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The elastic interaction of high-spin and low-spin complex molecules in spin-crossover compounds

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Abstract. Several transition metal compounds show a transition from the low-spin (LS) to the high-spin (HS) electronic state with increasing temperature. The cooperative nature of the transition is usually parametrised by an interaction constant Γ, the origin of which is still under discussion. In the frame of the lattice expansion mode, the interaction Γ is attributed to the elastic interaction between the spin-changing ions as a result of the deformation of the crystal accompanying the transition. In this work the complete elastic energy originating from the so-called image pressure is calculated in closed form by considering the crystal as an isotropic homogeneous elastic medium with the spin-changing ions as incompressible inclusions described by the full elastic dipole tensors $\mathbf{P}^{HS}$ and $\mathbf{P}^{LS}$, respectively. The calculated values of Γ based on x-ray data and reasonable estimates of the elastic constants of the compounds $[Fe(2\text{-pic})_3]Cl_2\cdot Sol$ (2-pic = 2-aminomethylpyridine, Sol = MeOH, EtOH) and $[Fe(2\text{-pic-}ND_2)_3]Cl_2\cdot EtOD$ are compared with the experimental values of Γ.

1. Introduction

The phenomenon of thermally induced high-spin (HS) $\leftrightharpoons$ low-spin (LS) transitions 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. A large variety of transition curves $\gamma(T)$ have been observed (Gütlich 1981, Haddad *et al* 1981, Ewald *et al* 1969). 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. Different interaction mechanisms that lead to the cooperative nature of the (HS) $\leftrightharpoons$ (LS) transition in crystalline solids have been suggested:

(i) coupling to lattice vibrations (Zimmermann and König 1977),

(ii) a cooperative Jahn–Teller type of interaction of the HS ions (Kambara 1979, 1980, 1981), and

(iii) elastic interaction between HS and LS ions via an image pressure that arises from the stress-free boundary condition (Ohnishi and Sugano 1981, Spiering *et al* 1982).

The starting point of all these considerations is the observed volume change of the lattice accompanying the transition of the ions from the LS to the HS state. This volume change leads to a change of the phonon frequencies of the lattice, which are considered by Zimmermann and König (1977). With increasing volume, the Debye frequency ω_D

states and the unit-cell volume of the isomorphic compound with the spin-changing ions substituted by the metal ions M, and V_C is the volume of the crystal per complex molecule. The quantity $\Delta V_{HL} = V_{HS} - V_{LS}$ is the volume change of the compound due to the spin transition and is related to the volume difference of the 'hard spheres' $\Delta v_{HL} = v_{HS} - v_{LS}$ by

$$\Delta V_{HL} = \gamma_0 \Delta v_{HL} . \tag{1.3}$$

Different features of the HS ⇆ LS transition in solid compounds, like the metal dilution effect (Sanner *et al* 1984), the influence of external pressure (Meissner 1983) and the specific heat (Jakobi *et al* 1988), are correctly predicted by the proposed treatment of the lattice expansion model. But unsatisfactorily there is a great discrepancy between the calculated value for the interaction parameter Γ and the value resulting from experiment. The calculated value is about a factor of 5–10 too small, which means that only a minor part of the relevant interaction is captured by the described approximation of the lattice expansion model (Adler *et al* 1986).

So far the calculations within the framework of this model have only taken into consideration the volume change of the crystal due to the spin transition. Detailed x-ray measurements (Mikami *et al* 1980) revealed that the crystal undergoes not only a change in size but also a change in shape owing to the HS ⇆ LS transition, both proportional to the HS fraction γ. Every lattice vector $\boldsymbol{x}(T)$ can be expressed as (Wiehl *et al* 1986)

$$\boldsymbol{x}(T) = (\mathbf{1} + \boldsymbol{\alpha} \cdot \Delta T + \boldsymbol{\varepsilon}_0 \cdot \Delta\gamma) \cdot \boldsymbol{x}(T_0) \tag{1.4}$$

with $\Delta T = T - T_0$ and $\Delta\gamma = \gamma(T) - \gamma(T_0)$. The tensor $\boldsymbol{\alpha}$ describes the thermal lattice expansion and $\boldsymbol{\varepsilon}_c$ the deformation accompanying the spin transition, the trace of which entered into the previous calculations: $\mathrm{Tr}(\boldsymbol{\varepsilon}_c) = \Delta V_{HL}/V_C$. In the present paper we have taken into account the full tensor $\boldsymbol{\varepsilon}_c$ for our calculations. The spin-changing ions and the corresponding metal ions are, therefore, treated as anisotropic defects characterised by tensors $\mathbf{P}^n$ (n = HS, LS, M) instead of isotropic spheres. The traces of these tensors are proportional to the respective misfits $(v_n - v_0)$.

From the viewpoint of elasticity theory, this extension of the previous calculation is imposed for mathematical reasons. Every displacement field $\boldsymbol{U}(\boldsymbol{r})$ in an isotropic elastic medium satisfies the differential equation

$$(1 - 2\sigma)\Delta\boldsymbol{U} + \mathrm{grad}(\mathrm{div}\,\boldsymbol{U}) = \mathbf{0}. \tag{1.5}$$

A multipole expansion in terms of vector spherical harmonics $\boldsymbol{Y}^L_{JM}$ (for definition see Appendix 1) of the six independent solutions of this equation has been given by Shuey and Beyeler (1969), revealing directly the $\boldsymbol{r}$ dependence of the displacement field $\boldsymbol{U}$. Displacement fields proportional to the same power of r are of the same multipole order. A field varying as r^{-2} is called an elastic dipole field. The dipole field satisfying (1.5) has the form (Shuey and Beyeler 1969)

$$\boldsymbol{U}(\boldsymbol{r}) = \frac{1}{\lambda + 2\mu}\frac{1}{r^2}\left(\frac{\boldsymbol{Y}^1_{00}}{(4\pi)^{1/2}}P_s + \frac{3\lambda + 8\mu}{10\mu}\sum_M \frac{\boldsymbol{Y}^1_{2M}}{(3\pi)^{1/2}}P^*_M - \frac{3(\lambda+\mu)}{10\mu}\sum_M \frac{\boldsymbol{Y}^3_{2M}}{(2\pi)^{1/2}}P^*_M\right). \tag{1.6}$$

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 characterised by six parameters: P_s and P_M ($M = -2, -1, 0, 1, 2$), which are combined into a symmetric tensor $\mathbf{P}$. In the previous treatment of the lattice expansion model only the contribution to the displacement field $\boldsymbol{U}$ proportional to P_s, which describes the volume change of the

N point defects within an isotropic elastic medium of volume V_a and a stress-free surface S_a. The elastic energy is obtained by the volume integral

$$W = \tfrac{1}{2} \int \boldsymbol{\varepsilon} \cdot \boldsymbol{\sigma} \, \mathrm{d}V_a \tag{2.3}$$

or according to Gauss' law by the surface integral

$$W = -\tfrac{1}{2} \int \boldsymbol{U}\boldsymbol{\sigma} \, \mathrm{d}\boldsymbol{S}_a$$

where $\mathrm{d}\boldsymbol{S}_a$ is the outward-directed surface element of V_a. Following Eshelby, W is computed in three steps:

