 1, 2$). The average tensor of a concentration x of spin-changing ions, a fraction γ of which are in the HS state and a concentration $(1 - x)$ of metal ions M is given by

$$\bar{P}_{\alpha} = x\gamma P_{\alpha}^{\text{HS}} + x(1-\gamma)P_{\alpha}^{\text{LS}} + (1-x)P_{\alpha}^{\text{M}} \qquad \alpha = \text{s}, M. \tag{1.4}$$

Taking into account only the image pressure of the spin-changing ions the interaction constant $\Gamma(x)$ and the parameter $\Delta(x)$ of the interaction part G_{int}, equation (1.1), of the Gibbs free energy $G(\gamma, p, T)$ could be expressed by the tensor components $\varepsilon_{\text{c,s}}^{\nu}$ and $\varepsilon_{\text{c,M}}^{\nu}$ (ν = HL, ML). The parameters are proportional to the concentration x of the spin changing ions so that we could write (subscript im stands for image pressure) $\Gamma(x) = x\Gamma_{\text{im}}$ and $\Delta(x) = x\Delta_{\text{im}}$ with

$$\Gamma_{\text{im}}/K = \tfrac{1}{2}V_{\text{c}}(\gamma_0 - 1)\gamma_0^{-1}[(\boldsymbol{\varepsilon}_{\text{c,s}}^{\text{HL}})^2 + \tfrac{3}{10}(2\gamma_0 + 1)(\boldsymbol{\varepsilon}_{\text{c},d}^{\text{HL}}\boldsymbol{\varepsilon}_{\text{c},d}^{\text{HL}})_{\text{s}}] \tag{1.5a}$$

$$\Delta_{\text{im}}/K = V_{\text{c}}(\gamma_0 - 1)\gamma_0^{-1}[\boldsymbol{\varepsilon}_{\text{c,s}}^{\text{HL}}\varepsilon_{\text{c,s}}^{\text{ML}} + \tfrac{3}{10}(2\gamma_0 + 1)(\boldsymbol{\varepsilon}_{\text{c,d}}^{\text{HL}}\boldsymbol{\varepsilon}_{\text{c,d}}^{\text{ML}})_{\text{s}}] \tag{1.5b}$$

$V_{\text{c}} = V_{\text{a}}/N$ is the volume per complex molecule. $(\boldsymbol{\varepsilon}^{\text{a}}\boldsymbol{\varepsilon}^{\text{b}})_{\text{s}} = \sum_m \boldsymbol{\varepsilon}_m^{\text{a}*}\boldsymbol{\varepsilon}_m^{\text{b}}$ denotes the

invariant of the product of two tensors $\boldsymbol{\varepsilon}^{a}$, $\boldsymbol{\varepsilon}^{b}$ and $\gamma_0 = 3(1-\sigma)/(1+\sigma)$ is the Eshelby constant.

This interaction Γ compares quite well with the experimental values at first sight. A close inspection however shows that the range of the interaction constant Γ does not completely cover the measured values for reasonable elastic constants K and σ of these compounds (Willenbacher *et al* 1988). In order to complete the theory of elastic interaction and hopefully improve the agreement with the experimental values the calculation of the direct interaction between the dipoles has become necessary.

The separation of the interaction in an image part resulting from a stress-free boundary and a direct part which is calculated summing over all pairs of dipoles embedded in a boundary-free infinite medium is a separation in a long (infinite) range and a 'short' range (R^{-3}) part. The long-range behaviour of the image pressure does not give rise to clustering effects on the microscopic scale. Therefore it is the average dipole tensor which enters the equations of the elastic energy of the crystal. From Mössbauer, susceptibility, or x-ray measurements there is indeed no hint at such clustering for the compounds under consideration. For the calculation of the short range part of the interaction in this paper we assume that the random distribution of defects is preserved by this interaction. We start with the elastic energy expression (Shuey *et al* 1969) of two arbitrary dipole defects $\mathbf{P}^{a}$ and $\mathbf{P}^{b}$ in an infinite medium separated by the distance R. One lies on the origin of the coordinate system and the second on the z axes at $z = R$

$$E^{\infty}_{\text{int}} = (1/4\pi R^3)[1/(\lambda+2\mu)]\{\sqrt{6}(P^{a}_0 P^{b}_s + P^{b}_0 P^{a}_s) + [(4\mu+3\lambda)/\mu]P^{a}_0 P^{b}_0 - (2\mu+3\lambda)/2\mu(P^{a}_1 P^{b*}_1 + P^{a}_{-1}P^{b*}_{-1}) - (P^{a}_2 P^{b*}_2 + P^{a}_{-2}P^{b*}_{-2})\}. \tag{1.5}$$

This equation will be generalised for arbitrary positions of the second defect in § 2. Then the summation procedure used for a computer calculation will be described in § 3. The deformation tensors as obtained from x-ray measurements are taken from our previous paper. In § 4 it is shown that all components of the dipole tensor difference $\mathbf{P}^{\text{HL}}$ of the complex molecule $[\text{Fe(2-pic)}_3]^{2+}$ can be unequivocally determined from the deformation tensors of the two compounds under consideration so that the direct interaction can be calculated as a function of the elastic constants. The total interaction constant Γ and the energy shift Δ which can also be estimated are compared with experimental results in § 5.

2. Elastic energy of point defects in an infinite medium

In order to generalise the geometrical situation of the defects leading to (1.5) we change the coordinate system from system S′ to system S. The vector $\boldsymbol{R} = R\boldsymbol{e}_{z'}$ points from defect (a) located at the origin to defect (b). With respect to the coordinate system S which is rotated by the Euler angles $\boldsymbol{\beta} = (\alpha, \beta, \gamma)$ onto the system S′ the dipole tensor components P'_N are expressed in terms of P_M by means of the Wigner rotation matrix, $P'_N = \Sigma P_M D^2_{MN}(\boldsymbol{\beta})$, so that (1.5) reads

$$E^{\infty}_{\text{int}} = \frac{1}{4\pi R^3}\frac{1}{\lambda+2\mu}\Bigg[\sqrt{6}\sum_M (P^{a}_M P^{b}_s + P^{b}_M P^{a}_s)D^2_{M0} + \sum_{MM'}\Bigg(\frac{4\mu+3\lambda}{\mu}D^2_{M0}D^{2*}_{M'0} - \frac{2\mu+3\lambda}{2\mu}(D^2_{M1}D^{2*}_{M'1} + D^2_{M,-1}D^{2*}_{M',-1}) - (D^2_{M2}D^{2*}_{M'2} + D^2_{M,-2}D^{2*}_{M',-2})\Bigg)P^{a}_M P^{b*}_{M'}\Bigg]. \tag{2.1}$$

Using the expansion series of the product of two Wigner rotation matrices, the interaction energy is finally written as

$$E^{\infty}_{\text{int}}(\boldsymbol{R}) = \sum_{M} (P^{\text{a}}_{M}\mathbf{V}(\boldsymbol{R})_{M}P^{\text{b}}_{\text{s}} + P^{\text{b}}_{M}\mathbf{V}(\boldsymbol{R})_{M}P^{\text{a}}_{\text{s}}) + \sum_{MM'} P^{\text{a}}_{M}\mathbf{W}(\boldsymbol{R})_{MM'}P^{\text{b}*}_{M'}$$
$$= \mathbf{P}^{\text{a}}\mathbf{V}(\boldsymbol{R})P^{\text{b}}_{\text{s}} + P^{\text{a}}_{\text{s}}\mathbf{V}(\boldsymbol{R})^{+}\mathbf{P}^{\text{b}+} + \mathbf{P}^{\text{a}}\mathbf{W}(\boldsymbol{R})\mathbf{P}^{\text{b}+} \tag{2.2}$$

$$\mathbf{V}(\boldsymbol{R})_{M} = [1/(\lambda + 2\mu)]\mathbf{V}(\boldsymbol{R})^{2}_{M} \tag{2.3a}$$

$$\mathbf{W}(\boldsymbol{R})_{MM'} = [1/(\lambda + 2\mu)]\{-[(10\mu + 3\lambda)/7\mu]\mathbf{W}(\boldsymbol{R})^{2}_{MM'} + [18(\mu + \lambda)/7\mu]\mathbf{W}(\boldsymbol{R})^{4}_{MM'}\}. \tag{2.3b}$$

