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Dynamical Jahn-Teller coupling of Fe$^{2+}$ in the cluster approach applied to the Mössbauer quadrupole data of $^{57}$Fe doped K$_2$ZnF$_4$ and Ba$_2$ZnF$_6$

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Résumé. — Nous avons analysé les données Mössbauer de l'interaction quadripolaire de l'ion Fe$^{2+}$ à spin fort dans les octaèdres à distorsion quadratique de K$_2$ZnF$_4$ et Ba$_2$ZnF$_6$. Nous avons introduit le couplage Jahn-Teller dynamique linéaire entre les états orbitaux excités E$_g$, en symétrie D$_{4h}$, par les modes de vibration A$_{1g}$, B$_{1g}$, B$_{2g}$ du cluster FeF$_6$. Nous effectuons une résolution rigoureuse tenant compte de ce couplage et du couplage spin-orbite, dans une base de dimension 5 (orbite) × 5 (spin) × 10 (vibrations). Il en résulte une amélioration spectaculaire des courbes de variation thermique de la séparation quadripolaire, dans les deux composés, par rapport aux résultats antérieurs du champ cristallin statique.

Abstract. — We have analysed the Mössbauer quadrupole data of high-spin Fe$^{2+}$ located in the tetragonally distorted octahedra of K$_2$ZnF$_4$ and Ba$_2$ZnF$_6$. The dynamical linear Jahn-Teller coupling between the orbital excited states E$_g$, in D$_{4h}$ symmetry, involves the vibrational modes A$_{1g}$, B$_{1g}$, B$_{2g}$ of the cluster FeF$_6$; spin-orbit coupling is introduced, and a full mathematical treatment is performed in a basis of dimension 5 (orbit) × 5 (spin) × 10 (vibrations). This leads to a spectacular improvement of the calculated thermal variations of the quadrupole splitting in both systems, when compared to the results of the static crystal field model.

1. Introduction.

Previous works [1-6] have shown that Mössbauer spectroscopy provides useful data for investigating (although somewhat indirectly) the electronic level scheme of the high-spin Fe$^{2+}$ ion (3d$^6$, D). The quadrupole splitting $Q_S$ (and more generally the whole set of electric field gradient components) is chiefly due to the partially filled 3d$^6$ shell and its thermal variation reflects the thermal population of the electronic level scheme.

Numerous investigations in cubic, trigonal and tetragonal symmetries (reviewed in [7]) have used a static crystal field model, following the pioneering works of Ingalls [4] and Ono-Ito [3].

Vibronic coupling was first introduced into Mössbauer spectroscopy by Ham [8], and primarily developed for cubic symmetry and low-temperature data [9-10]. The first thermal investigation using a vibronic model was performed by Bacci [11] in the case of oxy-and deoxyhaemoglobin, following Val- lin’s approach [12] of a molecular cluster with located modes.

Also, the shortcomings of the static crystal field for obtaining a detailed analysis of the thermal curves $Q_S(T)$ were progressively recognized [13-17]. A vibronic calculation in the cluster model with a frequence continuum, but neglecting the spin orbit coupling, was developed by Price and Srivastava [14, 17], for trigonal systems such as ferrous fluorosilicate and siderite.

Here we report the general treatment of a molecular cluster with located modes, including spin-orbit coupling, linear dynamical Jahn-Teller coupling and thermal population effects, adapted to D$_{4h}$ symmetry. This treatment provides a very good account of experimental data for two different systems over a large temperature range.

2. High-spin Fe$^{2+}$ in K$_2$ZnF$_4$ and Ba$_2$ZnF$_6$.

Both fluorides K$_2$MF$_4$ and Ba$_2$MF$_6$ (with M = Fe, Zn, Co, Ni) have a tetragonal, layered structure [18-19] derived from the perovskite type, with point group $I_4/m$ ($D_{4h}$) around the M$^{2+}$ site.
The magnetic and Mössbauer properties of K$_2$FeF$_4$ have been reported by Thurlings et al. [20], those of Ba$_2$FeF$_6$ by Renaudin et al. [19, 21].