(i) The starting point of his considerations is an infinitely extended elastic medium with a closed surface $\boldsymbol{S}_a$ marked out and a distribution of N point defects localised inside $\boldsymbol{S}_a$. The displacement field caused by the defect i shall be $\boldsymbol{U}_i^\infty$ and the corresponding stress and strain tensors $\boldsymbol{\varepsilon}_i^\infty$ and $\boldsymbol{\sigma}_i^\infty$, respectively. The elastic energy W_1 of the described system is composed of the sum of the elastic self-energies $W_\infty(i)$ of the particular defects and the sum of all interaction energy terms $W_{\mathrm{int}}(i,j)$ for two different defects i and j. The displacement in the neighbourhood of the defects is not necessarily described by elasticity theory. Therefore a spherical region of volume v_0 and radius R_0 around each defect is excluded. The energy inside v_0 is composed of the electronic and vibrational energies, which are assumed to be independent of the stress on the surface of v_0 and of a small elastic energy contribution as a result of the finite compressibility of the sphere. This contribution is neglected. This point has been discussed by Shuey and Beyeler (1969). On grounds of these considerations we get for the self-energy of defect i:

$$W_\infty(i) = -\tfrac{1}{2} \int \boldsymbol{U}_i^\infty \, \boldsymbol{\sigma}_i^\infty \, \mathrm{d}\boldsymbol{S}_i \tag{2.4}$$

where $\mathrm{d}\boldsymbol{S}_i = R_0 \, \mathrm{d}\boldsymbol{\Omega}_i \boldsymbol{e}_{r_i}$ is the outward normal vector to the surface $\boldsymbol{S}_i$ of v_0. This expression is independent of the particular position of the defect i. The interaction energy of the so-called direct interaction between two defects depends on the relative positions and orientations of the defects:

$$W_{\mathrm{int}}(i,j) = -\int (\boldsymbol{U}_i^\infty \boldsymbol{\sigma}_j^\infty - \boldsymbol{U}_j^\infty \boldsymbol{\sigma}_i^\infty) \, \mathrm{d}\boldsymbol{S}_{ij} \tag{2.5}$$

where $\boldsymbol{S}_{ij}$ is an arbitrary closed surface in the elastic medium separating the two defects i and j. The elastic energy W_1 for N defects is the sum

$$W_1 = \sum_{i=1}^{N} \left(W_\infty(i) + \tfrac{1}{2} \sum_{j \neq i} W_{\mathrm{int}}(i,j) \right). \tag{2.6}$$

W_{int} will be calculated for several compounds in a forthcoming paper.

(ii) The displacement field on the surface is the superposition of the fields of all defects so that $\boldsymbol{U}^\infty = \Sigma_i \boldsymbol{U}_i^\infty$ and $\boldsymbol{\sigma}^\infty = \Sigma_i \boldsymbol{\sigma}_i^\infty$. The elastic energy outside $\boldsymbol{S}_a$ is obtained by

$$W_2 = -\tfrac{1}{2} \int \boldsymbol{U}^\infty \boldsymbol{\sigma}^\infty \, \mathrm{d}\boldsymbol{S}_a . \tag{2.7}$$

Removing the elastic medium outside $\boldsymbol{S}_a$ one obtains a finite crystal containing N defects in equilibrium by surface tractions $\boldsymbol{\sigma}^\infty \, \mathrm{d}\boldsymbol{S}_a$.

We have introduced the mean-squared dipole tensor components:

$$\overline{|P_\alpha|^2} = \frac{1}{N}\sum_i |P_\alpha^i|^2 = c^{\mathrm{HS}}|P_\alpha^{\mathrm{HS}}|^2 + c^{\mathrm{LS}}|P_\alpha^{\mathrm{LS}}|^2 + c^{\mathrm{M}}|P_\alpha^{\mathrm{M}}|^2. \tag{3.3}$$

When passing from an infinite elastic medium to a crystal of finite size, the displacement field on the surface has to be calculated:

$$\boldsymbol{U}^\infty(\boldsymbol{r}) = \sum_{i=1}^{N} \boldsymbol{U}_i^\infty(\boldsymbol{r}_i'). \tag{3.4}$$

The vectors r and r' are directed to an arbitrary point outside or on the surface of the crystal from the origin of the coordinate system and from the defect i at $\boldsymbol{R}_i$, respectively, so that $\boldsymbol{r}_i' = \boldsymbol{r} - \boldsymbol{R}_i$. Since the distance between neighbouring defects (i.e. the lattice spacing) is sufficiently small compared with the dimensions of the crystal, the discrete distribution of dipole defects can be treated as a continuous distribution with dipole tensor density $\boldsymbol{\pi}(\boldsymbol{R})$, so that the sum in (3.4) is replaced by an integration:

$$\boldsymbol{U}^\infty(\boldsymbol{r}) = \int_{V_\mathrm{a}} \boldsymbol{U}_\pi^\infty(\boldsymbol{r}')\,\mathrm{d}V(\boldsymbol{R}). \tag{3.5}$$

$\boldsymbol{U}_\pi^\infty$ is given by (1.6) replacing P_α by π_α, $\alpha = \mathrm{s}, M$. For a homogeneous distribution of defects, the density $\boldsymbol{\pi}$ does not depend on $\boldsymbol{R}$. The components are $\pi_\alpha = \bar{P}_\alpha/V_\mathrm{C}$, where $V_\mathrm{C} = V_\mathrm{a}/N$ is the crystal volume per defect and $\bar{P}_\alpha$ is the mean tensor component

$$\bar{P}_\alpha = c^{\mathrm{HS}}P_\alpha^{\mathrm{HS}} + c^{\mathrm{LS}}P_\alpha^{\mathrm{LS}} + c^{\mathrm{M}}P_\alpha^{\mathrm{M}}.$$

The integration in (3.5) is performed assuming V_a to be a spherical volume of radius R_a. The following integrals have to be calculated:

$$V_\mathrm{a}^{-1}\int_0^{R_\mathrm{a}}\int_\Omega r^{-2}\boldsymbol{Y}_{JM}^L(\boldsymbol{r}')\,\mathrm{d}V(\boldsymbol{R}) \qquad \mathrm{d}V(\boldsymbol{R}) = R^2\,\mathrm{d}R\,\mathrm{d}\Omega \tag{3.6}$$

with indices $\{(LJM)\} = \{(100), (12M), (32M); M = -2, -1, 0, 1, 2\}$. These integrals were solved by interchanging integration and differentiation of the functions r' and r'^{-1} by suitable differential vector operators $\boldsymbol{D}_{JM}^L$ ($\boldsymbol{D}_{JM}^1 r'^{-1} = r'^{-2}\boldsymbol{Y}_{JM}^1$ and $\boldsymbol{D}_{JM}^3 r' = r'^{-2}\boldsymbol{Y}_{JM}^3$). For the explicit expressions for the $\boldsymbol{D}_{JM}^L$ see Appendix 2. With the known solutions of the integrals of r' and r'^{-1} we obtain for $r \geqslant R_\mathrm{a}$

$$V_\mathrm{a}^{-1}\boldsymbol{D}_{JM}^1\int_{V_\mathrm{a}} r'^{-1}\,\mathrm{d}V = \boldsymbol{D}_{JM}^1 r^{-1} = r^{-2}\boldsymbol{Y}_{JM}^1(\boldsymbol{r}) \tag{3.7a}$$

$$V_\mathrm{a}^{-1}\boldsymbol{D}_{JM}^3\int_{V_\mathrm{a}} \boldsymbol{r}'\,\mathrm{d}V = \boldsymbol{D}_{JM}^3(r + \tfrac{1}{5}R_\mathrm{a}^2 r^{-1}) = (r^{-2} - R_\mathrm{a}^2 r^{-4})\boldsymbol{Y}_{JM}^3(\boldsymbol{r}). \tag{3.7b}$$

Finally the displacement outside V_a is given by

$$\boldsymbol{U}^\infty(\boldsymbol{r}) = \frac{N}{\lambda + 2\mu}\frac{1}{r^2}\left\{-\frac{Y_{00}^1}{(4\pi)^{1/2}}\bar{P}_\mathrm{s} + \sum_M \bar{P}_M^* \times\left[\frac{3\lambda + 8\mu}{10\mu}\frac{\boldsymbol{Y}_{2M}^1}{(3\pi)^{1/2}} - \frac{3(\lambda+\mu)}{10\mu}\frac{\boldsymbol{Y}_{2M}^3}{(2\pi)^{1/2}}\left(1 - \frac{R_\mathrm{a}^2}{r^2}\right)\right]\right\}. \tag{3.8}$$

and the trace $\varepsilon_{c,s} = \varepsilon_{c,xx} + \varepsilon_{c,yy} + \varepsilon_{c,zz}$. The displacement $\boldsymbol{U}_c$ is then given by

$$\boldsymbol{U}_c = R_a(\Sigma\varepsilon^*_{c,M}\boldsymbol{a}_M\boldsymbol{e}_r + \tfrac{1}{3}\varepsilon_{c,s}\boldsymbol{e}_r). \tag{4.2}$$

The displacement $\boldsymbol{U}(R_a)$ of (3.12) can also be written as a product of a second-rank tensor times $\boldsymbol{e}_r$. With $\boldsymbol{Y}^1_{00} = -\boldsymbol{e}_r(4\pi)^{1/2}$ and $\boldsymbol{Y}^1_{2M} = [3/(4\pi)]^{1/2}\boldsymbol{a}_M\boldsymbol{e}_r$, comparison of the coefficients gives the desired relation:

$$\varepsilon_{c,s} = 3NV_a^{-1}(3\lambda + 2\mu)^{-1}P_s \qquad \varepsilon_{c,M} = NV_a^{-1}(2\mu)^{-1}P_M \tag{4.3}$$

where V_a is the volume of the spherical crystal.