The tensors $\mathbf{V}(\boldsymbol{R})^{2}_{M}$, $\mathbf{W}(\boldsymbol{R})^{2}_{MM'}$ and $\mathbf{W}(\boldsymbol{R})^{4}_{MM'}$ are independent of the elastic constants λ and μ

$$\mathbf{V}(\boldsymbol{R})^{2}_{M} = (1/4\pi R^{3})\sqrt{6}C^{*}_{2M} \qquad C_{kM} = \sqrt{[4\pi/(2k+1)]}Y_{kM}$$
$$\mathbf{W}(\boldsymbol{R})^{2}_{MM'} = \frac{1}{4\pi R^{3}}(-1)^{M}\sqrt{\frac{35}{2}}\begin{pmatrix}2 & 2 & 2\\ M & -M & M'-M\end{pmatrix}C^{*}_{2M,-M'} \tag{2.4}$$
$$\mathbf{W}(\boldsymbol{R})^{4}_{MM'} = \frac{1}{4\pi R^{3}}(-1)^{M}\sqrt{\frac{35}{2}}\begin{pmatrix}2 & 2 & 2\\ M & -M & M'-M\end{pmatrix}C^{*}_{4M,-M'}.$$

The $Y(\boldsymbol{R})_{kM}$ are the spherical harmonics. The interaction does not depend on an inversion of the direction of $\boldsymbol{R}$ (interchanging defects a and b). This behaviour is guaranteed by the even k-values of the spherical harmonics. The rotation around the z' axes by the Euler angle γ does also not change the interaction energy. The spherical harmonics depend only on the angle α and β.

Hirsekorn and Siems (1981) gave general formulae for the interaction of point defects at positions $\boldsymbol{r}$ and $\boldsymbol{r}'$ in an infinite medium (equation (3.11) therein) and the image interaction in a finite medium of spherical shape (equation (4.18)). We were not able to reduce their general equation (3.11) to the special equation (1.5) given by Shuey and Beyeler (1969), which has been confirmed. Their equation (4.18) can be used to integrate the image interaction of arbitrary defects homogeneously distributed over a sphere, the situation considered in our previous paper (Willenbacher and Spiering 1988). The result is identical with that independently derived by us without use of the advanced tools of elasticity theory (up to that time we did not know the paper of Hirsekorn and Siems).

3. The lattice sum

The sum of the interaction energies between all pairs of lattice sites is carried out assuming a random distribution of the different types of defects over the lattice sites of the metal atoms. The following sum has to be evaluated:

$$E_{\text{direct}} = \tfrac{1}{2}\sum_{a\neq b}^{N} E^{\infty}_{\text{int}}(\boldsymbol{R}_{ab}). \tag{3.1}$$

This double sum will be carried out in such a way that the average dipole tensors $\bar{\mathbf{P}}^{i}$ at

the n sites in the unit cell can be introduced in (3.1). The indices a, b are replaced by pairs u, i and v, j, where u, v count the unit cells and $i, j = 1, \ldots, n$ the sites within the unit cells. $\boldsymbol{R}^{ij}_{uv}$ is a vector pointing from site i of unit cell u to site j of cell v. The dipole tensors of the defects at these sites are $\mathbf{P}^{ui}$ and $\mathbf{P}^{vj}$ respectively. Then the double sum can be arranged as:

$$E_{\text{direct}} = \tfrac{1}{2}\sum_{u\neq v}\sum_{i,j}^{n} E_{\text{int}}(\boldsymbol{R}^{ij}_{uv}) + \tfrac{1}{2}\sum_{u}\sum_{i\neq j}^{n} E_{\text{int}}(\boldsymbol{R}^{ij}_{uu}). \tag{3.2}$$

We consider first vectors between different unit cells $u \neq v$ and fixed i, j. The sum u, v can be rearranged using the translational symmetry of the lattice. Vectors between unit cells u' and v' the positions of which differ from the cells u and v by the same translation vector of the lattice shall be denoted $\boldsymbol{R}^{ij}_{\tau}$ where the index τ counts all translation vectors. The index τ is unequivocally determined by u and v: $\tau = \tau(u, v)$ and also vice versa v by τ and u: $v = v(\tau, u)$. In order to have not so long formulae we consider one of the terms of (3.2) exemplarily. Substituting (2.2) the $\mathbf{W}$ term of the first term of (3.2) is given by

$$E^{\text{wl}}_{\text{direct}} = \tfrac{1}{2}\sum_{u\neq v}\sum_{i,j}^{n} \mathbf{P}^{ui}\mathbf{W}(\boldsymbol{R}^{ij}_{\tau})\mathbf{P}^{vj+}. \tag{3.3}$$

Here we made use of the fact that the tensor $\mathbf{W}$ does not depend on the absolute position u, i and v, j of the defects. The double sum will be rearranged by a sum over three indices α, u_α, and τ. The sum over u, v is replaced by u, τ and u is further split into α, u_α so that $\mathbf{P}^{u_\alpha j}$ denotes one of the tensors of type $\alpha = \text{HS}, \text{LS}$ and M and can be taken out of the sum over u_α. If c^α is the concentration of α-complexes u_α runs from 1 to N/nc^α.

$$E^{\text{wl}}_{\text{direct}} = \tfrac{1}{2}\sum_{i,\alpha}\mathbf{P}^{u_\alpha i}\left(\sum_{\tau,j}\mathbf{W}(\boldsymbol{R}^{ij}_{\tau})\sum_{u_\alpha}\mathbf{P}^{v(\tau,u_\alpha)j+}\right). \tag{3.4}$$

The sum u_α can be carried out since all types of defects are met at site $v(\tau, u_\alpha)$, j. According to their random distribution we obtain the average tensor $\bar{\mathbf{P}}^j$ at site j multiplied by N/nc^α. The sum α of the three types of defects gives again the average tensor $\sum_\alpha c^\alpha \mathbf{P}^{u_\alpha i} = \bar{\mathbf{P}}^i$ so that

$$E^{\text{wl}}_{\text{direct}} = \tfrac{1}{2}N\frac{1}{n}\sum_{i}^{n}\bar{\mathbf{P}}^i\sum_{\tau}\sum_{j}^{n}\mathbf{W}(\boldsymbol{R}^{ij}_{\tau})\bar{\mathbf{P}}^{j+}. \tag{3.5}$$

The other terms of (3.2) are treated in the same manner. In the case of the second term E^2_{direct} of (3.2) the sum over all unit cells u again gives the factor N/n and the tensors are replaced by their average values.

