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# Susceptibility formalism for magnetic and quadrupolar interactions in hexagonal and tetragonal rare-earth compounds

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A susceptibility formalism is developed for analyzing the magnetic and quadrupolar interactions in hexagonal and tetragonal rare-earth compounds. Symmetrized expressions are given for the one-ion magnetoelastic coupling and for the two-ion quadrupolar interactions. This formalism, derived from perturbation theory, leads to specific magnetic, strain, and quadrupolar susceptibilities considering both the crystalline-electric-field effects and quadrupolar interactions. It allows an analytical description of physical properties, such as the first- and third-order paramagnetic susceptibilities, the parastriction, and the elastic constants.

## I. INTRODUCTION

Magnetoelastic effects and, in a more general way, quadrupolar interactions have been extensively studied over recent years in cubic rare-earth intermetallic compounds.[1,2] In particular, the paramagnetic phase has been found to be a fruitful range of investigation, since it allows: (i) alignment of the $4f$ magnetic moment anywhere in space by applying a magnetic field along the proper direction; (ii) the consequent study of properties for any symmetry, while often the only properties associated with the easy magnetization direction are those of the ordered state; (iii) derivation of a susceptibility formalism from a perturbation theory, leading to an analytical description of several experiments related to magnetic and magnetoelastic properties, such as the elastic constants, the parastriction, and the third-order magnetic susceptibility.[3-5] These studies have been successfully performed in numerous concentrated and diluted cubic rare-earth compounds,[1,3-8] leading to the determination of magnetoelastic and possibly quadrupolar pair-interaction parameters. Thus, a consistent understanding of the quadrupolar interactions has been achieved in several intermetallic compounds.[1,2,9]

These quadrupolar properties have been studied less thoroughly in rare-earth intermetallic compounds with a symmetry lower than cubic, e.g., in hexagonal and tetragonal compounds, due to the greater number of parameters involved in the crystalline-electric-field (CEF) Hamiltonian as well as in the quadrupolar couplings. Only a few systems have been investigated, such as diluted yttrium- and scandium-based rare-earth compounds,[10] Pr metal[11] and recently the PrNi$_5$ compound.[12] The magnetoelastic and quadrupolar properties of these systems present behavior with new interesting features, related to the fact that the main quadrupolar component, namely $\langle O_2^0 \rangle$, is already ordered by the crystal field, unlike the case in cubic symmetry.

In the present work, the full Hamiltonian is first described, including all the relevant terms of the one-ion magnetoelastic coupling, as well as of the various two-ion quadrupolar interactions, for hexagonal and tetragonal symmetries (Sec. II). Section III is devoted to the perturbation theory which allows us to obtain the different magnetic and strain susceptibilities involved in the magnetization, the parastriction, and the elastic constants. Section IV presents the behavior of the various susceptibilities according to different situations (singlet or doublet as CEF ground state, case of Kramers or non-Kramers rare-earth ions) and shows how the susceptibility formalism may be fruitful for determining the quadrupolar interactions as well as the CEF itself.

## II. THE HAMILTONIAN

The Hamiltonian used for describing the magnetic properties of a $4f$ shell including magnetoelastic and two-ion quadrupolar pair couplings has been extensively described for cubic symmetry in the last decade.[5,13] Here, two other simple symmetries, namely hexagonal and tetragonal, are considered. By using the operator-equivalent method and the molecular-field approximation (MFA) for the two-ion bilinear and quadrupolar pair interactions, the complete Hamiltonian, for one $4f$ ion, is written as

$$\mathcal{H}=\mathcal{H}_{\mathrm{CEF}}+\mathcal{H}_Z+\mathcal{H}_B+\mathcal{H}_Q+\mathcal{H}_{\mathrm{ME}}+(E_{\mathrm{el}}+E_B+E_Q) \ . \tag{1}$$

In this expression, $\mathcal{H}_{\mathrm{CEF}}$ is the crystalline electric field (CEF) Hamiltonian written, in the axes system with the $z$ axis parallel to the $c$ axis of the hexagonal and tetragonal unit cell, as respectively

$$\mathcal{H}_{\mathrm{CEF}}^{\mathrm{hex}}=B_2^0O_2^0+B_4^0O_4^0+B_6^0O_6^0+B_6^6O_6^6 \ , \tag{2}$$

$$\mathcal{H}_{\mathrm{CEF}}^{\mathrm{tet}}=B_2^0O_2^0+B_4^0O_4^0+B_4^4O_4^4+B_6^0O_6^0+B_6^4O_6^4 \ , \tag{3}$$

where the $O_l^m$'s are the Stevens equivalent operators,[14] and the $B_l^m$'s the CEF parameters.

$$\mathcal{H}_Z=-g_J\mu_B\mathbf{H}\cdot\mathbf{J} \tag{4}$$

represents the Zeeman coupling between the $4f$ magnetic moment and the internal magnetic-field **H** (external field corrected for demagnetization effects).

$$\mathcal{H}_B = -g_J \mu_B \mathbf{H}_B \cdot \mathbf{J} \tag{5}$$

is the Heisenberg-type isotropic bilinear interaction Hamiltonian written in the MFA as a function of the exchange field $\mathbf{H}_B$ acting on a given ion ($n$ is the bilinear exchange parameter):

$$\mathbf{H}_B = n\mathbf{M} = n g_J \mu_B \langle \mathbf{J} \rangle \ . \tag{6}$$

Here the anisotropic bilinear coupling is neglected; it would induce different $n$ values only parallel and perpendicular to the $c$ axis. Note that this MFA treatment leads us to consider a corrective energy term

$$E_B = \tfrac{1}{2} n M^2 \tag{7}$$

in the Hamiltonian for one ion since, when summing the pair interactions over the whole crystal to obtain Eq. (6), the energy relative to a pair of rare-earth elements is counted twice.

$$\begin{aligned}\mathcal{H}_Q^{\text{hex}} = &-K^{\alpha}\langle O_2^0\rangle O_2^0 - K^{\epsilon}(\langle O_2^2\rangle O_2^2 + 4\langle P_{xy}\rangle P_{xy}) \\ &-K^{\zeta}(\langle P_{yz}\rangle P_{yz} + \langle P_{zx}\rangle P_{zx}) \ ,\end{aligned} \tag{8}$$

and

$$\begin{aligned}\mathcal{H}_Q^{\text{tet}} = &-K^{\alpha}\langle O_2^0\rangle O_2^0 - K^{\gamma}\langle O_2^2\rangle O_2^2 - K^{\delta}\langle P_{xy}\rangle P_{xy} \\ &-K^{\epsilon}(\langle P_{yz}\rangle P_{yz} + \langle P_{zx}\rangle P_{zx}) \ ,\end{aligned} \tag{9}$$

represent the two-ion quadrupolar Hamiltonian written in the MFA as a function of the linear combinations of the products of second-order Stevens operators, which are invariant under the symmetry operations of the hexagonal or tetragonal point groups. The expression for these second-order operators are

$$\begin{aligned}&O_2^0 = 3J_z^2 - J(J+1) \ , \\ &O_2^2 = J_x^2 - J_y^2 \ , \\ &P_{ij} = \tfrac{1}{2}(J_i J_j + J_j J_i) \ \ (ij = xy, yz, zx) \ .\end{aligned} \tag{10}$$

This type of coupling has been extensively studied in cubic CsCl-type rare-earth intermetallic compounds[1] where it is responsible for the ferroquadrupolar ordering observed in TmZn and TmCd for example.[15,16] It is worth noting that, in hexagonal and tetragonal compounds, the $O_2^0$ quadrupolar component is already ordered (i.e., $\langle O_2^0\rangle \neq 0$) by the crystal field, but that does not exclude the possible existence of quadrupolar pair interactions. The MFA treatment again leads to corrective quadrupolar energy terms in the Hamiltonian:

$$\begin{aligned}E_Q^{\text{hex}} = &\tfrac{1}{2}K^{\alpha}\langle O_2^0\rangle^2 + \tfrac{1}{2}K^{\epsilon}(\langle O_2^2\rangle^2 + 4\langle P_{xy}\rangle^2) \\ &+\tfrac{1}{2}K^{\zeta}(\langle P_{zx}\rangle^2 + \langle P_{yz}\rangle^2) \ ,\end{aligned} \tag{11}$$

$$\begin{aligned}E_Q^{\text{tet}} = &\tfrac{1}{2}K^{\alpha}\langle O_2^0\rangle^2 + \tfrac{1}{2}K^{\gamma}\langle O_2^2\rangle^2 + \tfrac{1}{2}K^{\delta}\langle P_{xy}\rangle^2 \\ &+\tfrac{1}{2}K^{\epsilon}(\langle P_{zx}\rangle^2 + \langle P_{yz}\rangle^2) \ .\end{aligned} \tag{12}$$