Since $\boldsymbol{\varepsilon}_c$ describes the strain at all points of the homogeneous medium, the tensor $\mathbf{P}$ has the same property. If there are equivalent lattice sites in a unit cell of a real crystal, only the average tensor of the different sites can be determined by the tensor $\boldsymbol{\varepsilon}_c$. This fact has consequences for the calculation of the direct interaction where all tensor components of $\mathbf{P}$ at all lattice sites are needed.

5. Application of the lattice expansion model to the HS ⇆ LS transition in mixed crystals

Essential results concerning the spin transition phenomenon have been obtained from investigations of mixed crystal compounds such as, for example, $[Fe_xZn_{1-x}(2-pic)_3]Cl_2.EtOH$. For such compounds the mean tensor components are given by

$$\bar{P}_\alpha = x\gamma P^{HS}_\alpha + x(1-\gamma)P^{LS}_\alpha + (1-x)P^M_\alpha \qquad \alpha = s, M. \tag{5.1}$$

All complexes in the lattice, HS, LS and metal complexes M, are considered as defects even in the case of a pure lattice of only one species. So every lattice has a deformation tensor $\boldsymbol{\varepsilon}_c$ which is referred to a fictitious lattice containing complexes of vanishing tensor $\mathbf{P}$. This lattice can be defined by the minimum elastic energy achieved by the special shape and size of complexes. As long as only tensor differences are considered, the fictitious lattice, which is a reference for the absolute strain energy, plays no role. Only changes of a lattice can be measured. The tensor difference $\boldsymbol{\varepsilon}^{HS}_c - \boldsymbol{\varepsilon}^{LS}_c$, which will be denoted by the index HL ($\boldsymbol{\varepsilon}^{HL}_c$), describes the deformation as a result of the transition from the LS to the HS state. Similarly we obtain the differences $\boldsymbol{\varepsilon}^{ML}_c$ and $\boldsymbol{\varepsilon}^{MH}_c$ comparing the lattice of the isomorphic metal compound with the pure LS and HS compounds (at the same temperature), respectively.

Defining an average tensor $\bar{\boldsymbol{\varepsilon}}_c$ in the same way as $\bar{\mathbf{P}}$ and inserting (4.3) in the expression for the energy $W = W_\infty - W_2 - W_3$ of (3.2) and (3.12) we obtain ($V_c = V_a/N$)

$$\begin{aligned} W = {} & NV_c^2 v_0^{-1}\tfrac{1}{2}K(\gamma_0 - 1)\gamma_0^{-2}\left(\overline{\varepsilon_{c,s}}^2 + \tfrac{3}{50}(9\gamma_0^2 + 19\gamma_0 + 26)\sum_M \overline{|\varepsilon_{c,M}|^2}\right) \\ & - NV_c\tfrac{1}{2}K(\gamma_0 - 1)\gamma_0^{-1}\left(\overline{\varepsilon^2_{c,s}} + \tfrac{3}{10}(2\gamma_0 + 1)\sum_M \overline{|\varepsilon_{c,M}|^2}\right) \end{aligned} \tag{5.2}$$

where the bulk modulus K and the Eshelby constant γ_0 are introduced instead of the Lamé coefficients λ and μ. If we omit terms that are independent of the HS fraction γ, the strain energy per spin-changing complex $G = W/xN$ valid for all x and γ is given by

$$G = \gamma E + x\gamma\Delta' - x\gamma^2\Gamma'. \tag{5.3}$$

Table 1. The deformation tensors $\boldsymbol{\varepsilon}^{AB}$ of the lattice A with respect to the lattice B ($\boldsymbol{\varepsilon}^{HL} \equiv \boldsymbol{\varepsilon}^{HS} - \boldsymbol{\varepsilon}^{LS}$ and $\boldsymbol{\varepsilon}^{ZnH} \equiv \boldsymbol{\varepsilon}^{Zn} - \boldsymbol{\varepsilon}^{HS}$; see § 5) and the volume V_c at room temperature of the lattice per complex molecule are obtained from x-ray data (Wiehl 1987, Wiehl *et al* 1986). The angle α is included by the monoclinic a axis and the x axis of that system to which the $\boldsymbol{\varepsilon}$ tensor is referred. The interaction parameter Γ and the ratio $q = \Delta/(2\Gamma)$ (see text) are determined from the HS ⇆ LS transition curves of the mixed crystals (M = Zn, Co).

	$[Fe(M)(2\text{-pic})_3]Cl_2 \cdot EtOH$		$[Fe(2\text{-pic-}ND_2)_3]Cl_2 \cdot EtOD$	$[Fe(2\text{-pic})_3]Cl_2 \cdot MeOH$
	$\boldsymbol{\varepsilon}^{HL}$	$\boldsymbol{\varepsilon}^{ZnH}$	$\boldsymbol{\varepsilon}^{HL}$	$\boldsymbol{\varepsilon}^{HL}$
$\varepsilon_{xx} \times 10^2$	2.93	−0.39	2.23	0.18
$\varepsilon_{yy} \times 10^2$	1.57	−0.42	1.18	1.43
$\varepsilon_{zz} \times 10^2$	−2.07	0.63	−1.53	0.83
$\varepsilon_{xz} \times 10^2$	0	−0.15	0	0
α (deg)	14.0	14.0	15.6	0
V_c (Å^3)	621	—	620	577
Γ (cm^{-1})	130	—	152	98
q(Zn)	0.93	—	0.88	0.80
q(Co)	0.73	—	—	0.69

The lattice expansion model in the approximation of dipole defects in a homogeneous elastic medium obviously does not give a complete explanation of the observed interaction energy between the Fe complexes in the HS and LS states. We cannot expect an improvement by using higher-order terms of the multipole expansion of the displacement vector $\boldsymbol{U}$. The next terms describing a uniform dilatation are proportional to r^{-4}. The displacement $\boldsymbol{U}(R_a)$ on the surface is then proportional to R_a^{-1} and therefore vanishes for macroscopic crystals.

We are, however, convinced that the interaction between the complexes is of elastic origin. Therefore we shall discuss in a forthcoming paper the direct interaction (2.5). Preliminary computer calculations have been started. For the lattice parameters of the deuterated compound we obtained Γ values of about 60 cm^{-1} with a bulk modulus and an Eshelby constant as has been determined by the Mössbauer measurements. On the one hand, such a large value is encouraging in explaining the large interaction constant but on the other hand one runs into the difficulty of explaining the absence of clustering effects in these phase transitions.

7. Conclusions

Eshelby discussed the interaction energy of a solid solution of defects by the so-called 'sphere-in-a-hole model'. The spherical defects interact via the image pressure of the stress-free boundary. The interaction energy depends on the concentration of the homogeneously distributed defects but not on the shape of the crystal. The defects are considered as spherical elastic inclusions with elastic constants different from the surrounding material, which is approximated by a homogeneous isotropic elastic medium. The direct elastic interaction between spherical defects vanishes. The problem solved in this paper is as follows. The inclusion is described by a general dipole defect with vanishing compressibility. The defects are homogeneously distributed over the crystal and have the same orientation. The defects interact via the image pressure of a stress-free spherical surface. The spherical shape of the crystal is deformed by the coherently oriented defects. The expressions combining the deformation tensor and the tensor components of the defects are explicitly given.