The Mössbauer data of K$_2$ZnF$_4$ and Ba$_2$ZnF$_6$, $^{57}$Fe doped [22] have already been reported in two theses [23, 24], and the $QS(T)$ curves (plotted in Fig. 3), are similar to those of their ferrous isotypes (above $T_N$). This similarity allows the same treatment to be followed for both concentrated magnetic or doped systems.

It is worth noting that the barium compounds have increased 2-D character compared to the potassium compounds and, which is of major interest here, they show a more important shortening of the octahedra along their 4-fold axis (the axial/equatorial ratios being respectively 0.97 and 0.93 in K$_2$FeF$_4$ and Ba$_2$FeF$_6$).

Figure 1 shows the orbital scheme, with ground state $B_{2g}$ (deduced from the positive value of the EFG); the tetragonal splitting $\delta$ between the ground state $B_{2g}$ and the first excited states $E_g$ is large (from a preliminary analysis of the $QS(T)$ data using a static model, it amounts $\sim 500 - 1500$ cm$^{-1}$ for K$_2$ZnF$_4$ and Ba$_2$ZnF$_6$ respectively, with these values clearly related to the distortions quoted above). The rather well isolated ground orbital singlet allows the use of the spin Hamiltonian formalism $DS_2^2$ and of the magnetic hyperfine tensor $[A]$. $D$ was measured as $\sim 3$ or 4 cm$^{-1}$ in K$_2$FeF$_4$ from magnetic studies [20b, c, d] and in K$_2$ZnF$_4$, from high field Mössbauer spectroscopy [23]; the magnetic structure of Ba$_2$FeF$_6$ [21], shows a negative $D$ in the barium systems [23].

A static crystal-field approach, restricted to the low-temperature range (as in [13] for the fluosilicates) led to satisfactory sets of values for $D$ and $[A]$; on the other hand, the calculated $QS(T)$ departed greatly from the experimental data at higher temperatures [23]. The analysis consequently assumed a temperature dependent crystal field, whose possible origins have been discussed in [16], and which would appear here as an ad hoc explanation.

3. The static crystal field.

The static situation is sketched on the left part of figure 1. The exact solution consists in diagonalizing the matrix of the following Hamiltonian:

$$\mathcal{H}(r, s) = \mathcal{H}_{\text{C.F.}}(r) + \mathcal{H}_{\text{LS}}(r, s)$$

$$= \frac{1}{5} B'_4 (O^4_0 + 5 O^2_0) + B'_2 O^0_0 + \left( B'_4 - \frac{B'_2}{5} \right) O^0_4$$

$$+ \lambda L \cdot S - \rho \left[ (L \cdot S)^2 + \frac{1}{2} L \cdot S \right]$$

$$- \frac{1}{3} L(L+1) S(S+1)$$

whose successive terms are:

- the tetragonal crystal field, developed with the Stevens’ operators $O^n_{\ell}(r)$,
- the spin-orbit coupling, with $\lambda \sim -100$ cm$^{-1}$ (free-ion value) slightly reduced by covalency, and
- the spin-spin coupling with $\rho \sim +1$ cm$^{-1}$ (experimental value for the free-ion also including 2nd order spin-orbit coupling with excited LS terms).

The matrix elements are computed in the standard basis $\{| L, L_z \rangle \}$ of dimension 25; the resulting matrix is diagonalized, and the contribution of each level to the EFG components is calculated (as explained in [7]).

In axial symmetry, and accounting for the lattice contribution, then

$$QS(T) = QS_0 + QS_M \left( \frac{3 L^2 + L(L+1)}{6} \right),$$

where:

- $QS_0$ stands for the lattice contribution,
- $QS_M = -\frac{2}{7} e^2 Q \langle r^{-3} \rangle_{3d} (1 - R)$ represents the
maximum contribution of an orbital singlet belonging to the cubic T2g triplet, and $\frac{1}{6} \langle 3L_z^2 - L(L+1) \rangle_T$, Ingalls' reduction factor (≈ 1), describes the thermal population of the electronic scheme.