The full one-ion magnetoelastic coupling, linear in strain (harmonic approximation) and limited to the second-rank terms, may be written, in symmetrized notation,[17] as

$$\begin{aligned}\mathcal{H}_{\text{ME}}^{\text{hex}} = &-(B^{\alpha1}\epsilon^{\alpha1} + B^{\alpha2}\epsilon^{\alpha2})O_2^0 - B^{\epsilon}(\epsilon_1^{\epsilon}O_2^2 + 2\epsilon_2^{\epsilon}P_{xy}) \\ &-B^{\zeta}(\epsilon_1^{\zeta}P_{zx} + \epsilon_2^{\zeta}P_{yz})\end{aligned} \tag{13}$$

$$\begin{aligned}\mathcal{H}_{\text{ME}}^{\text{tet}} = &-(B^{\alpha1}\epsilon^{\alpha1} + B^{\alpha2}\epsilon^{\alpha2})O_2^0 - B^{\gamma}\epsilon^{\gamma}O_2^2 - B^{\delta}\epsilon^{\delta}P_{xy} \\ &-B^{\epsilon}(\epsilon_1^{\epsilon}P_{zx} + \epsilon_2^{\epsilon}P_{yz}) \ .\end{aligned} \tag{14}$$

In these expressions the $\epsilon^{\mu}$'s are the symmetrized strains (see Table I) and the $B^{\mu}$'s the magnetoelastic coefficients associated with the corresponding normal strain modes. The related elastic energy is written as

$$\begin{aligned}E_{\text{el}}^{\text{hex}} = &\tfrac{1}{2}C_0^{\alpha1}(\epsilon^{\alpha1})^2 + C_0^{\alpha12}\epsilon^{\alpha1}\epsilon^{\alpha2} + \tfrac{1}{2}C_0^{\alpha2}(\epsilon^{\alpha2})^2 \\ &+\tfrac{1}{2}C_0^{\epsilon}[(\epsilon_1^{\epsilon})^2 + (\epsilon_2^{\epsilon})^2] + \tfrac{1}{2}C_0^{\zeta}[(\epsilon_1^{\zeta})^2 + (\epsilon_2^{\zeta})^2] \ ,\end{aligned} \tag{15}$$

$$\begin{aligned}E_{\text{el}}^{\text{tet}} = &\tfrac{1}{2}C_0^{\alpha1}(\epsilon^{\alpha1})^2 + C_0^{\alpha12}\epsilon^{\alpha1}\epsilon^{\alpha2} + \tfrac{1}{2}C_0^{\alpha2}(\epsilon^{\alpha2})^2 \\ &+\tfrac{1}{2}C_0^{\gamma}(\epsilon^{\gamma})^2 + \tfrac{1}{2}C_0^{\delta}(\epsilon^{\delta})^2 + \tfrac{1}{2}C_0^{\epsilon}[(\epsilon_1^{\epsilon})^2 + (\epsilon_2^{\epsilon})^2] \ ,\end{aligned} \tag{16}$$

TABLE I. Symmetrized strains in hexagonal and tetragonal symmetry.

| Hexagonal Representation | Strain | Tetragonal Representation | Strain | Expression |
|---|---|---|---|---|
| $\Gamma_1$ | $\epsilon^{\alpha1}$ | $\Gamma_1$ | $\epsilon^{\alpha1}$ | $\frac{1}{\sqrt{3}}(\epsilon_{xx}+\epsilon_{yy}+\epsilon_{zz})$ |
| $\Gamma_1$ | $\epsilon^{\alpha2}$ | $\Gamma_1$ | $\epsilon^{\alpha2}$ | $(\frac{2}{3})^{1/2}\left[\epsilon_{zz}-\frac{\epsilon_{xx}+\epsilon_{yy}}{2}\right]$ |
| $\Gamma_5$ | $\epsilon_1^{\epsilon}$ | $\Gamma_3$ | $\epsilon^{\gamma}$ | $\frac{1}{\sqrt{2}}(\epsilon_{xx}-\epsilon_{yy})$ |
| | $\epsilon_2^{\epsilon}$ | $\Gamma_4$ | $\epsilon^{\delta}$ | $\sqrt{2}\epsilon_{xy}$ |
| $\Gamma_6$ | $\epsilon_1^{\zeta}$ | $\Gamma_5$ | $\epsilon_1^{\epsilon}$ | $\sqrt{2}\epsilon_{zx}$ |
| | $\epsilon_2^{\zeta}$ | | $\epsilon_2^{\epsilon}$ | $\sqrt{2}\epsilon_{yz}$ |

where the $C_0^\mu$'s are the symmetrized background elastic constants without magnetic interactions[17] (see Table II).

Minimizing the free energy with regard to the strains leads to their equilibrium values as a function of the expectation values of the following quadrupolar operators

(a) *Hexagonal:*

$$\epsilon^{\alpha 1}=\frac{B^{\alpha 1}C_0^{\alpha 2}-B^{\alpha 2}C_0^{\alpha 12}}{C_0^{\alpha 1}C_0^{\alpha 2}-(C_0^{\alpha 12})^2}\langle O_2^0\rangle=A^{\alpha 1}\langle O_2^0\rangle\ ,$$
$$\epsilon^{\alpha 2}=\frac{B^{\alpha 2}C_0^{\alpha 1}-B^{\alpha 1}C_0^{\alpha 12}}{C_0^{\alpha 1}C_0^{\alpha 2}-(C_0^{\alpha 12})^2}\langle O_2^0\rangle=A^{\alpha 2}\langle O_2^0\rangle\ , \tag{17}$$

$$\epsilon_1^\epsilon=\frac{B^\epsilon}{C_0^\epsilon}\langle O_2^2\rangle;\quad \epsilon_2^\epsilon=2\frac{B^\epsilon}{C_0^\epsilon}\langle P_{xy}\rangle\ , \tag{18}$$

$$\epsilon_1^\zeta=\frac{B^\zeta}{C_0^\zeta}\langle P_{zx}\rangle;\quad \epsilon_2^\zeta=\frac{B^\zeta}{C_0^\zeta}\langle P_{yz}\rangle\ . \tag{19}$$

(b) *Tetragonal:*

$\epsilon^{\alpha 1},\epsilon^{\alpha 2}$ as in Eqs. (17),

$$\epsilon^\gamma=\frac{B^\gamma}{C_0^\gamma}\langle O_2^2\rangle\ , \tag{20}$$

$$\epsilon^\delta=\frac{B^\delta}{C_0^\delta}\langle P_{xy}\rangle\ , \tag{21}$$

$$\epsilon_1^\epsilon=\frac{B^\epsilon}{C_0^\epsilon}\langle P_{zx}\rangle;\quad \epsilon_2^\epsilon=\frac{B^\epsilon}{C_0^\epsilon}\langle P_{yz}\rangle\ . \tag{22}$$

After replacing these $\epsilon^\mu$ values in Eqs. (13) and (14), $\mathcal{H}_{\mathrm{ME}}$ appears to be indistinguishable from $\mathcal{H}_Q$ [Eqs. (8) and (9)], and both terms can be gathered in the total quadrupolar Hamiltonian:

$$\mathcal{H}_{QT}^{\mathrm{hex}}=-G^\alpha\langle O_2^0\rangle O_2^0-G^\epsilon(\langle O_2^2\rangle O_2^2+4\langle P_{xy}\rangle P_{xy})-G^\zeta[\langle P_{zx}\rangle P_{zx}+\langle P_{yz}\rangle P_{yz}]\ , \tag{23}$$

$$\mathcal{H}_{QT}^{\mathrm{tet}}=-G^\alpha\langle O_2^0\rangle O_2^0-G^\gamma\langle O_2^2\rangle O_2^2-G^\delta\langle P_{xy}\rangle P_{xy}-G^\epsilon[\langle P_{zx}\rangle P_{zx}+\langle P_{yz}\rangle P_{yz}]\ . \tag{24}$$

The total quadrupolar coefficients $G^\mu$ then receive contribution from both the one-ion magnetoelasticity and the quadrupolar pair interactions:

(a) *Hexagonal:*

$$G^\alpha=\frac{(B^{\alpha 1})^2C_0^{\alpha 2}-2B^{\alpha 1}B^{\alpha 2}C_0^{\alpha 12}+(B^{\alpha 2})^2C_0^{\alpha 1}}{C_0^{\alpha 1}C_0^{\alpha 2}-(C_0^{\alpha 12})^2}+K^\alpha$$
$$=G_{\mathrm{ME}}^\alpha+K^\alpha\ , \tag{25}$$

$$G^\epsilon=\frac{(B^\epsilon)^2}{C_0^\epsilon}+K^\epsilon=G_{\mathrm{ME}}^\epsilon+K^\epsilon\ , \tag{26}$$

$$G^\zeta=\frac{(B^\zeta)^2}{C_0^\zeta}+K^\zeta=G_{\mathrm{ME}}^\zeta+K^\zeta\ . \tag{27}$$