The sum over τ and j in (3.5) can be looked at as the negative of the strain field $\boldsymbol{\varepsilon}^i$ at lattice site i so that the average energy E^{ui} of a dipole tensor $\mathbf{P}^{ui}$ at site u, i has the familiar form $E^{ui} = -\mathbf{P}^{ui}\boldsymbol{\varepsilon}^i$. The calculation of the $\boldsymbol{\varepsilon}^i$ for the finite spherical crystal embedded in an infinite medium is carried out in two steps. First $\boldsymbol{\varepsilon}^i$ is summed up over a small sphere of radius R_ε taking into account the crystal structure of the compound under consideration. This sum converges as a result of the angular dependence of the $\mathbf{V}$ and $\mathbf{W}$ terms which are proportional to the spherical harmonics. At sufficiently large distance R the number of points on a spherical surface becomes so large that the sum can be replaced by an integral $\int \mathrm{d}\Omega$ which vanishes integrating over the spherical harmonics with $k > 0$. Outside R_ε the vector $\boldsymbol{R}^{ij}_{\tau}$ is almost independent of i and j and we replace the

summation by an integration so that the strain field at site (u, i) in the spherical crystal is a sum of $\boldsymbol{\varepsilon}^i(V_\varepsilon)$ which is independent of u and the integral

$$\boldsymbol{\varepsilon}^{ui} = \int_{V_a - V_\varepsilon} \mathrm{d}V_\tau \, \mathbf{W}(\boldsymbol{R}_\tau(u)) \sum_j \bar{\mathbf{P}}^{j+} \tag{3.6}$$

which depends on the position (u, i) in the crystal. It will be shown in the appendix that this integral vanishes independently of the position (u, i) and the radius R_ε.

For the calculation of $\varepsilon^i(V_\varepsilon)$ the symmetry of the compounds under consideration is taken into account. The n sites of the unit cell are equivalent and the average tensors at different sites are related to each other by a transformation $T^2_{MM'}$. Starting with site 1 we can write:

$$\bar{P}^i_M = \sum_{M'} \bar{P}^1_{M'} \mathbf{T}^{2i}_{M'M} \qquad \bar{P}^i_s = \bar{P}^1_s \qquad \bar{\mathbf{P}}^i = \bar{\mathbf{P}}^1 \mathbf{T}^{2i}. \tag{3.7}$$

With these relations the direct interaction is finally given by:

$$E_{\text{direct}} = N(\bar{\mathbf{P}}^1 \mathbf{V}_c \bar{P}^1_s + \bar{\mathbf{P}}^1 \mathbf{W}_c \bar{\mathbf{P}}^{1+}) \tag{3.8}$$

$$\mathbf{V}_c = \frac{1}{2}\frac{1}{n}\left[\sum_\tau \sum_{i,j}^{n} [\mathbf{T}^{2i}\mathbf{V}(\boldsymbol{R}^{ij}_\tau) + \mathbf{T}^{2j}\mathbf{V}(\boldsymbol{R}^{ij}_\tau)] + \sum_{i \neq j}^{n} \mathbf{T}^{2i}\mathbf{V}(\boldsymbol{R}^{ij}_{uu})\right] \tag{3.9a}$$

$$\mathbf{W}_c = \frac{1}{2}\frac{1}{n}\left[\sum_\tau \sum_{i,j}^{n} \mathbf{T}^{2i}\mathbf{W}(\boldsymbol{R}^{ij}_\tau)\mathbf{T}^{2j+} + \sum_{i \neq j}^{n} \mathbf{T}^{2i}\mathbf{W}(\boldsymbol{R}^{ij}_{uu})\mathbf{T}^{2j+}\right]. \tag{3.9b}$$

The total tensors $\mathbf{V}_c$ and $\mathbf{W}_c$ of the lattice are determined by the crystallographic structure and the elastic constants of the compounds. For practical calculations the lattice sums of the tensors of (2.4) are carried out.

The interaction parameters $\Gamma(x)$ and $\Delta(x)$ are obtained by inserting the average tensor of (1.4) into the expression of E_{direct}. The average tensor element $\bar{P}_\alpha$ is expressed by the tensor differences $P^{\text{HL}}_\alpha = P^{\text{HS}}_\alpha - P^{\text{LS}}_\alpha$ and $P^{\text{ML}}_\alpha = P^{\text{M}}_\alpha - P^{\text{LS}}_\alpha$ so that $\bar{P}_\alpha = x\gamma P^{\text{HL}}_\alpha - xP^{\text{ML}}_\alpha + P^{\text{M}}_\alpha$, $\alpha = \text{s}, M$. This tensor shall belong to site 1 whereby the index 1 is dropped. Collecting only terms dependent on the fraction γ the interaction energy per iron complex E_{direct}/Nx can be written in the form of (1.1) with $\Gamma(x) = x\Gamma_d$, $\Delta(x) = x\Delta_d$ and:

$$\Gamma_d = -(\mathbf{P}^{\text{HL}}\mathbf{V}_c P^{\text{HL}}_s + \mathbf{P}^{\text{HL}}\mathbf{W}_c\mathbf{P}^{\text{HL}+}) \tag{3.10a}$$

$$\Delta_d = -(\mathbf{P}^{\text{HL}}\mathbf{V}_c P^{\text{ML}}_s + \mathbf{P}^{\text{ML}}\mathbf{V}_c P^{\text{HL}}_s + \mathbf{P}^{\text{HL}}\mathbf{W}_c\mathbf{P}^{\text{ML}+} + \mathbf{P}^{\text{ML}}\mathbf{W}_c\mathbf{P}^{\text{HL}+}). \tag{3.10b}$$

The average dipole tensor at each lattice site cannot be completely evaluated from experiment. The tensor components obtained experimentally from the average deformation tensor ε_c according to (1.2) are those that are invariant with respect to the transformations $\mathbf{T}^{2i}$ $(i = 1, 2, \ldots, n)$. Therefore several tensor components remain as hidden variables for the calculation of the direct interaction.

4. Results

4.1. The elastic dipole tensor

The symmetry of the crystals under consideration is monoclinic for the compound $[\text{Fe(2-pic)}_3]\text{Cl}_2 \cdot \text{EtOH}$ and orthorhombic for $[\text{Fe(2-pic)}_3]\text{Cl}_2 \cdot \text{MeOH}$. In the following

sections the compounds will be abbreviated by their solvent molecules EtOH and MeOH, respectively. Corresponding to symmetry only a few linear combinations of the components P_M of the dipole tensor of the complexes can be derived from the macroscopic deformation of the crystal described by the tensor $\boldsymbol{\varepsilon}_c$. These are the trace P_s, P_0 and the real linear combinations $P_{2c} = (1/\sqrt{2})(P_{22} + P_{2,-2})$, $P_{1c} = (1/\sqrt{2})(P_{21} - P_{2,-1})$ for the monoclinic crystal and P_s, P_0 and P_{2c} for the orthorhombic crystal. The linear combinations $P_{1s} = (\mathrm{i}/\sqrt{2})(P_{21} - P_{2,-1})$ and $P_{2s} = -(\mathrm{i}/\sqrt{2})(P_{22} - P_{2,-2})$ are hidden parameters for the monoclinic crystal and P_{1c}, P_{1s} and P_{2s} for the orthorhombic crystal. In order to reduce the number of unknown parameters we have made the rigorous assumption that the shape of the complex and especially the change of the shape on going from the HS to the LS state is independent of the lattice they are built in. The displacement field $\boldsymbol{U}(\boldsymbol{r})$ produced by the change of spin state of the complex embedded in an infinite medium has the form (Shuey *et al* 1969)

$$\boldsymbol{U}(\boldsymbol{r}) = \frac{1}{\lambda+2\mu}\frac{1}{r^2}\left[-\frac{\boldsymbol{Y}^1_{00}}{\sqrt{4\pi}}P_s + \frac{3\lambda+8\mu}{10\mu}\sum_M \frac{\boldsymbol{Y}^1_{2M}}{\sqrt{3\pi}}P^*_M - \frac{3(\lambda+\mu)}{10\mu}\sum_M \frac{\boldsymbol{Y}^3_{2M}}{\sqrt{2\pi}}P^*_M\right]. \tag{4.1}$$

The $\boldsymbol{Y}^L_{JM}$ are the vector spherical harmonics. In the approximation of a homogeneous lattice the displacement field $\boldsymbol{U}(\boldsymbol{r})$ describes for example the change of the nitrogen positions $\boldsymbol{r}_N$ in the complex molecule. According to (4.1) equal displacements $\boldsymbol{U}(\boldsymbol{r}_N)$ result in the same dipole tensor $\mathbf{P}$ if the elastic constants are identical in the two compounds. The proportionality of λ and μ with the bulk modulus K leads to the weaker conclusion that $\mathbf{P}/K$ is preserved if the Poisson ratio σ or equivalently the Eshelby constant ($\gamma_0 = 3(1-\sigma)/(1+\sigma)$) is the same for the different compounds and vice versa.