$Q_{So}$ can be calculated using polarizable point-charge summations [25]; it is rather large in layered structures [≈ 1.4 mms$^{-1}$ in KFeF$_4$], and calculations give –1.0 and –1.3 mms$^{-1}$ for K$_2$FeF$_4$ and Ba$_2$FeF$_6$ respectively [23]. $Q_{SM}$ should be slightly smaller than the free-ion value, and according to literature data [7], should be in the range 4 – 4.4 mms$^{-1}$ for highly ionic systems.

The best application of the static model over the whole temperature range led to the fits shown as dashed lines in figure 3 (all parameters have been systematically spanned, and all resources of the model have been investigated including reductions of $\Delta$, $\beta$, and the 4th order term [26]). Except for the initial increase of $QS(T)$ in K$_2$ZnF$_4$, due to thermal population of the spin Hamiltonian levels, the remainder of the data are poorly reproduced; particularly, the decrease of $QS(T)$ of Ba$_2$ZnF$_6$ in the range 60-200 K cannot be accounted for (similar discrepancies are observed in siderite [14, 16] and ferrous fluosilicate [13, 17]): this suggests that low-energy excited states, as low as ≈ 50-60 K, exist such as can be found in the vibrational scheme.

4. The vibronic Hamiltonian in the cluster approach.

The Hamiltonian accounting for the electrons of the central atom (positions $r$, spins $s$) and the neighbouring nuclei (positions $Q$), is usually written:

$$\mathcal{H}(r, Q, s) = \mathcal{H}_c(r) + \mathcal{H}_N(Q) + \mathcal{H}_{en}(r, Q) + \mathcal{H}_{LSS}(r, s).$$

Here we closely follow a treatment described by [27]: in the harmonic approximation, developing the electro-nuclear potential to first-order of nuclear displacements, then:

$$\mathcal{H}(r, Q, s) \sim \mathcal{H}(r, Q_0) + \mathcal{H}_{CF}(Q_0) + \sum_k \frac{\partial V}{\partial Q_k} (Q_k - Q_k^0) + \mathcal{H}_{LSS}(r, s).$$

Here $\mathcal{H}(r, Q_0)$ is the crystal field for the equilibrium positions, which has already been quoted above as $\mathcal{H}_{CF}$.

This is transformed by using symmetrised coordinates (having the symmetry of irreducible representations of $D_{4h}$):

$$\mathcal{H}(r, Q, s) = \mathcal{H}_{CF}(r) + \mathcal{H}_{N}(Q) + \sum_{\Gamma} V_{\Gamma}(r) \mathcal{C}_{\Gamma} + \mathcal{H}_{LSS}(r, s).$$

with $V_{\Gamma}(r) = \left( \frac{\partial V(r, Q)}{\partial Q_{\Gamma}} \right)_{Q_0}$.

The atomic motions in the cluster FeF$_6$, in $D_{4h}$ symmetry, are decomposed as follows:

$$\Gamma^{(21)} = \Gamma_{tr} + \Gamma_{rot} + \Gamma_{vb}$$

$$\Gamma_{vb} = 2A_{1g} + B_{1g} + B_{2g} + E_g + 2A_{2u} + B_{2u} + 3E_u.$$

The active modes $\Gamma_{\gamma}$ for Jahn-Teller coupling are determined according to the selection rule $\Gamma_i \times \Gamma_j \times \Gamma_j \Rightarrow A_{1g}$, since the dynamical Jahn-Teller coupling does not lower the symmetry. For the proper Jahn—Teller coupling, $\Gamma_i$, $\Gamma_j$ are two representations of the orbital doublet $E_g$; for the pseudo-Jahn-Teller coupling, one belongs to the ground orbital $B_{2g}$, and the other to $E_g$. This leads to 3 possible modes, represented in figure 2:

$$E_r - b_{1g} - E_g, E_r - b_{2g} - E_g \ (\text{Jahn-Teller})$$

$$B_{2g} - E_g - E_{r, g} \ (\text{pseudo Jahn-Teller}).$$

The latter mode is dropped here, but has been considered in [24]. Matrix elements of $\mathcal{H}(r, Q, s)$ are determined by successive application of the Wigner-Eckart theorem to the electronic part of the operators, and using second quantization for the remaining part (nuclear positions).