(b) *Tetragonal:*

$G^\alpha$ as in Eq. (25)

$$G^\gamma=\frac{(B^\gamma)^2}{C_0^\gamma}+K^\gamma=G_{\mathrm{ME}}^\gamma+K^\gamma\ , \tag{28}$$

$$G^\delta=\frac{(B^\delta)^2}{C_0^\delta}+K^\delta=G_{\mathrm{ME}}^\delta+K^\delta\ , \tag{29}$$

$$G^\epsilon=\frac{(B^\epsilon)^2}{C_0^\epsilon}+K^\epsilon=G_{\mathrm{ME}}^\epsilon+K^\epsilon\ . \tag{30}$$

TABLE II. Symmetrized elastic constants in hexagonal and tetragonal symmetry.

| Hexagonal | Tetragonal | Expression |
|---|---|---|
| $C^{\alpha 1}$ | $C^{\alpha 1}$ | $\frac{1}{3}(2C_{11}+2C_{12}+4C_{13}+C_{33})$ |
| $C^{\alpha 12}$ | $C^{\alpha 12}$ | $-\frac{\sqrt{2}}{3}(C_{11}+C_{12}-C_{13}-C_{33})$ |
| $C^{\alpha 2}$ | $C^{\alpha 2}$ | $\frac{1}{3}(C_{11}+C_{12}-4C_{13}+2C_{33})$ |
| $C^\epsilon$ | $C^\gamma$ | $C_{11}-C_{12}$ |
| $C^\zeta$ | $C^\epsilon$ | $2C_{44}$ |
|  | $C^\delta$ | $2C_{66}$ |

It is worth noting that only the expectation value $\langle O_2^0\rangle$ is different from zero in hexagonal and tetragonal symmetry, and in the absence of any external stress. As a consequence, the $\alpha$ term in $\mathcal{H}_{QT}$ [Eqs. (23) and (24)] gives an additional quadrupolar contribution to the pure CEF second-order term in Eq. (2) as soon as $B^{\alpha 1}$,$B^{\alpha 2}$, or $K^\alpha$ are present. As $\langle O_2^0\rangle$ this contribution is temperature dependent, thus the CEF level spacing also. Therefore, in case of strong quadrupolar coupling, it is worth taking into account this contribution explicitly besides the pure CEF one.

On the other hand, from Eq. (17) and Table I, there is a spontaneous quadrupolar contribution to the volume (through $\epsilon^{\alpha 1}$) and to the ratio $c/a$ (through $\epsilon^{\alpha 2}$) of the hexagonal or tetragonal unit cell. This feature manifests itself through the thermal expansion, as seen in Pr and $\mathrm{PrNi_5}$ for example.[18,19] Applying a magnetic field modifies $\langle O_2^0\rangle$ then $\epsilon^{\alpha 1}$ and $\epsilon^{\alpha 2}$, and the same relations as Eq. (17) may be written between the corresponding increments $\delta\epsilon^{\alpha 1}$, $\delta\epsilon^{\alpha 2}$, and $\delta\langle O_2^0\rangle$. These new relations will be actually used in the description of the magnetostriction and the parastriction (see below). At last, in Eqs. (23) and (24), the $\langle O_2^2\rangle$ and $\langle P_{ij}\rangle$ expectation values vanish in the absence of external stress. However, the corresponding $G^\mu$'s may drive a phase transition towards a lower symmetry, e.g., orthorhombic, as observed in rare-earth insulators.[20]

## III. PERTURBATION THEORY

The Hamiltonian [Eq. (1)] may be used in two ways for describing the magnetic properties of the $4f$ shell. First, a direct diagonalization of the full Hamiltonian may be performed, in particular, in the presence of a magnetic field, and all the expectation values of the $J_i$'s ($i=x,y,z$) and $O_2^0,O_2^2,P_{ij}$'s ($ij=xy,yz,zx$) operators can be deduced, whence the magnitude and position of the rare-earth magnetic moment $\mathbf{M}=g_J\mu_B\langle \mathbf{J}\rangle$ and the values of the strains $\epsilon^{\mu}$ [Eq. (17)–(22)]. This is the usual way for describing the magnetization and the magnetostriction curves, in particular, in the ordered state.

The second way of using this Hamiltonian is to apply a perturbation theory for the paramagnetic state.[4,5,13] This method is developed here to hexagonal and tetragonal systems. By applying this theory to the zeroth-order Hamiltonian, it is possible to analytically expand the generalized free energy $F=-kT\ln Z$, where $Z=\mathrm{Tr}\exp(-\mathcal{H}/kT)$ is the partition function, up to second order for the $\epsilon^{\mu}$'s and the various quadrupolar operators, and to fourth order for $H$ and $M$. All the magnetic properties may be then derived from the thermodynamical analysis of the free energy $F$, namely the first- and third-order magnetic susceptibilities, the parastriction, and the elastic constants. In this calculation, the modes $\zeta(\epsilon)$ in hexagonal (tetragonal) symmetry will not be taken into account, as their investigation would require us to apply a magnetic field out of the main symmetry directions. We will restrict ourselves to a magnetic field parallel and perpendicular to the $c$ axis, successively.

### A. Magnetic field along the *c* axis

First, we apply the perturbation theory for a magnetic field $\mathbf{H}$ along the $c$ axis, i.e., the [001] direction, where only the operators $J_z$ and $O_2^0$ are involved. The zeroth-order Hamiltonian ($H=0$) takes the following form, identical for the hexagonal and the tetragonal symmetries:

$$\mathcal{H}_0=\mathcal{H}_{\mathrm{CEF}}-G^{\alpha}Q_0O_2^0 \ , \tag{31}$$

where $Q_0=\langle O_2^0\rangle_0$ is the spontaneous ($H=0$) expectation value of the involved quadrupolar component. The full Hamiltonian $\mathcal{H}_c$ then includes $\mathcal{H}_0$ and perturbation terms arising from Eqs. (4), (5), (8), or (9), (13), or (14):

$$\begin{aligned}\mathcal{H}_c=\ &\mathcal{H}_0-g_J\mu_B(H+nM)J_Z-(B^{\alpha1}\delta\epsilon^{\alpha1}+B^{\alpha2}\delta\epsilon^{\alpha2}+K^{\alpha}\delta Q_0)O_2^0+\tfrac{1}{2}nM^2+\tfrac{1}{2}K^{\alpha}(Q_0+\delta Q_0)^2\\&+\tfrac{1}{2}C_0^{\alpha1}(\epsilon_0^{\alpha1}+\delta\epsilon^{\alpha1})^2+C_0^{\alpha12}(\epsilon_0^{\alpha1}+\delta\epsilon^{\alpha1})(\epsilon_0^{\alpha2}+\delta\epsilon^{\alpha2})+\tfrac{1}{2}C_0^{\alpha2}(\epsilon_0^{\alpha2}+\delta\epsilon^{\alpha2})^2 \ ,\end{aligned} \tag{32}$$

where, according to Eq. (17), $\epsilon_0^{\alpha i}=A^{\alpha i}Q_0$. The expression for the free energy $F_c$ is then derived (see Appendix A):

$$\begin{aligned}F_c=\ &F_0-\tfrac{1}{2}\chi_0(H+nM)^2-Q_0(B^{\alpha1}\delta\epsilon^{\alpha1}+B^{\alpha2}\delta\epsilon^{\alpha2}+K^{\alpha}\delta Q_0)-\tfrac{1}{2}\chi_{\alpha}(B^{\alpha1}\delta\epsilon^{\alpha1}+B^{\alpha2}\delta\epsilon^{\alpha2}+K^{\alpha}\delta Q_0)^2\\&-\chi_{\alpha}^{(2)}(H+nM)^2(B^{\alpha1}\delta\epsilon^{\alpha1}+B^{\alpha2}\delta\epsilon^{\alpha2}+K^{\alpha}\delta Q_0)-\tfrac{1}{4}\chi_0^{(3)}(H+nM)^4\\&+\tfrac{1}{2}nM^2+\tfrac{1}{2}K^{\alpha}(Q_0+\delta Q_0)^2+\tfrac{1}{2}C_0^{\alpha1}(\epsilon_0^{\alpha1}+\delta\epsilon^{\alpha1})^2+C_0^{\alpha12}(\epsilon_0^{\alpha1}+\delta\epsilon^{\alpha1})(\epsilon_0^{\alpha2}+\delta\epsilon^{\alpha2})+\tfrac{1}{2}C_0^{\alpha2}(\epsilon_0^{\alpha2}+\delta\epsilon^{\alpha2})^2 \ .\end{aligned} \tag{33}$$

This expression involves four single-ion CEF susceptibilities which may be calculated from the spontaneous CEF level scheme, obtained by diagonalization of the zeroth-order Hamiltonian $\mathcal{H}_0$ (see Appendix A): they depend only on the energies of the CEF levels and on the exact composition of the corresponding CEF wave functions, through matrix elements of $J_Z$ and $O_2^0$ between the CEF levels. By analogy with the cubic symmetry,[4,5,13] $\chi_0$ is the usual (first-order) magnetic susceptibility; $\chi_0^{(3)}$ is the third-order paramagnetic susceptibility, i.e., the following term in the field expansion of the magnetization curves. $\chi_{\alpha}$ is a strain susceptibility associated with $O_2^0$ and occurring in the elastic constants; $\chi_{\alpha}^{(2)}$ is a quadrupolar field susceptibility appearing in the parastriction. Note that the presence of a spontaneous quadrupolar moment $Q_0$ drives here additional terms in Eq. (33) compared to the expression in cubic symmetry; one term appears explicitly and the other ones are included in the expressions of $\chi_{\alpha}$ and $\chi_{\alpha}^{(2)}$.