For the EtOH and MeOH compounds the parameters are as follows. The volume change $\varepsilon^{\mathrm{HL}}_{c,s} \cdot V_c$ given in table 1 are the same so that for these two compounds which have different crystallographic structures the ratio $P^{\mathrm{HL}}_s/K = \varepsilon^{\mathrm{HL}}_{c,s} \cdot V_c$ (according to (1.2)) is also the same. With the rigorous assumption above of the same local displacement $\boldsymbol{U}$ we conclude the Eshelby constants of both compounds to be the same too: $\gamma_0^{\mathrm{EtOH}} = \gamma_0^{\mathrm{MeOH}}$. Since the orientations of the Fe complexes in both structures are different we can principally calculate, applying (1.2) to both crystals, the local tensor $\mathbf{P}^{\mathrm{HL}}/K$ from the $\boldsymbol{\varepsilon}^{\mathrm{HL}}_c$ tensors by the following system of linear equations (M = 2c, 1c, 0, 1s, 2s):

$$\frac{1}{n}\sum_i^n P^{\mathrm{HL},i}_M/K = \varepsilon^{\mathrm{HL}}_{c,M} V_c^{\frac{3}{2}}(\gamma_0 - 1). \tag{4.2}$$

The index i runs over all sites n in the unit cell. In order to solve this system the components of the tensors $\mathbf{P}^{\mathrm{HL},i}/K$ in (4.2) related to the crystal system S_c have to be expressed in a local coordinate system S_{loc} which is fixed to the complex molecule. If the Euler angles $\boldsymbol{\beta}$ rotate the system S_c onto S_{loc} of site $i = 1$ the local tensor components are given by

$$P^{\mathrm{HL}}_M = \sum_m P^{\mathrm{HL},i}_m D^2_{m,M}(\boldsymbol{\beta}) \qquad i = 1. \tag{4.3}$$

Inserting the transformation matrices $\mathbf{T}^{2i}$ of (3.8), which relate the equivalent lattice sites to site 1, (4.3) reads

$$\frac{1}{n}\sum_i^n \left(\sum_{M'}\sum_m P^{\mathrm{HL}}_m D^{2*}_{m,M'}(\boldsymbol{\beta}) T^{2i}_{M'M}\right)/K = \varepsilon^{\mathrm{HL}}_{c,M} V_c^{\frac{3}{2}}(\gamma_0 - 1). \tag{4.4}$$

For the monoclinic structure two equations (M = 1s, 2s) and for the orthorhombic

Table 1. The deformation tensors $\boldsymbol{\varepsilon}^{AB}$ of the lattice A with respect to the lattice B (A, B = H(S), L(S) and ZnL(S)), obtained from x-ray data (Wiehl 1987). The carthesian crystal system S_c of the monoclinic crystal (EtOH) is oriented such that the z axis is parallel to the c axis and y parallel to the twofold b axis. The axes of the orthorhombic system S_c correspond to the (x, y, z) fractional coordinates (Katz *et al* 1979). The system S_{loc} is fixed to the complex molecule $[Fe(2\text{-pic})_3]$ as described in the text. The elastic dipole tensor components P_M^{HL} of the $[Fe(2\text{-pic})_3]$ complex changing from the LS- to the HS-state has been calculated from the deformation tensors $\boldsymbol{\varepsilon}_c^{HL}$ of the EtOH and MeOH crystal. Two components P_M^{ZnL} (M = 1s, 2s) are guessed (italic bold numbers) to be smaller by the same fraction (0.8) as the components M = 1c, 0 in the system S_c^{EtOH}.

		S_c^{EtOH}		S_c^{MeOH}		S_{loc}		S_c^{EtOH}		S_c^{MeOH}	
	M	$\boldsymbol{\varepsilon}_c^{HL}$	$\boldsymbol{\varepsilon}_c^{ZnL}$	$\boldsymbol{\varepsilon}_c^{HL}$	α	HL	ZnL	HL	ZnL	HL	ZnL
$\varepsilon_{c,M}$ (10^{-2})	2c	−0.53	−0.11	−0.88	$\dfrac{P_M^\alpha}{K(\gamma_0 - 1)}$	+15.6	14.3	−4.7	−1.0	−7.7	−6.9
	1c	3.49	2.75	0		−26.4	−19.8	30.6	24.1	−11.6	−9.5
	0	−0.94	−0.78	0.02		−21.4	−17.0	−8.2	−6.9	0.2	−0.1
	1s	0	0	0		1.7	1.3	−9.6	***−7.7***	7.3	8.1
	2s	0	0	0		7.1	4.1	−18.2	***−14.6***	−34.7	−26.4
$\varepsilon_{c,s}$ (10^{-2})		2.43	2.25	2.44	P_s^α/K (Å^3)	14.2	13.7	14.2	13.7	14.1	13.7

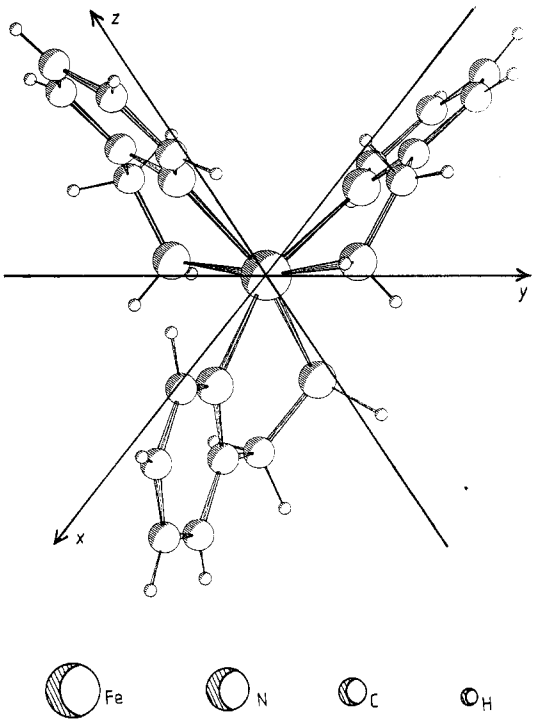

Figure 1. Configuration of the complex molecule $[Fe(2\text{-pic})_3]^{2+}$ and the local coordinate system S_{loc} which can be unequivocally fixed to the orientation of the three bidentate 2-aminomethylpyridine ligands of the central Fe^{2+} ion. The sizes of the atoms were chosen such that Fe > N > C > H.

structure three equations (M = 1c, 1s, 2s) vanish identically so that just five equations are left to determine the local tensor components P_m^{HL}. The system S_{loc} can be fixed at the iron complex unequivocally as indicated in figure 1. The z axis points from the iron atom to that amino nitrogen atom which is opposite to a pyridine nitrogen atom. The x axis connects two pyridine nitrogen atoms and points in the direction of the pyridine ring which is bonded to the amino group defining the z axis. Since the six nitrogen do not exactly form an octahedron the coordinate system is chosen such that $s = \Sigma_j^6 \cos^2(\alpha_j)$ becomes minimal where α_j is the angle between the direction from iron to nitrogen atom j and the corresponding coordinate axis. The crystallographic data of the compounds in the LS state were taken for the calculation. These are the data at 90 K of the EtOH compound (Mikami *et al* 1980) and at 115 K of the MeOH compound (Katz *et al* 1979). The estimations of the Eshelby constant γ_0 of these compounds based on the theory restricted to spherical defects (Adler *et al* 1987) shall not be used. Therefore the tensor components P_M^{HL} divided by $K(\gamma_0 - 1)$ are given in table 2. The components with respect to the crystal system S_c belong to site $i = 1$ which has the fractional coordinates (x, y, z) in the unit cell as tabulated in Mikami *et al* (1980) and Katz *et al* (1979), respectively.