This result has been applied to the HS $\leftrightarrows$ LS phenomenon. The cooperativity of the phase transition is understood by an interaction between the HS and LS complex molecules. The spin-changing ions are considered as dipole defects with the properties described above and an interaction constant is calculated from the deformation of the lattice accompanying the transition observed by x-ray measurements and the elastic constants of the crystal. Separating the contributions of the spherical part (according to Eshelby) and the anisotropic part of the dipole tensor of the defects to the interaction constants one finds the result that the spherical part is the smaller contribution.

At present the 'lattice expansion model' is the only approach that relates the interaction energy to the properties of the spin-changing ions and of their surrounding lattice, which are accessible by independent experimental methods. The examples known from the literature, where the interaction parameters were deduced from the transition curves and where x-ray data are available, are discussed. The spherical part of the dipole tensor is not sufficient to explain the size of the interaction observed. This was the difficulty of the 'lattice expansion model' in the approximation of the 'sphere-in-a-hole model' of Eshelby. The anisotropic part of the dipole tensor improves the situation considerably but still the interaction cannot be taken as understood. A quantitative understanding

and

$$\text{symgrad}\, \boldsymbol{Y}_{JM}^{J-1} = -\left(\frac{(J+1)(2J+3)}{6(2J-1)(2J+1)}\right)^{1/2} \boldsymbol{E}_{JM}^{J}\left(\frac{\partial}{\partial r} - \frac{J-1}{r}\right) + \left(\frac{J-1}{2J-1}\right)^{1/2} \boldsymbol{E}_{JM}^{J-2}\left(\frac{\partial}{\partial r} + \frac{J}{r}\right)$$

$$\text{symgrad}\, \boldsymbol{Y}_{JM}^{J} = -\left(\frac{J+2}{2(2J+1)}\right)^{1/2} \boldsymbol{E}_{JM}^{J+1}\left(\frac{\partial}{\partial r} - \frac{J}{r}\right) + \left(\frac{J-1}{2(2J+1)}\right)^{1/2} \boldsymbol{E}_{JM}^{J-1}\left(\frac{\partial}{\partial r} + \frac{J+1}{r}\right)$$

$$\text{symgrad}\, \boldsymbol{Y}_{JM}^{J+1} = -\left(\frac{J+2}{2J+3}\right)^{1/2} \boldsymbol{E}_{JM}^{J+2}\left(\frac{\partial}{\partial r} - \frac{J+1}{r}\right) + \left(\frac{J(2J-1)}{6(2J+3)(2J+1)}\right)^{1/2} \boldsymbol{E}_{JM}^{J}\left(\frac{\partial}{\partial r} + \frac{J+2}{r}\right). \tag{A1.4}$$

The tensor spherical harmonics $\boldsymbol{E}_{JM}^{L}$ are similarly defined as the $\boldsymbol{Y}_{JM}^{L}$ replacing the unit vectors $\boldsymbol{e}_n$ by the unit tensors

$$\boldsymbol{a}_M = \sum_{m,n} C_{1m1n}^{2M} \boldsymbol{e}_m \boldsymbol{e}_n. \tag{A1.5}$$

The $\boldsymbol{E}_{JM}^{L}$ obey the orthonormality relation

$$\mathrm{Tr}\left(\int (\boldsymbol{E}_{JM}^{L})^{*} \boldsymbol{E}_{JM'}^{L}\, \mathrm{d}\boldsymbol{\Omega}\right) = \delta_{LL'}\delta_{JJ'}\delta_{MM}.$$

The traction on the surface of a sphere is evaluated by use of the following formulae (Shuey and Beyeler 1969):

$$\boldsymbol{e}_r Y_{JM} = \left(\frac{J}{2J+1}\right)^{1/2} \boldsymbol{Y}_{JM}^{J-1} - \left(\frac{J+1}{2J+1}\right)^{1/2} \boldsymbol{Y}_{JM}^{J+1} \tag{A1.6}$$

and

$$\boldsymbol{e}_r \boldsymbol{E}_{JM}^{J+2} = -\left(\frac{J+2}{2J+3}\right)^{1/2} \boldsymbol{Y}_{JM}^{J+1} \qquad \boldsymbol{e}_r \boldsymbol{E}_{JM}^{J+1} = -\left(\frac{J+2}{2(2J+1)}\right)^{1/2} \boldsymbol{Y}_{JM}^{J}$$

$$\boldsymbol{e}_r \boldsymbol{E}_{JM}^{J} = \left(\frac{J(2J-1)}{6(2J+3)(2J+1)}\right)^{1/2} \boldsymbol{Y}_{JM}^{J+1} - \left(\frac{(J+1)(2J+3)}{6(2J-1)(2J+1)}\right)^{1/2} \boldsymbol{Y}_{JM}^{J-1} \tag{A1.7}$$

$$\boldsymbol{e}_r \boldsymbol{E}_{JM}^{J-1} = \left(\frac{J-1}{2(2J+1)}\right)^{1/2} \boldsymbol{Y}_{JM}^{J} \qquad \boldsymbol{e}_r \boldsymbol{E}_{JM}^{J-2} = \left(\frac{J-1}{2J-1}\right) \boldsymbol{Y}_{JM}^{J-1}.$$

Appendix 2. Differential operators $\boldsymbol{D}_{JM}^{L}$

The vector operators $\boldsymbol{D}_{JM}^{L}$ are constructed in the same manner as the vector spherical harmonics:

$$\boldsymbol{D}_{JM}^{L} = \sum_{m,n} C_{Lm1n}^{JM} \boldsymbol{e}_n D_{Lm}.$$

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The operators D_{1m} and D_{3m} generate the spherical harmonics Y_{1m} and Y_{3m} multiplied by r'^{-2} from the functions r'^{-1} and r', respectively ($r' = |\boldsymbol{r} - \boldsymbol{R}|$). The operator D_{1m} is very easily constructed. The functions $r'^{-2}Y_{1m}(\boldsymbol{r}')$ are linear combinations of $x_i' r'^{-3}$ ($i = 1, 2, 3$). Since $(\partial/\partial x_i)r'^{-1} = -x_i r'^{-3}$ the differential operator is the same linear combination of $-\partial/\partial x_i$:

$$D_{10} = -\frac{1}{2}\left(\frac{3}{\pi}\right)^{1/2}\frac{\partial}{\partial z} \qquad D_{1,\pm 1} = \mp\frac{1}{2}\left(\frac{3}{2\pi}\right)^{1/2}\left(\frac{\partial}{\partial x} \pm \mathrm{i}\frac{\partial}{\partial y}\right). \tag{A2.1}$$

The operators D_{3m} are more complicated:

$$\begin{aligned}
D_{30} &= \left(\frac{7}{4\pi}\right)^{1/2} D_z(-3, -3, 2) \\
D_{3,\pm 1} &= \mp\frac{1}{8}\left(\frac{21}{\pi}\right)^{1/2}[D_x(-1, -1, 4) \pm \mathrm{i}D_y(-1, -1, 4)] \\
D_{3,\pm 2} &= \frac{1}{4}\left(\frac{105}{4\pi}\right)^{1/2}[D_z(1, -1, 0) \pm 2\mathrm{i}\, D_{xyz}] \\
D_{3,\pm 3} &= \mp\frac{1}{8}\left(\frac{35}{\pi}\right)^{1/2}[D_x(1, -3, 0) \pm \mathrm{i}\, D_y(3, -1, 0)]
\end{aligned} \tag{A2.2}$$

where

$$\begin{aligned}
D_{xyz} &= \frac{1}{3}\frac{\partial^3}{\partial x\,\partial y\,\partial z} \\
D_z(a, b, c) &= -\frac{1}{6}\frac{\partial}{\partial z}\left((-a + b + 3c)\frac{\partial^2}{\partial x^2} + (a - b + 3c)\frac{\partial^2}{\partial y^2} + (a + b + c)\frac{\partial^2}{\partial z^2}\right).
\end{aligned} \tag{A2.3}$$

D_x and D_y are obtained by cyclic permutation of x, y, z. Application of these operators on r and r^{-1} (correspondingly r') gives ($x_i = x, y, z$):

$$\begin{aligned}
D_{x_i} r &= \frac{x_i}{r^5}(ax^2 + by^2 + cz^2) \\
D_{xyz} r &= \frac{xyz}{r^5}
\end{aligned} \tag{A2.4}$$

and

$$\begin{aligned}
D_x r^{-1} &= -\frac{5}{r^2}D_x r + (3a + b + c)\frac{x}{r^5} \\
D_y r^{-1} &= -\frac{5}{r^2}D_y r + (a + 3b + c)\frac{y}{r^5} \\
D_z r^{-1} &= -\frac{5}{r^2}D_z r + (a + b + 3c)\frac{z}{r^5} \\
D_{xyz} r^{-1} &= -\frac{5}{r^2}D_{xyz} r.
\end{aligned} \tag{A2.5}$$

requires a generalisation to (i) anisotropic elastic properties, (ii) non-spherical shapes of the crystals, and (iii) the calculation of the direct elastic interaction between the complexes. Another open question is the dependence of intra-molecular HS and LS states on the weak stress fields in the crystals and whether such a dependence gives significant contributions to the interaction as is assumed by Kambara (1981) and also by Ohnishi and Sugano (1981).