As said above (Sec. II), the equilibrium values for $M$, $\delta\epsilon^{\alpha1}$, $\delta\epsilon^{\alpha2}$, and $\delta Q_0$ are given by the conditions of minimization of the free energy:

$$\frac{\partial F_c}{\partial M}=\frac{\partial F_c}{\partial\delta\epsilon^{\alpha1}}=\frac{\partial F_c}{\partial\delta\epsilon^{\alpha2}}=\frac{\partial F_c}{\partial\delta Q_0}=0 \ .$$

That provides a system of four linear equations, the solution of which leads to the following expressions:

$$M=\chi_M H+\chi_M^{(3)}H^3+\dots \ , \tag{34}$$

$$\delta\epsilon^{\alpha1}=A^{\alpha1}\delta Q_0,\quad \delta\epsilon^{\alpha2}=A^{\alpha2}\delta Q_0 \ , \tag{35}$$

$$\delta Q_0=\delta\langle O_2^0\rangle=\chi_Q^{\alpha}H^2+\dots \ , \tag{36}$$

with

$$\chi_M=\frac{\chi_0}{1-n\chi_0} \ , \tag{37}$$

$$\chi_M^{(3)}=\frac{1}{(1-n\chi_0)^4}\left[\chi_0^{(3)}+2G^{\alpha}\frac{(\chi_{\alpha}^{(2)})^2}{1-G^{\alpha}\chi_{\alpha}}\right] , \tag{38}$$

$$\chi_Q^{\alpha}=\frac{\chi_{\alpha}^{(2)}}{(1-n\chi_0)^2(1-G^{\alpha}\chi_{\alpha})} \ . \tag{39}$$

$\chi_M$ is the usual total first-order magnetic susceptibility which is the single-ion one $\chi_0$ strengthened only by the isotropic bilinear exchange coupling $n$. $\chi_M^{(3)}$ is the total third-order magnetic susceptibility which represents the initial curvature of the magnetization curves in presence of bilinear exchange and quadrupolar interactions; it consists in two contributions, both reinforced in an identical manner by the bilinear interactions: (i) the first one corresponds to the pure CEF term $\chi_0^{(3)}$; (ii) the second one is the quadrupolar contribution which, according to the sign of $G^\alpha$, may strengthen or compete with the first one. Finally, $\chi_Q^\alpha$ is the total quadrupolar field susceptibility which is enhanced by both the bilinear exchange $n$ and the quadrupolar interactions $G^\alpha$.

### B. Magnetic field along the [100] direction

Now we apply the perturbation theory for a magnetic field perpendicular to the $c$ axis, and we investigate first the [100] ($a$) direction. Both symmetries (hexagonal and tetragonal) can be treated in a similar way, and all the expressions are the same, except that $B^\epsilon$, $K^\epsilon$, $G^\epsilon$, $\epsilon^\epsilon$, and $C_0^\epsilon$ (hexagonal) have to be replaced by $B^\gamma$, $K^\gamma$, $G^\gamma$, $\epsilon^\gamma$, and $C_0^\gamma$, respectively (tetragonal).

As soon as $H$ differs from zero, the initial symmetry is broken since both $M=g_J\mu_B\langle J_x\rangle$ and $Q_2=\langle O_2^2\rangle$ appear next to $Q_0=\langle O_2^0\rangle$. If the zeroth-order Hamiltonian $\mathcal{H}_0$ takes the same form as above [Eq. (31)], the full Hamiltonian includes additional terms with respect to Eq. (32) (where $J_z$ has to be replaced by $J_x$):

$$\mathcal{H}_{\rm add}^{\rm hex}=-(B^\epsilon\epsilon_1^\epsilon+K^\epsilon Q_2)O_2^2+\tfrac{1}{2}K^\epsilon(Q_2)^2+\tfrac{1}{2}C^\epsilon(\epsilon_1^\epsilon)^2 \ . \tag{40}$$

By again applying a perturbation theory (see details in Appendix B), the free energy $F_a$ associated with the $a$ axis is expressed as $F_c$ [Eq. (33)] *plus* additional terms related to the $O_2^2$ operator:

$$\begin{aligned}F_a=F_c&-\tfrac{1}{2}\chi_\epsilon(B^\epsilon\epsilon_1^\epsilon+K^\epsilon Q_2)^2\\&-\chi_\epsilon^{(2)}(H+nM)^2(B^\epsilon\epsilon_1^\epsilon+K^\epsilon Q_2)\\&+\tfrac{1}{2}K^\epsilon(Q_2)^2+\tfrac{1}{2}C_0^\epsilon(\epsilon_1^\epsilon)^2 \ .\end{aligned}\tag{41}$$

Two new CEF susceptibilities $\chi_\epsilon,\chi_\epsilon^{(2)}$ are defined in this expression, involving matrix elements of $O_2^2$ between CEF levels. In addition, it is worth noting that, if the expressions of all the CEF susceptibilities in Eq. (41) are formally the same as previously (Sec. III A) their numerical values differ through the new CEF wave functions used when the magnetic field is along the $a$ axis (see Appendix B). This feature is well known for the first-order magnetic susceptibility $\chi_0$ and this is true also for $\chi_0^{(3)}$ and various $\chi_\mu$ and $\chi_\mu^{(2)}$.

As in the previous case, the conditions of minimization of the free energy $F_a$ lead to a system of linear equations from which the following expressions are derived:

$M,\delta\epsilon^{\alpha 1},\delta\epsilon^{\alpha 2},\delta Q_0$ as in Eqs. (34)–(36),

$$\epsilon_1^\epsilon=\frac{B^\epsilon}{C_0^\epsilon}Q_2 \ , \tag{42}$$

$$Q_2=\chi_Q^\epsilon H^2+\dots \ , \tag{43}$$

whence the following relations for the total susceptibilities:

$\chi_M,\chi_Q^\alpha$ as in Eqs. (37) and (39),

$$\chi_M^{(3)}=\frac{1}{(1-n\chi_0)^4}\left[\chi_0^{(3)}+2G^\alpha\frac{(\chi_\alpha^{(2)})^2}{1-G^\alpha\chi_\alpha}+2G^\epsilon\frac{(\chi_\epsilon^{(2)})^2}{1-G^\epsilon\chi_\epsilon}\right] , \tag{44}$$

$$\chi_Q^\epsilon=\frac{\chi_\epsilon^{(2)}}{(1-n\chi_0)^2(1-G^\epsilon\chi_\epsilon)} \ . \tag{45}$$

The main difference, with regard to the case where $\mathbf{H}$ is applied along the $c$ axis, is the presence of both $\alpha$ and $\epsilon$ quadrupolar contributions to the total third-order magnetic susceptibility. On the contrary, each quadrupolar field susceptibility depends only on the quadrupolar parameter associated.

### C. Magnetic field in the basal plane (other than [100] direction)

When the magnetic field is applied in the basal plane in a direction other than the [100] direction, the calculation of the field dependence of the magnetic and quadrupolar moments may be simplified by symmetry considerations.

#### 1. *Hexagonal symmetry*

It is well known that the first-order magnetic susceptibility $\chi_M$ is isotropic within the basal plane. In the same way symmetry properties applied to the third-order magnetic susceptibility lead to the isotropy of $\chi_M^{(3)}$ perpendicularly to the $c$ axis.[21] In particular, the third-order susceptibility is the same for the $a$ and $b$ axes of the orthohexagonal unit cell. Note that the anisotropy between both axes, which depends on the $V_6^6$ CEF parameter, should appear only for the higher terms ($H^5,H^7\dots$) in the $H$ expansion of the magnetization.

For the $H^2$ dependence of the quadrupolar moments, symmetry considerations lead to expressions for $\delta Q_0$, $Q_2$, and $\langle P_{xy}\rangle$, which involve only two independent susceptibilities:

$$\begin{aligned}&\delta Q_0=\delta\langle O_2^0\rangle=\chi_Q^\alpha H^2 \ , \quad \text{as in Eq. (36)} \ ,\\&Q_2=\langle O_2^2\rangle=\chi_Q^\epsilon H^2\cos 2\phi \ ,\\&\langle P_{xy}\rangle=\tfrac{1}{2}\chi_Q^\epsilon H^2\sin 2\phi \ ,\end{aligned}\tag{46}$$

where $\phi$ is the angle between $\mathbf{H}$ and the $a$ ([100]) direction, and $\chi_Q^\alpha,\chi_Q^\epsilon$ are given in Eqs. (39) and (45). These relations will be useful in the expressions of the magnetostriction (see Sec. V C).