4.2. *The interaction*

In order to calculate the tensor components $V_{c,M}$, $W_{c,MM'}$ of (3.7) the tensor $\mathbf{W}_c$ is broken up into two tensors $\mathbf{W}_c^2$ and $\mathbf{W}_c^4$ and $\mathbf{V}_c$ replaced by $\mathbf{V}_c^2$ which are independent of the elastic constants according to (2.3). If we denote $\mathbf{P}^{HL}$ divided by $K(\gamma_0 - 1)$ and P_s/K by

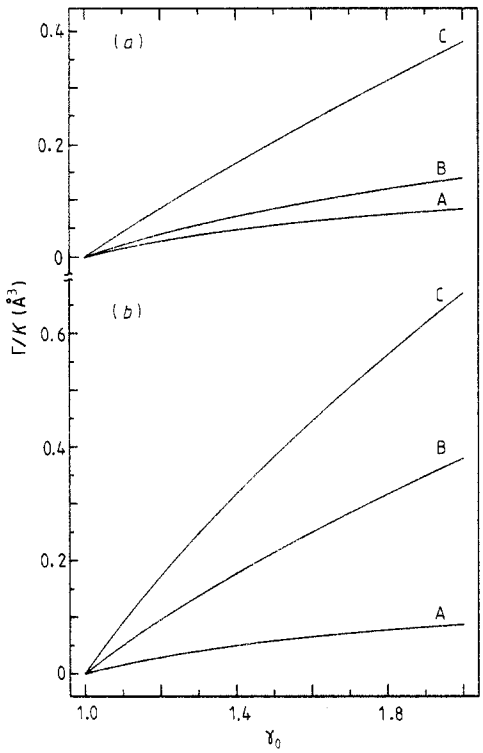

Figure 2. The interaction Γ divided by the bulk modulus K plotted versus the Eshelby parameter γ_0 for two compounds $[Fe(2\text{-pic})_3]Cl_2 \cdot Sol$ (2-pic-2-aminomethylpyridine; Sol = MeOH, EtOH). (*a*) MeOH compound, (*b*) EtOH compound. Γ/K has been calculated from the x-ray data of the two compounds. The three curves for each compound show the different contributions included in the calculation: curve A takes into account the image pressure of the isotropic part of the dipole tensor (P_s) of the HS defects in the LS lattice; curve B includes the image pressure of the full dipole tensor; curve C represents the total elastic interaction between the defects homogeneously distributed over the lattice sites of the crystals having a spherical shape.

the underlined symbols $\underline{\mathbf{P}}^{HL}$ and $\underline{P}_s$, respectively, then the direct interaction part Γ_d and the energy shift Δ_d can be written as

$$\Gamma_d/K = -[(\gamma_0 - 1)/\gamma_0][\underline{\mathbf{P}}^{HL}\mathbf{V}_c^2\underline{P}_s^{HL} - \tfrac{4}{7}(2\gamma_0 - 1)\underline{\mathbf{P}}^{HL}\mathbf{W}_c^2\underline{\mathbf{P}}^{HL+} + \tfrac{6}{7}(\gamma_0 + 3)\underline{\mathbf{P}}^{HL}\mathbf{W}_c^4\underline{\mathbf{P}}^{HL+}] \tag{4.5a}$$

$$\Delta_d/K = -[(\gamma_0 - 1)/\gamma_0][\underline{\mathbf{P}}^{ML}\mathbf{V}_c^2\underline{P}_s^{HL} + \underline{\mathbf{P}}^{HL}\mathbf{V}_c^2\underline{P}_s^{ML} - \tfrac{4}{7}(2\gamma_0 - 1)(\underline{\mathbf{P}}^{ML}\mathbf{W}_c^2\underline{\mathbf{P}}^{HL+} + \underline{\mathbf{P}}^{HL}\mathbf{W}_c^2\underline{\mathbf{P}}^{ML+}) + \tfrac{6}{7}(\gamma_0 + 3)(\underline{\mathbf{P}}^{ML}\mathbf{W}_c^4\underline{\mathbf{P}}^{HL+} + \underline{\mathbf{P}}^{HL}\mathbf{W}_c^4\underline{\mathbf{P}}^{ML+})]. \tag{4.5b}$$

For the calculation of the tensors $\mathbf{V}_c^2$, $\mathbf{W}_c^2$ and $\mathbf{W}_c^4$ sufficiently large lattice sums have to be performed. The convergence of the sums appears to be relatively slow. A change of 5% is still obtained if already 10^4 lattice sites are included which corresponds to a radius of 110 Å. The tensors were calculated up to a radius of 30 times the largest lattice constants b including more than 10^6 defects. Figure 2 shows the different contributions to the interaction constant as calculated for the EtOH compound versus the unknown Eshelby constant γ_0. The first approach of Spiering *et al* (1982) considered only the spherical part of the defect P_s which does not contribute to the direct interaction. The total image part Γ_{im}/K was calculated in our last work (Willenbacher *et al* 1988). The complete interaction $\Gamma/K = \Gamma_{im}/K + \Gamma_d/K$ includes the direct part which turns out to be a considerable contribution (about 30% of Γ).

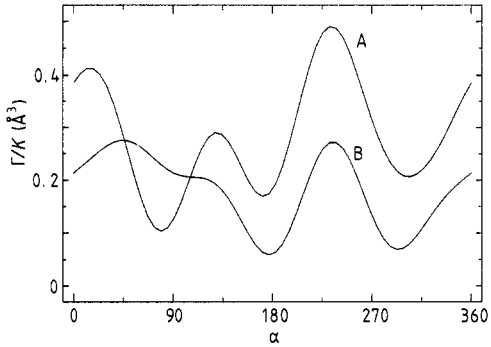

Figure 3. The dependence of the interaction on the orientation of the dipole tensor $\mathbf{P}^{HL}$ with respect to the lattice of the EtOH compound. The interaction constants divided by the bulk modulus K are plotted versus a rotation angle α about an axis with polar angle $\varphi = 240°$ and $\vartheta = 60°$ in the coordinate system S_{loc}. Curve A, total interaction; curve B, image part.

5. Discussion

A straightforward comparison of the experimental with the calculated interaction constants Γ and the energy shifts Δ is not possible because there are no reliable data of the elastic properties of the compounds. Moreover, for the calculation of the energy shift Δ the dipole tensor $\mathbf{P}^{ZnH}$ describing the difference of the shapes of the Zn- and HS-complex molecule could not be completely determined because of the missing crystallographic data of the Zn compound $[Zn(2\text{-pic})_3]Cl_2 \cdot MeOH$. But the consistency of the different experimental results with the theory and with reasonable ranges of the unknown parameters shall be discussed in detail. To begin with several general facts will be stated.