Acknowledgment

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Appendix 1. Elastic multipoles in an isotropic medium

Shuey and Beyeler (1969) have given a multipole expansion in terms of vector spherical harmonics $\boldsymbol{Y}^L_{JM}$ for the equilibrium displacements of the second-order differential equation (1.6). For a given JM with $J \neq 0$ there are six independent solutions:

$$\begin{aligned}
\boldsymbol{U}^1_{JM}(\boldsymbol{r}) &= r^{J+1}\{[2\mu(3J+1)+2\lambda J]\boldsymbol{Y}^{J+1}_{JM} + (\lambda+\mu)(2J+3)[J(J+1)]^{1/2}\boldsymbol{Y}^{J-1}_{JM}\} \\
\boldsymbol{U}^2_{JM}(\boldsymbol{r}) &= r^J\boldsymbol{Y}^J_{JM} \\
\boldsymbol{U}^3_{JM}(\boldsymbol{r}) &= r^{J-1}\boldsymbol{Y}^{J-1}_{JM} \\
\boldsymbol{U}^4_{JM}(\boldsymbol{r}) &= r^{-J}\{[2\mu(3J+2)+2\lambda(J+1)]\boldsymbol{Y}^{J-1}_{JM} \\
&\qquad - (\lambda+\mu)(2J-1)[J(J+1)]^{1/2}\boldsymbol{Y}^{J+1}_{JM}\} \\
\boldsymbol{U}^5_{JM}(\boldsymbol{r}) &= r^{-J-1}\boldsymbol{Y}^J_{JM} \\
\boldsymbol{U}^6_{JM}(\boldsymbol{r}) &= r^{-J-2}\boldsymbol{Y}^{J+1}_{JM}.
\end{aligned} \tag{A1.1}$$

The $\boldsymbol{Y}^L_{JM}$ are linear combinations of the products of the spherical harmonics and the spherical unit vectors $\boldsymbol{e}_0 = \boldsymbol{e}_z$, $\boldsymbol{e}_\pm = \mp(1/\sqrt{2})(\boldsymbol{e}_x \pm \mathrm{i}\boldsymbol{e}_y)$:

$$\boldsymbol{Y}^L_{JM}(\theta,\varphi) = \sum_{m,n} C^{JM}_{Lm1n}\boldsymbol{e}_n Y_{Lm}(\theta,\varphi) \tag{A1.2}$$

where the C^{JM}_{Lm1n} are the Clebsch–Gordan coefficients. The $\boldsymbol{Y}^L_{JM}$ obey the orthonormality relation

$$\int (\boldsymbol{Y}^L_{JM})^*\boldsymbol{Y}^{L'}_{J'M'}\,\mathrm{d}\boldsymbol{\Omega} = \delta_{LL'}\delta_{JJ'}\delta_{MM'}.$$

For the calculation of the strain tensor $\boldsymbol{\varepsilon}$ the divergence (div) and the symmetric gradient (symgrad) applied to the $\boldsymbol{Y}^L_{JM}$ are needed:

$$\begin{aligned}
\operatorname{div}\boldsymbol{Y}^{J-1}_{JM} &= \left(\frac{J}{2J+1}\right)^{1/2} Y_{JM}\left(\frac{\partial}{\partial r} - \frac{J-1}{r}\right) \qquad \operatorname{div}\boldsymbol{Y}^J_{JM} = 0 \\
\operatorname{div}\boldsymbol{Y}^{J+1}_{JM} &= -\left(\frac{J+1}{2J+1}\right)^{1/2} Y_{JM}\left(\frac{\partial}{\partial r} + \frac{J+2}{r}\right)
\end{aligned} \tag{A1.3}$$

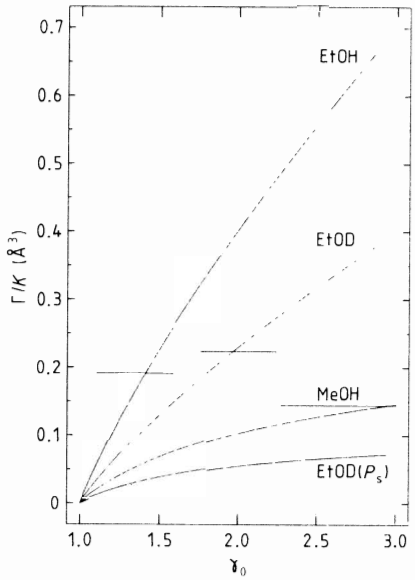

Figure 1. The theoretical expression for Γ/K according to equation (5.4*b*) ($\Gamma' = \Gamma(x = 1)$) is plotted using the x-ray data of the three compounds as given in table 1. The ratio Γ/K with a bulk modulus of $K = 1.35 \times 10^{10}$ N m^{-2} and the experimental value of the interaction constant Γ (table 1) are shown as horizontal lines. For the deuterated compound the theoretical value of Γ/K, which takes into account only the isotropic part of the dipole tensor (P_s), is plotted to demonstrate the larger contribution of the anisotropic tensor components.

magnitude between these contributions. The actual values are the result of the large anisotropic deformation of the lattice. A vanishing isotropic part is even conceivable. In that case the crystal changes its shape but not its volume.

The anisotropic dipole interaction treated in this paper improves the calculation considerably but still the size of Γ cannot be explained completely by the image pressure. In figure 1 the ratio Γ/K with a bulk modulus of $K = 1.35 \times 10^{10}$ N m^{-2} and the experimental Γ values of table 1 are shown as horizontal lines. The value of K was determined by Mössbauer measurements of the Debye–Waller factor f in the deuterated compound (Meissner *et al* 1987). For the EtOH compound Γ/K leads to a reasonable Eshelby constant of $\gamma = 1.46$ ($\sigma = 0.35$). The value of $\gamma = 2.0$ for the deuterated compound is not in agreement with $\gamma_0 = 1.25$ also determined by the Mössbauer work of Meissner *et al* (1987). In the case of the MeOH compound Γ/K is obviously too large ($\gamma_0 \sim 3$).

The ratio $q = \Delta/(2\Gamma)$ for a mixed crystal system depends on the tensors $\boldsymbol{\varepsilon}_c^{HL}$ and $\boldsymbol{\varepsilon}_c^{ML}$ and the Eshelby constant γ_0 according to (5.4*a*, *b*). A rather good agreement between the ratio of the experimental values Δ and Γ and the ratio $\varepsilon_{c,s}^{ML}/\varepsilon_{c,s}^{HL}$, which is the q value in the isotropic approximation, was found for the three compounds. For example the calculated value of the EtOH compound $q = 0.926$ corresponds to a ratio $\Delta/(2\Gamma) = 0.93$. These agreements are remarkable because the calculated value of Γ is too small by a factor of 5–10 if only the isotropic approximation is applied. Since the discrepancy in the size of Γ could not be removed we do not expect an agreement of the ratios on the basis of the improved theory. The tensor $\boldsymbol{\varepsilon}_c^{ZnL}$ is known from x-ray work of Mikami *et al* (1980) (see table 1). The q-values calculated with (5.4*a*, *b*) are now in the range 0.83–0.80 for $1 \leq \gamma_0 \leq 3$, which is much less than the measured value of 0.93.