#### 2. *Tetragonal symmetry*

If the first-order magnetic susceptibility $\chi_M$ remains isotropic in the basal plane for tetragonal symmetry, the same considerations as above show that $\chi_M^{(3)}$ is anisotropic perpendicularly to the $c$ axis.[21] Two independent susceptibilities are now involved, i.e., those relative to the two sets of twofold axes in the basal plane. The expressions for the [110] direction may be easily derived through perturbation theory (see Appendix C); it is formally the same as for the [100] direction but includes now a $\delta$-quadrupolar contribution instead of a $\gamma$ one:

$$\chi_M^{(3)}(H\|[110])=\frac{1}{(1-n\chi_0)^4}\left[\chi_0^{(3)}+2G^{\alpha}\frac{(\chi_\alpha^{(2)})^2}{1-G^{\alpha}\chi_\alpha}+2G^{\delta}\frac{(\chi_\delta^{(2)})^2}{1-G^{\delta}\chi_\delta}\right] . \qquad (47)$$

For the quadrupolar operators, general expressions for a magnetic field within the basal plane, involve three independent quadrupolar susceptibilities:

$$\begin{aligned}\delta Q_0&=\langle O_2^0\rangle=\chi_Q^{\alpha}H^2 \text{ [Eq. (36)]} ,\\ Q_2&=\langle O_2^2\rangle=\chi_Q^{\gamma}H^2\cos2\phi ,\\ \langle P_{xy}\rangle&=\chi_Q^{\delta}H^2\sin2\phi ,\end{aligned} \qquad (48)$$

where $\phi$ is the angle between **H** and the [100] direction, and $\chi_Q^{\alpha},\chi_Q^{\gamma}$ are given in Sec. III B. The third quadrupolar susceptibility $\chi_Q^{\delta}$ is associated with the quadrupolar operator $P_{xy}$:

$$\chi_Q^{\delta}=\frac{\chi_\delta^{(2)}}{(1-n\chi_0)^2(1-G^{\delta}\chi_\delta)} . \qquad (49)$$

Thus the $\gamma$ and $\delta$ tetragonal strain modes can be separately investigated by applying a magnetic field successively along the [100] and [110] directions, the $\alpha$ contribution being the same in both cases.

### D. Elastic constants

The expressions describing the variation of the elastic constants including quadrupolar effects can be derived from the same perturbation theory by considering the $\epsilon^{\mu}$'s as external variables and by taking $H=0$.

Minimizing the corresponding free energy with regard to each of the remaining variables $\delta Q_0, Q_2, \langle P_{xy}\rangle$ provides the strain dependence of the expectation values of quadrupolar operators:

$$\delta Q_0=(B^{\alpha1}\delta\epsilon^{\alpha1}+B^{\alpha2}\delta\epsilon^{\alpha2})\frac{\chi_\alpha}{1-K^{\alpha}\chi_\alpha} , \qquad (50)$$

$$Q_2=B^{\epsilon}\epsilon_1^{\epsilon}\frac{\chi_\epsilon}{1-K^{\epsilon}\chi_\epsilon} \text{ (Hexagonal)} , \qquad (51)$$

$$\begin{aligned}Q_2&=B^{\gamma}\epsilon^{\gamma}\frac{\chi_\gamma}{1-K^{\gamma}\chi_\gamma} ,\\ \langle P_{xy}\rangle&=B^{\delta}\epsilon^{\delta}\frac{\chi_\delta}{1-K^{\delta}\chi_\delta} \text{ (Tetragonal)} .\end{aligned} \qquad (52)$$

Finally the elastic constants $c^{\mu}$ are obtained by taking the total second-strain derivative of the free energies.

(a) $\alpha$ *mode*:

$$\begin{aligned}C^{\alpha1}&=\frac{d^2F}{d(\delta\epsilon^{\alpha1})^2}=C_0^{\alpha1}-(B^{\alpha1})^2\frac{\chi_\alpha}{1-K^{\alpha}\chi_\alpha} ,\\ C^{\alpha2}&=\frac{d^2F}{d(\delta\epsilon^{\alpha2})^2}=C_0^{\alpha2}-(B^{\alpha2})^2\frac{\chi_\alpha}{1-K^{\alpha}\chi_\alpha} ,\\ C^{\alpha12}&=\frac{d^2F}{d(\delta\epsilon^{\alpha1})d(\delta\epsilon^{\alpha2})}=C_0^{\alpha12}-B^{\alpha1}B^{\alpha2}\frac{\chi_\alpha}{1-K^{\alpha}\chi_\alpha} .\end{aligned} \qquad (53)$$

(b) $\epsilon$ mode (Hexagonal)

$$C^{\epsilon}=\frac{d^2F^{\text{hex}}}{d(\epsilon_1^{\epsilon})^2}=C_0^{\epsilon}-(B^{\epsilon})^2\frac{\chi_\epsilon}{1-K^{\epsilon}\chi_\epsilon} . \qquad (54)$$

(c) $\gamma$ mode (Tetragonal):

$$C^{\gamma}=\frac{d^2F^{\text{tet}}}{d(\epsilon^{\gamma})^2}=C_0^{\gamma}-(B^{\gamma})^2\frac{\chi_\gamma}{1-K^{\gamma}\chi_\gamma} . \qquad (55)$$

(d) $\delta$ mode (Tetragonal):

$$C^{\delta}=\frac{d^2F^{\text{tet}}}{d(\epsilon^{\delta})^2}=C_0^{\delta}-(B^{\delta})^2\frac{\chi_\delta}{1-K^{\delta}\chi_\delta} . \qquad (56)$$

## IV. BEHAVIOR OF THE DIFFERENT SINGLE-ION SUSCEPTIBILITIES

The different one-ion susceptibilities may allow one to determine the CEF level scheme throughout specific features. We propose here to discuss some behaviors according to the ground state for $Ce^{3+}$ and $Pr^{3+}$ ions in hexagonal symmetry.

### A. First- and third-order magnetic susceptibilities

It is well known that the first-order magnetic susceptibility is anisotropic between the $c$ axis and the basal plane, within which it remains isotropic. At high temperatures—high in comparison with the level spacing—the vertical splitting between the two corresponding reciprocal susceptibilities is only induced by the second-order CEF term, $V_2^0=B_2^0/\alpha_J$:

$$\frac{1}{\chi_0^c}-\frac{1}{\chi_0^a}=\frac{3}{2}\frac{(2J-1)(2J+3)}{5C}B_2^0 , \qquad (57)$$

where $C$ is the Curie constant.[22] Then the easy magnetization direction is only determined by the sign of the $B_2^0$ parameter (Fig. 1).

At low temperature, the thermal variation depends on the level spacing and the nature of each level. Along the easy magnetization direction, Curie or Van Vleck behavior, are observed in association with the magnetic or nonmagnetic character of the ground state. According to the temperature, the competition between Curie and Van Vleck terms may lead to a pronounced minimum for the reciprocal susceptibility as observed along the $a$ axis in Fig. 1(c) (this case is very close to the situation of $PrNi_5$)[12]. Along the difficult magnetization direction, a Van Vleck behavior is systematically observed (Fig. 1) except in the case of a Kramers ion with a ground state ex-

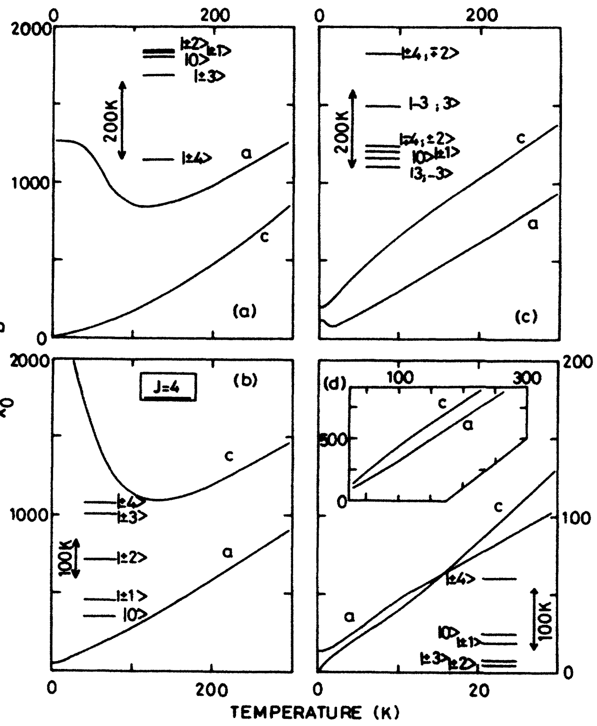

FIG. 1. Temperature variations of the first-order reciprocal susceptibility parallel and perpendicular to the $c$-axis of the hexagonal cell for a non Kramers ion ($J=4$). As indicated by the different level schemes, the variations are calculated for magnetic $a-d$ or non-magnetic $b-c$, pure $a,b,d$ or mixed $c$ ground state wave functions.