The curves of Γ/K versus γ_0 in figure 2 calculated with the same defect tensor $\mathbf{P}^{HL}$ obviously depend strongly on the symmetry of the crystal. Also the three contributions to Γ are different with respect to their relative size for different crystal symmetries. Γ_{im} which depends on the spherical and the anisotropic tensor components of the defect, is always positive as can be read from (1.5*a*). Γ_d, however, can also be negative. In figure 3 the dependence of Γ_{im}/K and $\Gamma/K = \Gamma_{im}/K + \Gamma_d/K$ on the orientation of the local tensor $\mathbf{P}^{HL}$ in the EtOH crystal is demonstrated. The orientations are obtained by rotating ($\alpha = 0°, \ldots, 360°$) the local tensor about an axis with polar angles $\varphi = 240°$ and $\vartheta = 60°$ in the local system. The Eshelby constant has been fixed to $\gamma_0 = 1.5$. Two facts are of importance, the total interaction constant Γ/K varies over a large range between 0.1 and 0.5 Å^3 and there are regions where Γ/K is smaller than Γ_{im}/K so that the direct contribution Γ_d/K is a negative one. This strong dependence on the orientation of the defect in the lattice and on the symmetry of the lattice provides an easy explanation for the range of interaction constants so far observed. The interaction may be large, in which case hysteresis is observed, or almost vanishing in another lattice as is the case for the $[Fe(2\text{-pic})_3]$ complex in $[Fe(2\text{-pic})_3]Br_2 \cdot EtOH$ (Wiehl *et al* 1987) and in $[Fe(2\text{-pic})_3](PF_6)_2$ (Adler *et al* 1989), respectively. So we can in fact state that the interaction in HS $\rightleftharpoons$ LS transitions can naturally be attributed to the elastic interaction between the spin changing ions.

In order to perform a more detailed comparison with the experimental interaction constants the value of Γ^{EtOH} shall be reevaluated. The known value of 130 cm^{-1} (Spiering *et al* 1982) was determined from the Mössbauer data of Sorai *et al* (1976) which do not show the characteristic step in the transition curve as was later found by Köppen *et al* (1982). The step turned out to be sensitive to the preparation procedure and mechanical treatment of the compound. Only samples which were not ground developed the full width of the step.

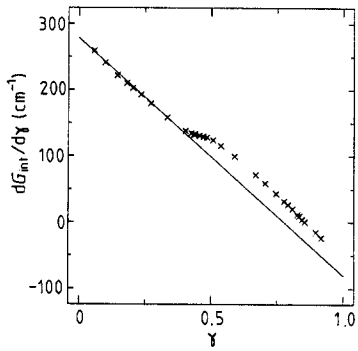

Figure 4. The derivative of the interaction part of the free enthalpy $dG_{int}/d\gamma = \Delta - 2\gamma\Gamma$ of the compound $[Fe(2\text{-pic})_3]Cl_2 \cdot EtOH$ versus the HS fraction γ. The step in the transition curve $\gamma(T)$ gives rise to shift of the derivative in the transition region. The slope below and above the step is the same and determines the interaction constant to be $\Gamma = 175\ cm^{-1}$.

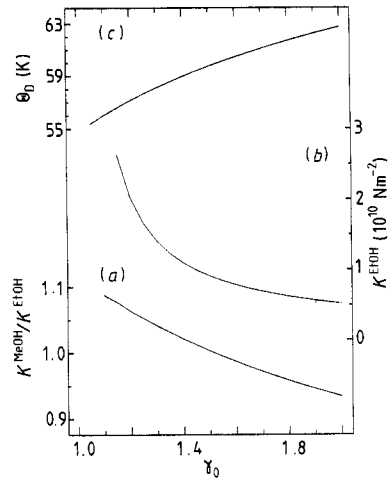

Figure 5. (*a*) The ratio of the theoretical values $(\Gamma/K)^{EtOH}$ and $(\Gamma/K)^{MeOH}$ plotted in figure 2 multiplied by the ratio of the experimental interaction constants Γ^{MeOH} and Γ^{EtOH} is equal to the ratio of the bulk moduli, K^{MeOH}/K^{EtOH}. (*b*) K^{EtOH} obtained from the ratio of the experimental value of $\Gamma = 175\ cm^{-1}$ divided by the theoretical values $(\Gamma/K)^{EtOH}$. (*c*) The Debye temperature Θ_D as calculated from K^{EtOH} and γ_0 (see text).

The interaction constant Γ and the energy shift Δ is evaluated as published elsewhere (Adler *et al* 1987). The derivative of the interaction part $dG_{int}/d\gamma = \Delta - 2\Gamma\gamma$ of (1.1) can be directly obtained from the transition curve $\gamma(T)$ by use of the data of the highly diluted compound ($x \to 0$) where the interaction term vanishes. The free energy $G(x \to 0, T)$ is determined by the free energies of the HS and LS state in the lattice, G^{HS} and G^{LS}, respectively, and by the mixing entropy $S_{mix}(\gamma) = -k_B[\gamma \ln \gamma + (1-\gamma)\ln(1-\gamma)]$

$$G(x \to 0, T) = \gamma G^{HS} + (1-\gamma)G^{LS} - TS_{mix}. \tag{4.6}$$

Application of the equilibrium condition $\partial G/\partial\gamma = 0$ leads to $(G^{HS}(T) - G^{LS}(T)) = k_B T \cdot \ln[(1-\gamma)/\gamma]$ which was measured by the HS fraction $\gamma(T)$ in the highly diluted compound $[Fe_xZn_{1-x}(2\text{-pic})_3]Cl_2 \cdot EtOH$ ($x = 0.009$). The experimental values of $(G^{HS} - G^{LS})$ were parametrised by an analytical function having the form of a free energy containing partition functions with different electronic and vibrational energies for the HS and LS states (Spiering *et al* 1982). Including the interaction term for $x = 1$ in (4.6) of the free energy the equilibrium condition changes to:

$$0 = (G^{HS} - G^{LS}) - k_B T \ln[(1-\gamma)/\gamma] + dG_{int}/d\gamma \tag{4.7}$$

where the HS fraction $\gamma(T)$ is measured on the pure iron ($x = 1$) compound. In figure 4 $dG_{int}/d\gamma$ is plotted versus $\gamma(T)$ which are taken from the work of Köppen (Köppen *et al* 1982). For a normal HS $\rightleftharpoons$ LS transition we expect a linear behaviour according to $dG_{int}/d\gamma = \Delta - 2\gamma\Gamma$. Here we have the linearity below and above the step in the transition curve. The step causes a parallel shift leading to different intercepts Δ above

($\Delta = 300\ \mathrm{cm}^{-1}$) and below ($\Delta = 275\ \mathrm{cm}^{-1}$) the step. From the slope an interaction of $\Gamma = 175\ \mathrm{cm}^{-1}$ can be determined. The origin of the step is not yet clear, but it is known that only a small change of the bulk modulus of 2% (i.e. by changes of the lattice) will cause changes of Δ of $\sim 30\ \mathrm{cm}^{-1}$ (Sanner *et al* 1984). We take the branch in the temperature range below 120 K where all other results have been derived. This part is correctly described by the free energy with $\Gamma = 175\ \mathrm{cm}^{-1}$ and $\Delta = 275\ \mathrm{cm}^{-1}$.

The theoretical values for Γ/K could be derived assuming the same Eshelby constant γ_0 for both the EtOH and MeOH compounds, a condition which has to be shown to be consistent with the experimental data. The three curves in figure 5 shall prove this consistency. The lower curve represents the γ_0 dependence of the ratio of the theoretical values $(\Gamma/K)^{\mathrm{EtOH}}/(\Gamma/K)^{\mathrm{MeOH}}$ of the total interaction (upper curves in figure 2) multiplied by the ratio of the experimental interaction constants $\Gamma^{\mathrm{MeOH}}/\Gamma^{\mathrm{EtOH}} = 98\ \mathrm{cm}^{-1}/175\ \mathrm{cm}^{-1} = 0.56$. This expression is equal to the ratio of the bulk moduli of the two compounds: $K^{\mathrm{MeOH}}/K^{\mathrm{EtOH}}$. The bulk modulus K^{EtOH} of the EtOH compound (second curve in figure 5) is obtained from the ratio of the experimental interaction constant $\Gamma = 175\ \mathrm{cm}^{-1}$ divided by the theoretical values $(\Gamma/K)^{\mathrm{EtOH}}$. The upper curve in figure 5 is a plot of the Debye temperature $\theta_{\mathrm{D}}^{\mathrm{EtOH}}$ versus γ_0 calculated from K^{EtOH} according to the equation (Meissner *et al* 1987)

$$K = (k_{\mathrm{B}}^2\Theta_{\mathrm{D}}^2/\hbar^2)\rho\left(\frac{V}{18\pi^2 N}\right)^{2/3}\frac{1}{\gamma_0}\{1 + (16/3\sqrt{3})[\gamma_0/(\gamma_0 - 1)]^{3/2}\}^{2/3} \tag{4.8}$$

where N/V is the number of vibrating masses per volume and ρ the density of the compound. As there are no direct measurements of the elastic constants of these compounds or similar ones, we will make use of the Debye temperatures Θ_{D} deduced from the Mössbauer Debye–Waller factor to prove the consistency of the data.