The « vibronic » wave functions are, in this frame where the Born-Oppenheimer approximation is no

Fig. 2. — Dynamical Jahn-Teller and pseudo Jahn-Teller modes, respectively acting in the $E_g$ doublet and between the $E_g$ and $B_{2g}$ orbital states; $A_{1g}$ modes can be dropped (see text).
longer valid, linear combinations of the following form:

$$|\psi\rangle = \sum_{i,j,k} a_{ijk} |\varphi_i\rangle |\chi_j\rangle |s_k\rangle,$$

respectively made of orbit, phonon, spin wave-functions. The optimum basis for factorization of the matrix is the real basis of $D_{4h}$ symmetry for orbit and spin; the phonon basis has genuinely the correct symmetry, and infinite dimension.

The matrix elements finally are:

$$\langle \varphi \chi_s | \mathcal{K}(r, Q, s) | \varphi' \chi' s' \rangle =$$

$$\delta_{\varphi \varphi'} \delta_{\chi \chi'} \delta_{s s'} \left( E(\varphi) + \sum_{r_{\gamma k}} \hbar \omega \left( v_{r_{\gamma k}} + \frac{1}{2} \right) \right)$$

$$+ \delta_{s s'} \left[ AK_1 U_{B_{1g}}(\varphi, \varphi') DB(v_1, v_1') \delta_{v_1 v_1'} \right]$$

$$+ \delta_{\chi \chi'} \langle \varphi s | \mathcal{K}_{LS} | \varphi' s' \rangle$$

where:

$E(\varphi)$ is a static crystal field energy,

$AK_{1,2}$ are coupling constants with vibrational modes $B_{1g}$, $B_{2g}$,

$v_{r_{\gamma k}}$ is the number of $r_{\gamma k}$ phonons in the state $|\chi\rangle$,

$U_{\gamma \gamma'}$ are electronic operator (listed in appendix) which generalize in total orbital space Ham’s $U_{\gamma \gamma'}$ operators [28].

$DB$ is the phonon « creation-annihilation » matrix, similarly used for each vibration mode, whose form (see in appendix) is associated with the linear Jahn-Teller coupling (such that $\mathcal{K}_{J} \sim Q \sim a^+ + a$); then only one-phonon processes are involved.

The multi-modal character of the problem implies vibrational states of the following form:

$$|\chi\rangle = |\chi_{v_1}(B_1) \chi_{v_2}(B_2)\rangle$$

labeled by the couple of integers $v_{1,2}$, representing the number of phonons of each mode in the considered basis state. (The totally symmetric modes $A_{1g}$ have been dropped since they only shift the orbital multiplets, and in practice add to the static crystal-field).

Figure 1 is an overall sketch of the starting point of problem; only one phonon type has been represented; vibronic interaction mixes the two halves of the scheme, and leads to complex diagrams which will be presented elsewhere.

5. Computation, results and discussion.

The phonon energies have been calculated by diagonalizing the dynamical matrix [29] of the cluster FeF$_6$, with force constants derived from lattice dynamics investigations in K$_2$ZnF$_4$ [30]; they are respectively 360 cm$^{-1}$, 45 cm$^{-1}$, 13 cm$^{-1}$ for the $B_{1g}$, $B_{2g}$, $E_g$ modes.

Preliminary calculations showed the necessity of spanning phonons states over the orbital splitting $\delta$; this is easily obtained with a few $B_{1g}$ phonons, but requires ~10 overtones of the $B_{2g}$ mode for K$_2$ZnF$_4$ and ~30 for Ba$_2$ZnF$_6$. The needed number of phonon states of the degenerate mode $E$ is very high, and this mode has not been considered here.

We developed a computer program using the largest finite basis consistent with available computer facilities [31]; we actually reached dimension 250 for the matrix, so that 10 vibrational states could be used conveniently for fitting procedure [32].

Some particularities of this computer program, which is optimized for lowering central unit time, are the following:

systematic use of matrix algebra inside the complete spin-orbit basis (dimension 25),

systematic research of the maximum factorization of the big matrix (usually into 4 sub-matrices), and

fast fitting procedure, denoted « barycentric », using linear combinations of $QS(T)$ curves calculated with successive sets of parameters.