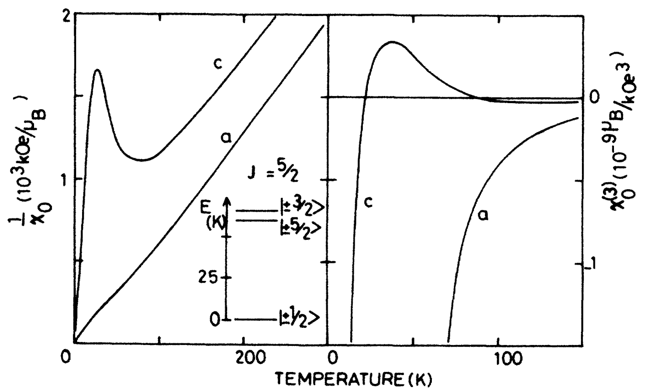

FIG. 2. Temperature variations of the first- and third-order magnetic susceptibilities parallel and perpendicular to the $c$-axis of the hexagonal cell for a Kramers ion ($J=\frac{5}{2}$) in the case of $|\pm 1/2\rangle$ ground state.

hibiting a $|\pm\frac{1}{2}\rangle$ component [Fig. 2(a)]. Note in Fig. 1(b) the divergence of $\chi_0^{-1}$ along the $c$ axis which is induced by the lack of Van Vleck matrix element from the nonmagnetic ground state $|0\rangle$. According to the level scheme, particular behaviors may occur as for instance in Fig. 1(d), where a change of easy magnetization direction is observed as a function of the temperature.

The third-order magnetic susceptibility is also anisotropic between the $c$ axis and the basal plane. Within this latter plane, it is isotropic in the hexagonal symmetry but anisotropic in the tetragonal one (see Sec. III C). Figure 3 gives the variations calculated along the $c$ and $a$ axis for

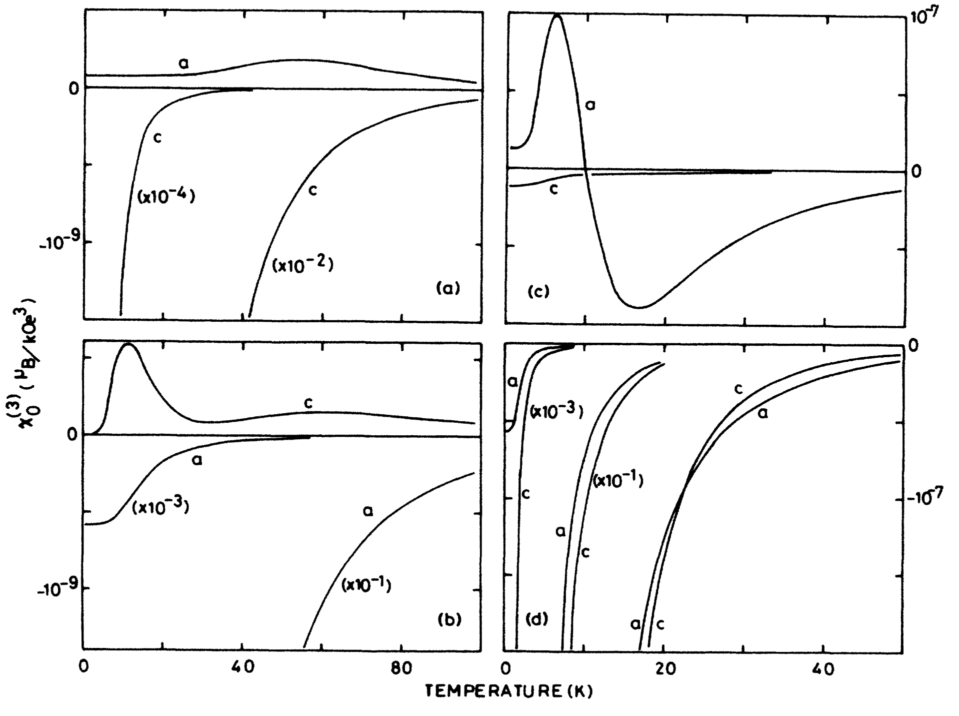

FIG. 3. Temperature variations of the third-order magnetic susceptibility parallel and perpendicular to the $c$-axis of the hexagonal cell for the same conditions as in Fig. 1.

the same level scheme as in Fig. 1. Along the easy magnetization direction, the temperature variation of $\chi_0^{(3)}$ is reminiscent of the behavior of the first-order one: for a magnetic ground state, $\chi_0^{(3)}$ is negative and diverges as classically expected for the expansion of a Brillouin function [Figs. 3(a) and 3(d)]. For a nonmagnetic ground state only the Van Vleck contribution is present at low temperature [Figs. 3(b) and 3(c)]. Positive $\chi_0^{(3)}$ values are even possible leading to unusual temperature variations [Fig. 3(c)].

Along the hard magnetization axis, the third-order susceptibility is of Van Vleck type and generally very weak [Fig. 3]. This corresponds to the difficulty to induce a magnetic moment on a nonmagnetic ground state due to the large anisotropy. As for $\chi_0$, the only exception is induced by the presence of the $|\pm\frac{1}{2}\rangle$ component in the ground state wave functions [Fig. 2(b)].

Thus, studying this susceptibility is very complementary of the study of the first-order susceptibility and may be also selective for determining the CEF level scheme throughout the observation of well defined anomalies in the temperature dependence as in Figs. 3(b) and 3(c).

### B. Strain and quadrupolar field susceptibilities

Here again, the susceptibilities associated with the various magnetoelastic modes may provide us with clear informations on the level scheme.

#### *1. α mode*

As an intrinsic quadrupolar moment $\langle O_2^0 \rangle$ is imposed by the symmetry, the strain susceptibility $\chi_\alpha$ exhibits a Van Vleck behavior at 0 K due to the cancellation of the Curie contributions. The 0 K value is null when there is no mixing at all or in the case of a mixed singlet [Fig. 4(b)]. In the case of a mixed doublet [Fig. 4(a)] as ground state, the Van Vleck value is different of zero.

For a [001] magnetic field, the quadrupolar field susceptibility also vanishes at 0 K for the same conditions as for $\chi_\alpha$ [Fig. 4(d)]. For a mixed doublet, frequent case for heavy rare earths, the quadrupolar field susceptibility diverges [Fig. 4(c)].

For a magnetic field along the *a* axis, $\chi_\alpha^{(2)}$ is negative at high temperature. At low temperature, the Curie terms vanish and the Van Vleck value at 0 K may be positive as well as negative, according to the sign and magnitude of the spontaneous quadrupolar moment (Fig. 5).

#### *2. Symmetry lowering modes*

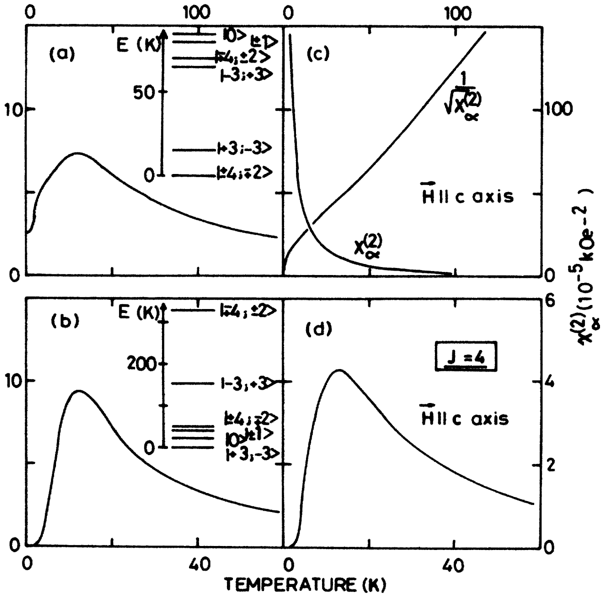

FIG. 4. Temperature variations of the strain susceptibility $\chi_\alpha$ (a) and (b) and of the quadrupolar field-susceptibility $\chi_\alpha^{(2)}$ (c) and (d) in hexagonal symmetry. Note that the ground state wave functions are mixed, corresponding to a doublet $(a-c)$ and a singlet $(b-d)$.

Similar features as for the α case are also possible as shown in Fig. 6 for the ϵ mode in the hexagonal symmetry. For a non-Kramers ion with a singlet ground state or in the absence of mixing terms, a Van Vleck behavior is calculated with a nonzero value at 0 K for $\chi_\epsilon$. On the contrary with a mixed doublet as ground state [Fig. 6(b)] a divergence occurs at 0 K. Parallel behavior is predicted for the quadrupolar field susceptibility $\chi_\epsilon^{(2)}$ [Fig. 6(c) and 6(d)].