An estimation of K and γ_0 of the deuterated compound $[\mathrm{Fe(2\text{-}pic\text{-}ND_2)_3}]\mathrm{Cl_2}\cdot\mathrm{EtOD}$ was obtained from the temperature and pressure dependence of the Mössbauer Debye–Waller factor f in the frame of the Debye approximation and simple Grüneisen relations for the volume dependence of the Debye temperature Θ_{D} (Meissner *et al* 1987). At low temperatures (115 K) a bulk modulus of $K = 1.4 \times 10^{10}\ \mathrm{Nm}^{-2}$ and $\gamma_0 = 1.25$ was evaluated. Consistency of the data was achieved if the recoil mass $\mathcal{M}$ had been taken as the mass of the Fe complex plus the Cl^- anions. This result was argued to be reasonable from the structure of the compound which forms a lattice of $[\mathrm{Fe(2\text{-}pic\text{-}ND_2)_3}]^{2+}$ complexes and Cl^- anions connected by hydrogen bridges. The ethanol molecules are bound to one of the Cl^- anions by an OH^- group and move independently in a lattice cage. A Debye temperature $\Theta_{\mathrm{D}} = 56$ K at 115 K was derived with these arguments. For the MeOH compound Adler *et al* (1987) reported $\Theta_{\mathrm{D}} = 48$ K calculated from the absolute value of the Mössbauer f-factor at room temperature taking, again the mass of $[\mathrm{Fe(2\text{-}pic)_3}]\mathrm{Cl_2}$ as the recoil mass $\mathcal{M}$. If the same increase of 13% in Θ_{D} from 300 K to 120 K found in the deuterated compound is assumed, a value of $\Theta_{\mathrm{D}}^{\mathrm{MeOH}}(120\ \mathrm{K}) = 54.5$ K has to be used. A value for the low temperature region can be directly obtained from Mössbauer factor $f(T)$ of the isomorphous mixed crystal $[\mathrm{Fe_{0.01}Zn_{0.99}(2\text{-}pic)_3}]\mathrm{Cl_2}\cdot\mathrm{EtOH}$ studied by Köppen (Köppen 1985). Θ_{D} is reliably estimated from the slope of $-\ln f(T) = [3E_\gamma^2/(k_{\mathrm{B}}c^2\mathcal{M}\Theta_{\mathrm{D}}^2)]T$ (high-temperature approximation of $f(T \gg \Theta_{\mathrm{D}})$ with $E_\gamma = 14.4$ eV the energy of the ^{57}Fe Mössbauer transition and c the velocity of light) since there are no extra changes of Θ_{D} in the diluted compound by a decreasing volume accompanying the HS $\rightarrow$ LS transition. In figure 6, $-\ln(f)$ is plotted against T. From the slope of the straight line fitting to the data around 120 K a Debye temperature of $\Theta_{\mathrm{D}} = 53$ K is determined which is almost the same as $\Theta_{\mathrm{D}}^{\mathrm{MeOH}}$.

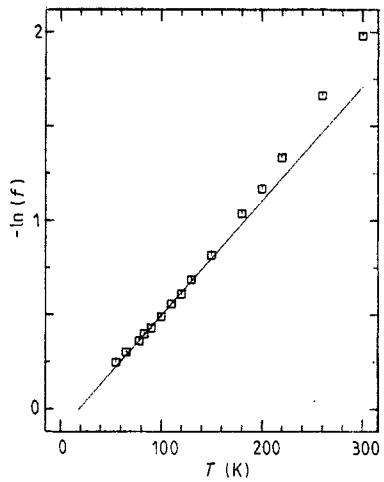

Figure 6. The negative logarithm of the Mössbauer Debye–Waller factor, $-\ln f$, of the mixed-crystal compound $[Fe_{0.01}Zn_{0.99}(2\text{-pic})_2]Cl_2 \cdot EtOH$ versus temperature T. From the slope at 120 K (straight line) the Debye temperature $\Theta_D = 53$ K is evaluated at that temperature.

First we can state that, as the bulk modulus is proportional to the square of Θ_D (equation (4.8)), the range of the ratios of the bulk moduli $0.93 < K^{MeOH}/K^{EtOH} < 1.1$ certainly covers the true value and therefore does not conflict with equal Eshelby constants γ_0 for both compounds. The values of the bulk moduli K^{EtOH} predicted from the interaction Γ range from 2.9×10^{10} N m^{-2} at $\gamma_0 = 1.1$ to 0.51×10^{10} N m^{-2} at $\gamma_0 = 2.0$. Within this range lies $K = 1.4 \times 10^{10}$ N m^{-2} determined from Mössbauer measurements for the deuterated EtOD compound. We can also compare with measured elastic constants of organic crystals which consist also of ring molecules like pyridine. The K-value of 0.45×10^{10} N m^{-2} calculated from the elastic compliances (Landolt–Börnstein 1969) at 250 K of benzene which is liquid at ambient temperature, can be considered as a lower limit for this type of compound. This limit almost agrees with the smallest predicted K^{EtOH} value at $\gamma_0 = 2.0$. Translating the bulk moduli and Eshelby constants to a Debye temperature the range $55\ K < \Theta_D^{EtOH} < 63$ K (upper curve of figure 5) is very narrow and compares well with the values estimated from the Mössbauer Debye–Waller factors. The different interaction constant of the two compounds obviously can be calculated with the same elastic dipole tensor, the same Eshelby constant γ_0 of the crystal, and quite reasonable values for the bulk moduli. The true value of γ_0, however, is not known. Nevertheless we arrived at a consistent description of the elastic interaction of the HS–LS compounds under discussion. Although many approximations are still involved in the theory of the isotropy of the elastic properties and spherical shapes of the crystals we consider this result as satisfactory.

A further parameter which has been predicted theoretically is the ratio $q = \Delta/(2\Gamma)$. The ratio is independent of the concentration x of spin-changing ions in a mixed-crystal-system and independent of the bulk modulus K. It depends according to (4.6) only on the tensors $\underline{\mathbf{P}}^{HL}$ and $\underline{\mathbf{P}}^{ML}$ and the Eshelby constant γ_0. $\underline{\mathbf{P}}^{ML}$ is obtained from the deformation tensor $\boldsymbol{\varepsilon}_c^{ML} = \boldsymbol{\varepsilon}_c^{MH} - \boldsymbol{\varepsilon}_c^{HL}$. In table 1 the tensor components $\boldsymbol{\varepsilon}_c^{ZnL}$ (M = Zn) of the EtOH compound are given as derived from x-ray data (Wiehl 1987). Since the corresponding tensor of the MeOH compound is not available the components $\underline{P}_{1s}^{ZnL}$ and $\underline{P}_{2s}^{ZnL}$ remain hidden parameters. We can, however, guess reliable ranges of the hidden parameters of the EtOH compound using the fact that the measured tensor components (2c, 1c, and 0) of the HS and Zn complex are not very different; in particular

their signs are the same (see table 1). Therefore limiting the range of these components by $|\underline{P}_m^{\mathrm{ZnL}}| < |\underline{P}_m^{\mathrm{HL}}|$ and preserving equal signs can be considered as a reasonable assumption. Then the calculated ratios vary within very narrow limits $0.80 < q < 0.82$ for $1.1 < \gamma_0 < 2$ and are close to the measured value of $q = 275\ \mathrm{cm}^{-1}/(2 \times 175\ \mathrm{cm}^{-1}) = 0.79$. This agreement can be taken as a parameter-free theoretical result.