This program is presently being adapted for a
vectorial computer, in order to enlarge the vibrational basis, so as to provide a better spanning of the orbital splitting (for Ba$_2$ZnF$_6$); this is also needed to introduce a significant number of $E_g$ phonon states.

Best fits of the experimental $QS(T)$ curves are shown in figure 3, as full lines, the vibration basis being made of 0, 1 (B$_1$), 1 to 8 (B$_2$) phonon states; the details of the fitting procedure [24] will be published elsewhere.

Fitted data for K$_2$ZnF$_4$ are listed in table I; their reliability is based on the convergence of the procedure (for all parameters except $h\omega_{B_{ij}}$) on the excellent data fit of the curve, and on the reasonable spanning of the phonon states over the orbital splitting. However they might be sizeably reassessed if the pseudo Jahn-Teller mode could be accounted for; in particular, the values of $QS_0$ obtained here do not fit the expected values given by lattice summation in section 3.

The fitted data for Ba$_2$ZnF$_6$, also listed in table I, despite providing a rather good fit of the curve, are less reliable because of the large orbital splitting which is not fully spanned by the phonon states (for instance, the $B_{1g}$ coupling does not sizeably affect the calculated curves).

The corresponding magnetic properties, also analysed in the vibronic approach [24], will be reported elsewhere.

6. Conclusion.

Despite of the reduced dimension of the vibrational basis, a spectacular improvement of the calculated $QS(T)$ curves is obtained using the vibronic approach. This suggests that many previous studies of the ferrous ion, particularly in the case of a small orbital splitting (such as in zinc fluosilicate) can be successfully reinterpreted using a full mathematical treatment mixing vibronic and spin-orbit coupling.

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Table I. — Dynamic crystal-field parameters of Fe$^{2+}$ in K$_2$ZnF$_4$ and Ba$_2$ZnF$_6$; underlined values have been fixed (when they did not influence sizeably the calculated curves); detailed description of the progressive analysis [24] will be published separately.

<table>
<thead>
<tr>
<th></th>
<th>K$_2$ZnF$_4$</th>
<th>Ba$_2$ZnF$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$</td>
<td>cm$^{-1}$</td>
<td>$-92 \pm 4$</td>
</tr>
<tr>
<td>$\rho$</td>
<td>cm$^{-1}$</td>
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</tr>
<tr>
<td>$E_{1g}$</td>
<td>cm$^{-1}$</td>
<td>$350$</td>
</tr>
<tr>
<td>$E_{2g}$</td>
<td>cm$^{-1}$</td>
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<td>$\Delta_{ob}$</td>
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<tr>
<td>$\delta$</td>
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<tr>
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<td>cm$^{-1}$</td>
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<tr>
<td>$AK_2$</td>
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<tr>
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</tr>
<tr>
<td>$QS_0$</td>
<td>mm s$^{-1}$</td>
<td>$0.53 \pm 0.08$</td>
</tr>
</tbody>
</table>

Appendix 1.

Orbital matrices for vibronic coupling in the orbital space with $D_{4h}$ basis: $A_{1g}, B_{1g}, B_{2g}, E_{g0}, E_{ge}$

$$
U_{B_{1}} = \begin{bmatrix}
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & -1 & 0
\end{bmatrix} \quad U_{B_{2}} = \begin{bmatrix}
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 1
\end{bmatrix}.
$$

Appendix 2.

Phonon creation-annihilation matrix elements $\langle x_v|DB|x_{v'}\rangle$, where $v$ and $v'$ are the number of phonons of a given mode in the basis states.

$$
v v' \rightarrow 0 1 2 3 \ldots .
$$

References

[22] Synthesized by G. Ferey et al. (UA CNRS 442, Le Mans).
[23] Pelaud, S., Thèse de 3e cycle, Université de Poitiers (1982).
[31] IBM 30-90 at CIRCE, Centre Inter-Régional de Calcul Electronique du CNRS.
[32] A typical diagonalization takes 40 s central computer unit, and a fit needs ~ 12 diagonalizations.