For Kramers ions, the degeneracy of the doublets is of spin origin whereas, for each quadrupolar mode, the levels are singlets. Thus a Van Vleck behavior is systematically calculated at low temperature, the strain susceptibility value being more or less large according to the level spacing and the nature of the ground state. The quadrupolar field susceptibility usually of Van Vleck type, may also diverge at low temperature through terms linear in $(1/T)$ in the expression $(\chi_\epsilon^{(2)})$.

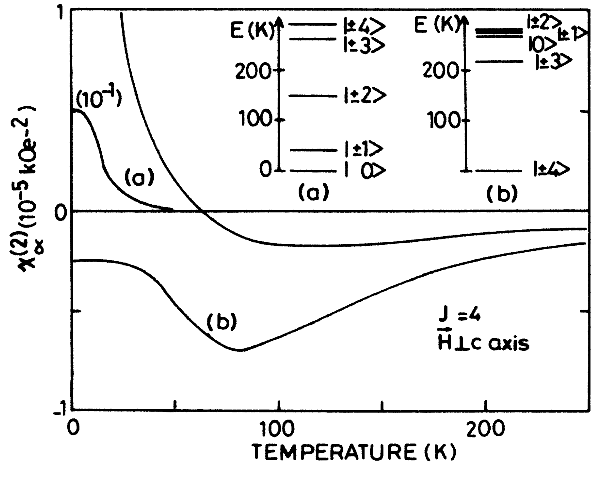

FIG. 5. Temperature variations of the quadrupolar field-susceptibility $\chi_\alpha^{(2)}$ for a magnetic field applied in the basal plane of the hexagonal cell for two characteristic level schemes of a non Kramers ion $(J=4)$.

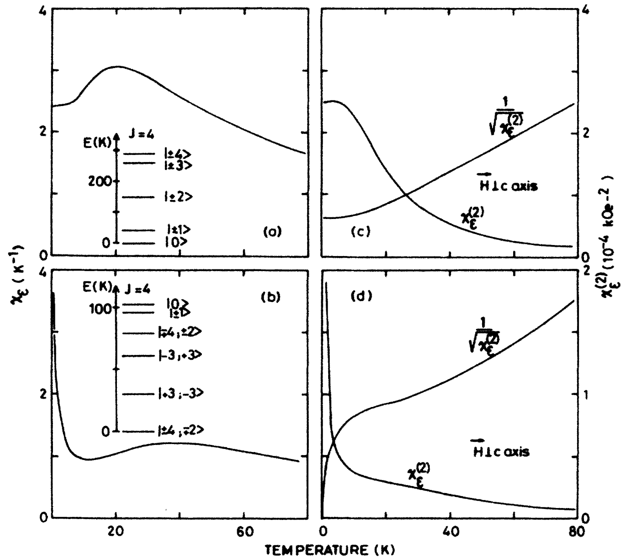

FIG. 6. Temperature variations of the strain susceptibility associated with the $\epsilon$-shear mode of the hexagonal symmetry for a non Kramers ion ($J=4$). The level schemes for (c) and (d) are given in (a) and (b), respectively.

## V. DETERMINATION OF THE PAIR INTERACTION AND MAGNETOELASTIC COEFFICIENTS

In the same time as the different susceptibilities may inform about the CEF throughout the single-ion contribution (previous section) they may also give the strength of the magnetoelastic and pair couplings associated with a given symmetry using specific experiments.

### A. Magnetization processes

It is well known that the bilinear interactions may be deduced from the vertical shift between the experimental reciprocal susceptibility $\chi_M^{-1}$ and the single-ion one, $\chi_0^{-1}$ along the $c$ and $a$ axes [Eq. (37)]. Note that for a ferromagnetic ordering, the reciprocal susceptibility vanishes at the Curie temperature, $T_c$, along the easy magnetization direction. In this case, the relation

$$\chi_0^{-1}(T_c)=n \tag{58}$$

provides us with another determination of the bilinear coefficient, $n$.

A first characterization of the quadrupolar interactions may be carried on for each symmetry by measuring the third-order magnetic susceptibility. The total quadrupolar coefficients [Eqs. (25)–(30)], or combinations of them, are achieved through Eqs. (38), (44), and (47). From an experimental point of view, it is fruitful to analyze the magnetization curve by plotting $(M/H)$ as a function of $H^2$.[5] The zero-field extrapolation gives the first-order magnetic susceptibility, whereas the initial slope defines the third-order one. Its temperature variation may then be described using Eq. (38), (44), or (47) according to the direction of the magnetic field. Such an analysis has been recently achieved in the case of $\mathrm{PrNi_5}$ (Ref. 12) and $\mathrm{TmNi_5}$ (Ref. 23).

### B. Elastic constants

The normal elastic modes deduced from ultrasonic velocity measurements may be described throughout Eqs. (53)–(56), the lattice background being measured in a nonmagnetic isomorphous compound. Both the pair interaction coefficient and the absolute value of the magnetoelastic parameter may be thus achieved. Many examples exist in the literature about rare earth zircons for example, although usually analyzed within a pseudo-spin formalism.[20,24]

In most cases, contrary to the cubic symmetry, the strain susceptibilities do not diverge at low temperature, that usually forbids a full softening of the corresponding elastic constants. However, the divergence of $\chi_\epsilon$ ($\chi_\gamma,\chi_\delta$ in tetragonal symmetry) for a mixed doublet as ground state [Fig. 6(b)] may induce a full softening of the $C^\epsilon$ ($C^\gamma,C^\delta$) elastic mode. In the absence of another stronger coupling, this would occur at a temperature corresponding to the $\langle O_2^2\rangle$ or $\langle P_{xy}\rangle$ quadrupolar ordering, the transition being second order. This agrees with the tetragonal-orthorhombic transition observed in rare-earth zircons.[20,24]

### C. Change of length measurements

In the presence of an applied magnetic field, an additional experimental probe, the parastriction, is based on the quadrupolar field susceptibilities. Indeed, applying a magnetic field along a $(\alpha_1\alpha_2\alpha_3)$ direction induces a change of length in the $(\beta_1\beta_2\beta_3)$ direction.[17] For example, in the tetragonal symmetry:

$$\lambda_{\alpha_1\alpha_2\alpha_3}^{\beta_1\beta_2\beta_3}=\left[\frac{\delta l}{l}\right]_{\alpha_1\alpha_2\alpha_3}^{\beta_1\beta_2\beta_3}=\frac{\epsilon^{\alpha 1}}{\sqrt{3}}+\frac{1}{\sqrt{6}}\epsilon^{\alpha 2}(2\beta_3^2-\beta_1^2-\beta_2^2)+\frac{1}{\sqrt{2}}\epsilon^{\gamma}(\beta_1^2-\beta_2^2)+\sqrt{2}\epsilon^{\delta}\beta_1\beta_2+\sqrt{2}\beta_3(\epsilon_1^{\epsilon}\beta_1+\epsilon_2^{\epsilon}\beta_2)\ . \tag{59}$$

According to equilibrium relations [Eqs. (17)–(22)] and to the quadrupolar field susceptibilities [Eqs. (39), (45), and (49)] the change of length may be simply described in particular along high-symmetry axes, for different directions of the applied magnetic field. Sets of measurements allow us to separately study the $\alpha$, $\gamma$, or $\delta$ modes and thus to determine the corresponding magnetoelastic and pair-interactions coefficients as previously done for the $\alpha$, $\gamma$, and $\epsilon$ modes in the cubic symmetry.[4,25] For instance, the experimental temperature variation

$$\frac{H}{(\lambda_{100}^{100}-\lambda_{100}^{010})^{1/2}}=(C_0^\gamma/B^\gamma)^{1/2}\frac{1}{(\chi_\gamma^{(2)})^{1/2}}[(1-G^\gamma\chi_\gamma)]^{1/2}(1-n\chi_0) \tag{60}$$

allows us to determine the $B^\gamma$ and $G^\gamma$ coefficients from the comparison with the $1/(\chi_\gamma^{(2)})^{1/2}$ variation. Note that the temperature variation is linear at least at high temperature (Figs. 4 and 6). Similar analysis has been recently performed in hexagonal $\mathrm{PrNi}_5$.[12]

In the absence of an applied magnetic field, Eq. (59) allows us to analyze the thermal expansion. Indeed the thermal expansion coefficients are the temperature derivatives of

$$\begin{aligned}\lambda^{001}&=\frac{1}{\sqrt{3}}\epsilon^{\alpha 1}+\frac{2}{\sqrt{6}}\epsilon^{\alpha 2}\ ,\\ \lambda^{010}=\lambda^{100}&=\frac{1}{\sqrt{3}}\epsilon^{\alpha 1}-\frac{1}{\sqrt{6}}\epsilon^{\alpha 2}\ ,\end{aligned}\tag{61}$$