We use the abbreviation $C_E = \frac{1}{2}KV_c(\gamma_0 - 1)\gamma_0^{-1}$, which has the dimension of an energy. Then the three terms are expressed as

$$E = C_E\left(\frac{V_c}{\gamma_0 V_0}(\varepsilon_{c,s}^{HS} + \varepsilon_{c,s}^{LS}) - 2\varepsilon_{c,s}^{M}\right)\varepsilon_{c,s}^{HL} + \tfrac{3}{5}C_E\left(\frac{V_c}{\gamma_0 V_0}\tfrac{1}{10}(9\gamma_0^2 + 19\gamma_0 + 26)\right.$$
$$\left.\times([\boldsymbol{\varepsilon}_{c,d}^{HS} + \boldsymbol{\varepsilon}_{c,d}^{LS}]\boldsymbol{\varepsilon}_{c,d}^{HL})_s - (2\gamma_0 + 1)(\boldsymbol{\varepsilon}_{c,d}^{M}\boldsymbol{\varepsilon}_{c,d}^{HL})_s\right) \tag{5.4a}$$

$$\Gamma' = C_E[(\boldsymbol{\varepsilon}_{c,s}^{HL})^2 + \tfrac{3}{10}(2\gamma_0 + 1)(\boldsymbol{\varepsilon}_{c,d}^{HL}\boldsymbol{\varepsilon}_{c,d}^{HL})_s] \tag{5.4b}$$

$$\Delta' = 2C_E[\boldsymbol{\varepsilon}_{c,s}^{HL}\boldsymbol{\varepsilon}_{c,s}^{ML} + \tfrac{3}{10}(2\gamma_0 + 1)(\varepsilon_{c,d}^{HL}\boldsymbol{\varepsilon}_{c,d}^{ML})_s] \tag{5.4c}$$

where the invariant of the product of two tensors $\boldsymbol{\varepsilon}^a$ and $\boldsymbol{\varepsilon}^b$ is denoted as $(\boldsymbol{\varepsilon}^a\boldsymbol{\varepsilon}^b)_s = \Sigma\, \boldsymbol{\varepsilon}_m^{a*}\boldsymbol{\varepsilon}_m^{b}$. The expression for E contains energy terms proportional to the strain tensors $\boldsymbol{\varepsilon}_c^{\alpha}$, α = M, HS, LS itself. This means that E is defined by the fictitious stress-free lattice, so that we have for pure states ($\gamma = x = 1$) non-vanishing strain energy G. This behaviour may be unexpected at first sight.

The relation to the thermodynamic description of the spin transition phenomenon is easily seen. The Gibbs free energy of the non-interacting stress-free spin-crossover complexes as can be observed in liquid solution is $G_{HL}(\gamma, p, T)$. In the solid solution of a highly diluted mixed crystal ($x \to 0$) the elastic self-energy G_s^n (n = HS, LS) of the complexes that are defects at their lattice sites has to be added so that $G_{x\to 0} = G_{HL}(\gamma, p, T) + \gamma G_s^{HS} + (1-\gamma)G_s^{LS}$. Omitting the energy shift G_s^{LS} the Gibbs free energy per spin-changing complex for $x > 0$ is obtained, including the interaction term G_{int} of (1.1), as

$$G(\gamma, p, T) = G_{HL}(\gamma, p, T) + \gamma(G_s^{HS} - G_s^{LS}) + \gamma\Delta(x) - \gamma^2\Gamma(x). \tag{5.5}$$

Comparison with (5.3) leads to theoretical expressions for the energy difference $G_s^{HS} - G_s^{LS} = E$, the parameter $\Delta(x) = x\Delta'$ and the interaction constant $\Gamma(x) = x\Gamma'$.

6. Discussion

The theoretical expression for $G_s^{HS} - G_s^{LS}$ cannot be compared with experiment without further assumptions since E depends on the strain tensor $\boldsymbol{\varepsilon}_c^{M}$ itself and on the sum $\boldsymbol{\varepsilon}_c^{HS} + \boldsymbol{\varepsilon}_c^{LS}$, which are not available experimentally. In the following we will discuss the parameters Δ and Γ, which depend on the differences (see (5.4)) $\boldsymbol{\varepsilon}_c^{HL} = \boldsymbol{\varepsilon}_c^{HS} - \boldsymbol{\varepsilon}_c^{LS}$ and $\boldsymbol{\varepsilon}_c^{ML} = \boldsymbol{\varepsilon}_c^{M} - \boldsymbol{\varepsilon}_c^{LS}$. The tensor $\boldsymbol{\varepsilon}_c^{HL}$ is given in table 1 for three compounds and for one of them the tensor $\boldsymbol{\varepsilon}_c^{ZnH} = \boldsymbol{\varepsilon}_c^{ZnL} - \boldsymbol{\varepsilon}_c^{HL}$.

The linear dependence of the parameters Δ and Γ on the concentration x of the spin-changing ions is in agreement with the experimental results. This fact was first proved under the assumption of isotropic dipole defects (Spiering *et al* 1982). The problem was the explanation of the size of the interaction constant Γ. In figure 1 the expression for Γ/K as derived from (5.4*b*) is plotted versus the Eshelby constant γ_0 for the three compounds of table 1 (in the following denoted as EtOH, MeOH and deuterated compound, respectively). Γ/K depends only on x-ray data, which are the volume V_c per complex molecule and the strain tensor $\boldsymbol{\varepsilon}_c^{HL}$. For the deuterated compound the isotropic part, which depends only on $\varepsilon_{c,s}^{HL}$, is plotted. This part is obviously less than 30% of the total calculated interaction. Normally anisotropic effects are small corrections to the main isotropic part, but here the opposite is true. Remembering the same r^{-2} dependence of the isotropic and anisotropic stress fields, we cannot expect different orders of

The displacement field $\boldsymbol{U}^{\mathrm{I}}$ is now obtained from the solution of the boundary-value problem of an isotropic elastic sphere subject to external tractions $\boldsymbol{\sigma}^{\mathrm{I}}\boldsymbol{e}_r = -\boldsymbol{\sigma}^{\infty}\boldsymbol{e}_r$ on the surface S_{a}. Applying (2.1) and (2.2) the traction $\boldsymbol{\sigma}^{\mathrm{I}}\boldsymbol{e}_r$ is calculated to be

$$\boldsymbol{\sigma}^{\mathrm{I}}\boldsymbol{e}_r|_{r=R_{\mathrm{a}}} = -NR_{\mathrm{a}}^{-3}(\lambda+\mu)^{-1}\left(4\mu\frac{\boldsymbol{Y}_{00}^{1}}{(4\pi)^{1/2}}\bar{P}_{\mathrm{s}} - \frac{9\lambda+14\mu}{10}\sum_{M}\bar{P}_{M}^{*}\frac{\boldsymbol{Y}_{2M}^{1}}{(3\pi)^{1/2}}\right). \tag{3.9}$$

Difficulties arise from the regions of volume v_0 enclosing the defects because the surface of each of these regions is an additional boundary of the elastic medium. This complication can be overcome by an argument due to Siems (1986). The defects together with their surrounding volumes v_0 are replaced by elastic material with the same properties (λ and μ) as the crystal in such a way that the original displacement field $\boldsymbol{U}^{\infty}$ is conserved so that the boundaries vanish. The displacement $\boldsymbol{U}^{\mathrm{I}}$ is a linear combination of the basic solutions $\boldsymbol{U}_{JM}^{i}$ (see Appendix 1), which are regular at $r = 0$:

$$\boldsymbol{U}^{\mathrm{I}}(\boldsymbol{r}) = \sum \alpha_{JM}^{1}\boldsymbol{U}_{JM}^{1} + \alpha_{JM}^{2}\boldsymbol{U}_{JM}^{2} + \alpha_{JM}^{3}\boldsymbol{U}_{JM}^{3}. \tag{3.10}$$