For the MeOH compound the situation is different. Transforming the tensor to the system S_c^{MeOH} the limits differ considerably: $0.63 < q < 0.86$. A definite prediction is achieved as follows. The hidden tensor components $\underline{P}_m^{\mathrm{ZnL}}$ (m = 1s, 2s) in the EtOH system are guessed to be smaller by the same percentage (in average) than the corresponding P_m^{HL} as is the case for the larger components m = 2, 1c, 0. These reduced components are given in table 1. The components are transformed to the local- and the MeOH systems and are also tabulated. The fact that all $\underline{P}_m^{\mathrm{ZnL}}$ components are smaller than the $\underline{P}_m^{\mathrm{HL}}$ components is preserved in the local system. For this choice the limits of q are $0.77 < q < 0.81$, fitting well to the experimental value of $q = 0.80$ (Adler *et al* 1987). We state that the ratio q or equivalently the energy shift Δ is also well explained by the elastic interaction between the HS and LS and metal complexes in mixed-crystal systems.

5. Conclusion

We have presented a theory for those HS $\rightleftharpoons$ LS transitions which are described by a phenomenological Gibbs free energy containing the interaction term $G_{\mathrm{int}} = \gamma\Delta(x) - \gamma^2\Gamma(x)$ of (1.1). The so called gradual transitions in mixed crystals with a concentration $0 < x \leqslant 1$ of the spin-changing ions have been successfully parametrised by such a phenomenological *ansatz*. The theory allows to calculate the energy shift $\Delta(x)$ and the interaction constant $\Gamma(x)$ from the crystallographic data and the elastic constants of the lattice. The theory uses simplifications in many respects but it is the first attempt to a quantitative understanding of the phenomenological parameter and appropriate to serve as a frame for future studies in the wide field of HS $\rightleftharpoons$ LS phenomena. So far there have been numerous suppositions and speculations on the origin of the cooperativity of the transition. The suppositions changed from compound to compound and never led to definite predictions which were suited to prove or disprove them. Concerning the structural changes accompanying the spin-state transitions the various experimental observations and suppositions about their relation to the HS $\rightleftharpoons$ LS transition have been reviewed in great detail by König (König 1987). Over several years Kambara and coworkers (Kambara 1979, 1980, 1981, Ogata *et al* 1983) worked out a completely different theory which certainly does not cover several experimental facts (Köppen *et al* 1988). They treated the spin-changing complex in the framework of ligand-field theory and introduced a Jahn–Teller type of coupling between them to account for the cooperativity. The essential problem namely the size of the interaction and its variation from compound to compound has not been treated by them. Beyond that their approximations contradict well established experimental results. In the framework of ligand-field theory a continuous variation of the isotropic strain (A_{1g}) of the ligands also changes the electronic energy separation between the HS and LS states continuously. From x-ray data (König 1987) and optical spectroscopy (Hauser *et al* 1986), however, it is known that the ligands have definite positions in the HS and LS states separated by a potential barrier so that the electronic energy separation does neither depend on x nor on the HS fraction γ. This fact was the starting point of our theory. We neglect completely the Jahn–Teller

coupling and take the whole shape of the complex as rigid in the two spin states. The HS, LS, and other metal complex molecules with their different but distinct shapes, which fit more or less to the crystal structure, are treated as defects. Each metal site of the crystal represents the position of a defect. In the theory the defects are treated as a point defect characterised by a second-rank tensor, the orientation of which is the same for lattice sites related by translational symmetry. The complete elastic interaction between the defects which are randomly distributed over the lattice sites has been calculated in this paper for the two compounds $[Fe(2\text{-pic})_3]Cl_2 \cdot EtOH$ and $[Fe(2\text{-pic})_3]Cl_2 \cdot MeOH$. The fact that the compounds have different structures and therefore different defect orientations in the unit cells turns out to be the reason for the very different interaction constants observed. The consistency of all experimental data in the frame of this theory encourages us to do work on other examples, especially on compounds which show abrupt transitions and those with hysteresis effects. It is well known that the phenomenological *ansatz* for the Gibbs free energy produces first-order transitions with hysteresis if the interaction constant Γ is sufficiently large (Drickamer *et al* 1973).

The severe simplifications in the theory are twofold: the lattice is approximated by a homogeneous isotropic elastic medium although the compounds have monoclinic and orthorhombic symmetry and the shape of the crystals is taken to be a sphere. In particular, the spherical shape that leads to an interaction constant which is independent of position in the crystal, simplifies the free-energy considerably. Extension of the theory to low-symmetry elastic media and crystals of arbitrary shape is difficult and can only be done by extensive numerical calculations. Such calculations may be justified if the complete set of elastic constants of the compounds are available. Another simplification concerns the elastic constants which are taken to be independent of temperature and of the volume of the crystal changing with the HS fraction γ. We believe, however, that these simplifications will not destroy the overall consistency of the picture obtained for the two examples discussed.

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Appendix

The integrals $\int_{V_a - V_\varepsilon} \mathrm{d}V_\tau\, \mathbf{W}(\boldsymbol{R}_\tau)$ and $\int_{V_a - V_\varepsilon} \mathrm{d}V_\tau\, \mathbf{V}(\boldsymbol{R}_\tau)$ have to be evaluated. According to (2.4) we have only to consider the spherical harmonics $Y_{2M}(\Omega_\tau)$ and $Y_{4M}(\Omega_\tau)$ divided by R_τ^3. The coordinates of $\boldsymbol{R}_\tau(R_\tau, \Omega_\tau)$ are with respect to a coordinate system S_τ fixed at the centre of the sphere $V_\varepsilon(R_\varepsilon)$ and S is fixed at the centre of the sphere $V_a(R_a)$. The system S is shifted to S_τ by the vector $\boldsymbol{R}^u$ ($R^u + R_\varepsilon \leqslant R_a$) and the z axes are chosen to be parallel so that we have rotational symmetry around the z axis. The volume integrals can be written as surface integrals by use of the divergence differential operator applied to the vector spherical harmonics

$$(1/R_\tau^3)Y_{LM}(\Omega_\tau) = -\sqrt{(2L+1)}/L[1/(L+1)]\,\mathrm{div}((1/R_\tau^2)\boldsymbol{Y}_{LM}^{L-1}(\Omega_\tau)). \tag{A1}$$

Using Gauss's law we obtain

$$I_{\mathrm{LM}} = \int_{V_{\mathrm{a}}-V_{\varepsilon}} \frac{1}{R_{\tau}^{3}} Y_{\mathrm{LM}}(\Omega_{\tau})\,\mathrm{d}V_{\tau} = -\sqrt{\frac{2L+1}{L}}\,\frac{1}{L+1}\int_{S_{\mathrm{a}}+S_{\varepsilon}} \frac{1}{R_{\tau}^{2}} Y_{\mathrm{LM}}^{L-1}(\Omega_{\tau})\,\mathrm{d}S \qquad \text{(A2)}$$

S_{a} and S_{ε} are the surfaces of the spheres V_{a} and V_{ε}, respectively. The axial symmetry immediately leads to $I_{\mathrm{LM}} = 0$ for $M \neq 0$ for both surfaces. Obviously I_{LO} $(L > 0)$ vanishes on S_{ε}. On S_{a} the integrals I_{20} and I_{40} have been calculated explicitly. They vanish independently of the relative values of R_{a} and R^{u}.

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