The coefficients α_{JM}^{i} are determined by comparison of the surface traction $\boldsymbol{\sigma}^{\mathrm{I}}(r = R_{\mathrm{a}})\boldsymbol{e}_r$ calculated from (3.10) with the surface traction of (3.9). The displacement field $\boldsymbol{U}^{\mathrm{I}}(\boldsymbol{r})$ of the boundary becomes proportional to r:

$$\boldsymbol{U}^{\mathrm{I}}(\boldsymbol{r}) = \frac{N}{\lambda+2\mu}\frac{r}{R_{\mathrm{a}}^{3}}\left(\frac{4\lambda}{3\lambda+2\mu}\frac{\boldsymbol{Y}_{00}^{1}}{(4\pi)^{1/2}}\bar{P}_{\mathrm{s}} + \frac{9\lambda+14\mu}{20\mu}\sum_{M}\bar{P}_{M}^{*}\frac{Y_{2M}^{1}}{(3\pi)^{1/2}}\right). \tag{3.11}$$

The total displacement $\boldsymbol{U} = \boldsymbol{U}^{\mathrm{I}} + \boldsymbol{U}^{\infty}$ of the surface of the sphere

$$\boldsymbol{U}(\boldsymbol{R}_{\mathrm{a}}) = 3NR_{\mathrm{a}}^{-2}\left(-(3\lambda+2\mu)^{-1}\frac{\boldsymbol{Y}_{00}^{1}}{(4\pi)^{1/2}}\bar{P}_{\mathrm{s}} + \frac{1}{4\mu}\sum_{M}\bar{P}_{M}^{*}\frac{\boldsymbol{Y}_{2M}^{1}}{(3\pi)^{1/2}}\right) \tag{3.12}$$

is inserted in the integral of (2.9):

$$W_2 + W_3 = N^2\left(\frac{4\pi}{3}R_{\mathrm{a}}^{3}\right)^{-1}\frac{2\mu}{(\lambda+2\mu)(3\lambda+2\mu)} \times\left(\bar{P}_{\mathrm{s}}^{2} + \frac{(9\lambda+14\mu)(3\lambda+2\mu)}{120\mu^2}\sum_{M}|\bar{P}_{M}|^2\right). \tag{3.13}$$

Subtraction of $W_2 + W_3$ from W_∞ gives the desired elastic energy W of the crystal. The small energy change of the crystal when replacing the elastic inclusions by the volumes v_0 that contain the defects is neglected.

4. The relation between P and $\boldsymbol{\varepsilon}_{\mathrm{c}}$

A homogeneous distribution of defects leads to a uniform deformation of the crystal measured by x-ray diffraction. The deformation is described by the tensor $\boldsymbol{\varepsilon}_{\mathrm{c}}$ so that a lattice vector $\boldsymbol{x}_0$ changes to $\boldsymbol{x} = \boldsymbol{x}_0 + \boldsymbol{\varepsilon}_{\mathrm{c}}\boldsymbol{x}_0$. The surface of a crystal of spherical shape with radius R_{a} is therefore displaced by $\boldsymbol{U}_{\mathrm{c}} = \boldsymbol{\varepsilon}_{\mathrm{c}}R_{\mathrm{a}}\boldsymbol{e}_r$. In order to compare $\boldsymbol{U}_{\mathrm{c}}$ with $\boldsymbol{U}(R_{\mathrm{a}})$ of (3.12), the Cartesian $\boldsymbol{\varepsilon}_{\mathrm{c}}$ tensor ($\varepsilon_{\mathrm{c},ik}$; $i, k = x, y, z$) is expressed by spherical unit tensors $\boldsymbol{a}_m$ (see equation (A1.5)). The traceless part $\boldsymbol{\varepsilon}_{\mathrm{c,d}}$ of $\boldsymbol{\varepsilon}_{\mathrm{c}}$ is written as $\boldsymbol{\varepsilon}_{\mathrm{c,d}} = \Sigma_m \varepsilon_{\mathrm{c,m}}^{*}\boldsymbol{a}_m$ with the spherical components

$$\varepsilon_{\mathrm{c},0} = \frac{1}{\sqrt{6}}(2\varepsilon_{\mathrm{c},zz} - \varepsilon_{\mathrm{c},xx} - \varepsilon_{\mathrm{c},yy}) \qquad \varepsilon_{\mathrm{c},\pm1} = \mp(\varepsilon_{\mathrm{c},xz} \pm \mathrm{i}\varepsilon_{\mathrm{c},yz})$$
$$\varepsilon_{\mathrm{c},\pm2} = \tfrac{1}{2}(\varepsilon_{\mathrm{c},xx} - \varepsilon_{\mathrm{c},yy}) \pm \mathrm{i}\varepsilon_{\mathrm{c},xy} \tag{4.1}$$

(iii) A stress-free crystal surface is achieved applying an additional so-called 'image traction' $\boldsymbol{\sigma}^{\mathrm{I}}\,\mathrm{d}S_{\mathrm{a}} = -\sigma^{\infty}\,\mathrm{d}S_{\mathrm{a}}$. Inside the crystal an additional displacement field $\boldsymbol{U}^{\mathrm{I}}$ is built up. The work done by the volume V_{a} in this step is

$$W_3 = \tfrac{1}{2}\int \boldsymbol{U}^{\mathrm{I}}\boldsymbol{\sigma}^{\mathrm{I}}\,\mathrm{d}\boldsymbol{S}_{\mathrm{a}}\,. \tag{2.8}$$

The total displacement field inside the crystal is the sum $\boldsymbol{U} = \boldsymbol{U}^{\infty} + \boldsymbol{U}^{\mathrm{I}}$. The sum $W_2 + W_3$ can be expressed by the displacement $\boldsymbol{U}$ and the image stress tensor $\boldsymbol{\sigma}^{\mathrm{I}}$:

$$W_2 + W_3 = \tfrac{1}{2}\int \boldsymbol{U}\boldsymbol{\sigma}^{\mathrm{I}}\,\mathrm{d}\boldsymbol{S}_{\mathrm{a}}. \tag{2.9}$$

The total elastic energy W_{a} of a system of N point defects embedded in a finite crystal with a stress-free surface $\boldsymbol{S}_{\mathrm{a}}$ is the sum $W = W_1 - W_2 - W_3$. In the framework of our treatment of the lattice expansion model, we are only concerned with dipole defects. The displacement field $\boldsymbol{U}^{\infty}$ of such a defect is given exactly by (1.6) so that the calculation of W_1 is straightforward. To compute W_2 and W_3 the displacement $\boldsymbol{U}$ on the crystal surface $\boldsymbol{S}_{\mathrm{a}}$ has to be determined. According to the arguments above we shall first execute $\boldsymbol{U}^{\infty} = \Sigma_i \boldsymbol{U}_i^{\infty}$ outside and on the surface of $\boldsymbol{S}_{\mathrm{a}}$. From $\boldsymbol{U}^{\infty}$ we easily derive $\boldsymbol{\sigma}^{\mathrm{I}}\,\mathrm{d}\boldsymbol{S}_{\mathrm{a}}$ and thus the calculation of $\boldsymbol{U}^{\mathrm{I}}$ can be reduced to the simple boundary-value problem of an isotropic medium to an external traction $\boldsymbol{\sigma}^{\mathrm{I}}\,\mathrm{d}\boldsymbol{S}_{\mathrm{a}}$. The difficulty to overcome is the execution of the sum $\Sigma \boldsymbol{U}_i^{\infty}$. We have carried out this sum for a homogeneous distribution of dipole defects in a medium with a spherical surface.

3. The elastic energy of a HS ⇆ LS compound

In order to describe the elastic energy in a mixed crystal of a spin-crossover compound, three types of dipole defects with dipole tensors $\mathbf{P}^n$ (n = HS, LS, M) representing the spin-changing ions in the HS and LS states and the metal ions M, respectively, have to be introduced. Each kind of defect is randomly distributed over the lattice sites with a concentration c^n.

The self-energy W_∞ of N defects in an infinite medium is calculated according to equation (2.4). The stress tensor $\boldsymbol{\sigma}^{\infty}$ times the radial vector $\boldsymbol{e}_r$ of the surface element of defect i is evaluated using (2.1), (2.2) and the formulae in the paper of Shuey and Beyeler (1969) (see Appendix 1):

$$\boldsymbol{\sigma}_i \boldsymbol{e}_{r_i} = \frac{1}{\sqrt{\pi}}\frac{1}{(\lambda + 2\mu)}\frac{1}{r^3}\left[2\mu \boldsymbol{Y}^1_{00}\boldsymbol{P}_{\mathrm{s}} - \sum_M \left(\frac{1}{10\sqrt{3}}(9\lambda + 14\mu)\boldsymbol{Y}^1_{2M} + \frac{6\sqrt{2}}{5}(\lambda + \mu)\boldsymbol{Y}^3_{2M}\right)P^*_M\right]. \tag{3.1}$$

The integration in (2.4) is easily performed using the orthogonality relations of the vector spherical harmonics. The result is also given in the paper mentioned but for one type of defect:

$$W_\infty = \frac{N}{2\pi R_0^3}\frac{\mu}{(\lambda + 2\mu)^2}\left(\overline{P_{\mathrm{s}}^2} + \frac{1}{(10\mu)^2}\left[\tfrac{1}{3}(3\lambda + 8\mu)(9\lambda + 14\mu) + 36(\lambda + \mu)^2\right]\sum_M \overline{|P_M|^2}\right). \tag{3.2}$$

defect, was taken into consideration. The terms proportional to P_M describing the dilatationless deformation were neglected. Therefore, a step towards a more complete calculation of the interaction energies in the framework of the lattice expansion model is naturally introduced by treating the spin-changing ions as dipole defects $\mathbf{P}^n$ still embedded in an isotropic elastic medium. Unfortunately, the solution of this more general problem could not be found in the literature. Eshelby has solved the case of spherical defects ($P_s \neq 0$, $P_M = 0$ for all M) embedded in arbitrary-shaped crystals approximated by isotropic elastic media (Eshelby 1956). In this contribution we present a calculation of the interaction energy taking into consideration three kinds of general dipole defects $\mathbf{P}^n$ (n = HS, LS, M), each type of defect being statistically distributed over the lattice sites. The statistical distribution is a reasonable assumption because the image pressure acts as an infinite-range interaction, which results in the proportionality of Γ to the concentraion x of the interacting complexes. This energy contribution does not prefer clusters. The calculations are done with the restriction to crystals with spherical surfaces for convenience. A general statement for arbitrary-shaped crystals as Eshelby found for spherical defects has not been obtained. In §§ 2 and 3 the elastic energy is evaluated on the grounds of the assumptions above. Following the arguments of Eshelby the contribution of the image stress to the elastic energy is calculated analytically by passing over to a continuous distribution of defects. Additionally there is a direct interaction mechanism between the defects at distance R, which is proportional to R^{-3}. The calculation of the corresponding elastic energy term is straightforward but lengthy and requires a summation over all lattice sites. This term, which is expected to be small at least for lower concentrations of the spin-changing ions, will be evaluated in a later paper. The direct interaction vanishes in the case of spherical defects (Bitter 1931), and therefore it did not appear in the previous treatment of the lattice expansion model.

2. Elastic energy of point defects

The deformation of an elastic medium is described mathematically by the displacement field vector $U(\boldsymbol{r})$. The associated strain tensor is separated into a traceless part $\boldsymbol{\varepsilon}_d$ and a part proportional to the unit matrix $\mathbf{1}$, $\boldsymbol{\varepsilon} = \boldsymbol{\varepsilon}_d + \frac{1}{3}\varepsilon_s\mathbf{1}$, where $\varepsilon_s = \mathrm{Tr}(\boldsymbol{\varepsilon})$. The traceless strain tensor is obtained by application of the symmetric gradient operator to the displacement field:

$$\boldsymbol{\varepsilon}_d = \mathrm{symgrad}\, \boldsymbol{U} \tag{2.1a}$$

and ε_s by the divergence of $\boldsymbol{U}$

$$\varepsilon_s = \mathrm{div}\, \boldsymbol{U}. \tag{2.1b}$$

The stress tensor $\boldsymbol{\sigma}$ is related to the strain tensor by Hooke's law, which in the case of an isotropic elastic medium reads

$$\boldsymbol{\sigma} = 2\mu\boldsymbol{\varepsilon}_d + \tfrac{1}{3}(3\lambda + 2\mu)\varepsilon_s\mathbf{1}. \tag{2.2}$$

In the absence of external forces, the equilibrium condition $\nabla\boldsymbol{\sigma} = \mathbf{0}$ leads to the differential equation (1.5) for the displacement vector $\boldsymbol{U}$. The boundary condition for a stress-free spherical surface is $\boldsymbol{e}_r\boldsymbol{\sigma} = \mathbf{0}$. If $\boldsymbol{U}$ is given in terms of vector spherical harmonics as in (1.6), the tensors $\boldsymbol{\varepsilon}$ and $\boldsymbol{\sigma}$ and the quantity $\boldsymbol{e}_r\boldsymbol{\sigma}$ are easily obtained by applying the formulae of Shuey and Beyeler (1969) referred to in Appendix 1.

Our problem to be solved is the calculation of the elastic energy of a distribution of

of the lattice decreases so that the resulting higher density of phonon states of the lattice decreases its free energy. The non-linear dependence of the free energy on the change of ω_D results in an interaction, which is, however, negligibly small. Kambara (1979, 1980, 1981) and also Ohnishi and Sugano (1981) have introduced a coupling between the lattice deformation and the electronic energies of the HS and LS states according to a cooperative Jahn–Teller interaction. In this case the electronic energy difference between the HS and LS states and the differences within the HS state are taken to be dependent on the fraction $\gamma(T)$. The coupling parameters are difficult to estimate and calculation of the parameters based on the molecular and crystal properties has never been tried.

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; 2-pic = 2-aminomethylpyridine; X = Cl, Br; Sol = MeOH, EtOH) (Adler *et al* 1986, Sanner *et al* 1984, Köppen *et al* 1982) and the corresponding deuterated compounds (Jakobi *et al* 1988, Meissner 1984), have been very successful with regard to uncovering the interaction mechanism responsible for the HS $\leftrightharpoons$ 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 these gradual spin transition behaviours in solid compounds are well described by a Gibbs free energy $G(\gamma, p\ T)$ that is the sum of two parts, the free energy $G_0(\gamma, p, T)$ of the isolated non-interacting ions ($x \to 0$) and an interaction part G_{int}, which has been parametrised as

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

An equivalent expression $G'_{\text{int}} = \Delta G\gamma + \Gamma\gamma(1-\gamma)$, so that $\Delta = (\Delta G - \Gamma)$, has already been extensively discussed by Slichter and Drickamer (1972). Large enough Γ values also produce first-order phase transitions. In order to relate the parameters Δ and Γ to the crystal properties, Spiering *et al* (1982) have discussed in more detail the elastic interaction between the HS and LS ions via the image pressure (Eshelby 1954, 1956), which was first introduced by Ohnishi and Sugano (1981). The spin-changing ions are considered as 'hard spheres' embedded in an isotropic homogeneous elastic medium characterised by elastic moduli K and σ. The 'hard-spheres' approximation has been justified in these molecular crystals by the fact that the intra-molecular frequencies (200–500 cm^{-1}) are an order of magnitude larger than the inter-molecular lattice frequencies (less than or equal to 50 cm^{-1}) (Meissner *et al* 1987). Within this so-called 'lattice expansion model', the intra-molecular degrees of freedom are not dependent on the stress field of the crystal. This point of view is opposite to that of Kambara (1980). So the interaction term G_{int} only depends on the volumes of the 'hard spheres' v_n (n = HS, LS, M) representing the spin-changing ions and the corresponding metal ions, respectively, and the elastic moduli K and σ. The interaction is a result of the stress field caused by the misfit of v_n to the lattice, which provides a volume v_0 for the considered ions in that lattice structure. The expressions for the interaction parameters Δ and Γ obtained from calculations based on this model are

$$\Gamma = \tfrac{1}{2}K\frac{\gamma_0 - 1}{\gamma_0}\frac{(\Delta V_{\text{HL}})^2}{V_{\text{C}}}x \tag{1.2a}$$

$$\Delta = 2q\Gamma \qquad q = (V_{\text{M}} - V_{\text{LS}})/(V_{\text{HS}} - V_{\text{LS}}) \tag{1.2b}$$

where $\gamma_0 = 3(1-\sigma)/(1+\sigma)$ is the so-called Eshelby constant. The quantity V_n (n = HS, LS, M) represents the respective unit-cell volume of the compound in the pure HS and LS