Thus using Eqs. (17)–(22), they read as:

$$\begin{aligned}\alpha_c&=\frac{1}{\sqrt{3}}\frac{(C_0^{\alpha 2}B^{\alpha 1}-C_0^{\alpha 12}B^{\alpha 2})+\sqrt{2}(C_0^{\alpha 1}B^{\alpha 2}-C_0^{\alpha 12}B^{\alpha 1})}{C_0^{\alpha 1}C_0^{\alpha 2}-(C_0^{\alpha 12})^2}\chi_{\alpha D}\ ,\\ \alpha_b=\alpha_a&=\frac{1}{\sqrt{3}}\frac{(C_0^{\alpha 2}B^{\alpha 1}-C_0^{\alpha 12}B^{\alpha 2})-\frac{1}{\sqrt{2}}(C_0^{\alpha 1}B^{\alpha 2}-C_0^{\alpha 12}B^{\alpha 1})}{C_0^{\alpha 1}C_0^{\alpha 2}-(C_0^{\alpha 12})^2}\chi_{\alpha D}\ ,\end{aligned}\tag{62}$$

with $\chi_{\alpha D}=\frac{1}{kT^2}(\langle EO_2^0\rangle-\langle E\rangle\langle O_2^0\rangle)$ . (63)

Measuring the thermal expansion parallel and perpendicular to the $c$ axis provides us with an additional experimental probe for determining $B^{\alpha 1}$ and $B^{\alpha 2}$, the magnetoelastic coefficients. Note that in this case the $\alpha$-quadrupolar interactions implicitly act on the starting level energies [Eq. (31)]. A similar feature has been previously discussed in cubic symmetry about high-order multipolar interactions.[26] Thermal expansion data have been analyzed in $\mathrm{PrNi}_5$ and Pr metal according to this formalism.[12,19]

## VI. CONCLUSION

We have presented the extension to the hexagonal and tetragonal symmetries of the susceptibility formalism, successfully used in the cubic symmetry. Two main possibilities are offered by this application of the perturbation theory. First, in addition to the first-order magnetic susceptibility, the single-ion strain and quadrupolar field susceptibilities provide us with novel fruitful experimental probes with regard to the CEF. Indeed, the entire set of CEF parameters is difficult to be accurately determined. This explains that studies in the literature usually consider only low-lying levels within a pseudo-spin formalism. The corresponding wave functions are not fully determined because mixing effects through $V_4^4$, $V_6^4$, or $V_6^6$ terms are not considered. As the neutron spectroscopy is not as powerful by itself as in the case of the cubic symmetry, a simultaneous analysis of all the available results is then necessary and magnetoelastic probes are well come. The possibility of separately studying the different symmetry modes may increase the number of possible informations.

On the other hand, the existence of magnetoelastic- and pair-interaction couplings may be here as common as for the cubic symmetry. Examples of quadrupolar orderings are numerous in rare earth zircons, such situations may also be expected in rare earth intermetallics. The determinations of the corresponding coefficients may be very fruitful for explaining all the magnetic properties as within the cubic symmetry.[1]

In this latter case, the order of the magnetic transition in particular has been successfully described by this simple mean-field approximation if the quadrupolar interactions were carefully determined: a first-order magnetic transition is observed as soon as the third-order magnetic susceptibility occurring in the Landau expansion of the free energy is positive.[2,13] In tetragonal and hexagonal symmetries, the existence of such a first-order transition may also be discussed in the same way. If driven by only a positive $\chi_0^{(3)}$ value in absence of quadrupolar interactions, it appears to be associated with a mixed wave function in the $J_Z$ basis [Fig. 3(c)] for a non-Kramers ion. This is the situation of $\mathrm{PrNi}_5$ (Ref. 12) where unfortunately the spin system is under critical. In all the other cases $\chi_0^{(3)}$ is negative and a first-order transition may be only driven by quadrupolar interactions, if their positive contribution dominates the $\chi_0^{(3)}$ term [Eqs. (38) and (44)]. Thus, a full understanding of the magnetic properties may be gained by the knowledge of the quadrupolar interactions in a given compound.

## ACKNOWLEDGMENT

E. Belorizky is gratefully acknowledged for fruitful discussions, in particular about the general symmetry properties of the third-order magnetic susceptibility.

## APPENDIX A

In a first step we define the eigenvalues $E_i$ and the eigenvectors $|ik\rangle$ corresponding to the zeroth-order Hamiltonian $\mathcal{H}_0$ [Eq. (31)]:

$$\mathcal{H}_0|ik\rangle=E_i|ik\rangle\ . \tag{A1}$$

In each subspace $i$ the eigenvectors $|\,ik\,\rangle$ must be adapted to the perturbating Hamiltonian $\mathcal{H}_c$-$\mathcal{H}_0$, in particular if the degeneracy is larger than one. This condition is always fulfilled if the CEF basis functions $|\,ik\,\rangle$ are chosen so that $\Delta M_J=6$ (four for tetragonal symmetry) in their $|\,J,M_J\,\rangle$ expansion:

$$\begin{aligned}|\,ik\,\rangle&=a_{M_J}\,|\,J,M_J\,\rangle+a_{M_J-6}\,|\,J,M_J-6\,\rangle\\&\quad+a_{M_J-12}\,|\,J,M_J-12\,\rangle\ldots\,.\end{aligned}\tag{A2}$$

The perturbation theory up to the second order for the $\epsilon^{\mu}$'s and to the fourth order for $H$ allows us to obtain analytical expressions for the perturbed energies $E_{ik}$:

$$E_{ik}=E_i+\sum_{n=1}^{4}E_{ik}^{(n)}+\ldots\,.\tag{A3}$$

Then the partition function

$$Z=\sum_{i,k}e^{-\beta E_{ik}}\tag{A4}$$

can be calculated, where $\beta=1/(k_BT)$, $k_B$ is the Boltzmann constant and $T$ is the temperature. One obtains

$$\begin{aligned}Z=Z_0\{\,&1+\tfrac{1}{2}\beta\chi_0(H+nM)^2+\beta Q_0(B^{\alpha 1}\delta\epsilon^{\alpha 1}+B^{\alpha 2}\delta\epsilon^{\alpha 2}+K^{\alpha}\delta Q_0)+\tfrac{1}{2}\beta(\chi_\alpha+\beta Q_0^2)(B^{\alpha 1}\delta\epsilon^{\alpha 1}+B^{\alpha 2}\delta\epsilon^{\alpha 2}+K^{\alpha}\delta Q_0)^2\\&+\beta(\chi_\alpha^{(2)}+\tfrac{1}{2}\beta\chi_0Q_0)(H+nM)^2(B^{\alpha 1}\delta\epsilon^{\alpha 1}+B^{\alpha 2}\delta\epsilon^{\alpha 2}+K^{\delta}\delta Q_0)+\tfrac{1}{4}\beta[\chi_0^{(3)}+\tfrac{1}{2}\beta(\chi_0)^2](H+nM)^4\}\;,\end{aligned}\tag{A5}$$

whence the expression of the total free energy $F=-k_BT\ln Z$ given in Eq. (33).

The expression of the four CEF susceptibilities $\chi_0$, $\chi_\alpha$, $\chi_\alpha^{(2)}$, and $\chi_0^{(3)}$ are given by

$$\chi_0=g_J^2\mu_B^2\sum_{i,k}f_i\left[-2\sum_{\substack{j\\ j\neq i,l}}\frac{|\,J_{ik,jl}\,|^2}{E_i-E_j}+\frac{1}{k_BT}\,|\,J_{ik,ik}\,|^2\right]\;,\tag{A6}$$

$$\chi_\alpha=\sum_{i,k}f_i\left[-2\sum_{\substack{j\\ j\neq i,l}}\frac{|\,Q_{ik,jl}\,|^2}{E_i-E_j}+\frac{1}{k_BT}\,|\,Q_{ik,ik}\,|^2\right]-\frac{1}{k_BT}(Q_0)^2\;,\tag{A7}$$

$$\begin{aligned}\chi_\alpha^{(2)}=-\frac{1}{2k_BT}\chi_0Q_0+g_J^2\mu_B^2\sum_{i,k}f_i\Bigg[&\sum_{\substack{j,j'\\ j\neq i,l\\ j'\neq i,l'}}\frac{J_{ik,jl}Q_{jl,j'l'}J_{j'l',ik}+2Q_{ik,jl}J_{jl,j'l'}J_{j'l',ik}}{(E_i-E_j)(E_i-E_{j'})}\\&-\sum_{\substack{j\\ j\neq i,l}}\frac{|\,J_{ik,jl}\,|^2Q_{ik,ik}+2Q_{ik,jl}J_{jl,ik}J_{ik,ik}}{(E_i-E_j)}\left[\frac{1}{E_i-E_j}+\frac{1}{k_BT}\right]\\&+\frac{1}{2(k_BT)^2}\,|\,J_{ik,ik}\,|^2Q_{ik,ik}\Bigg]\;,\end{aligned}\tag{A8}$$

and

$$\chi_0^{(3)} = -\frac{1}{2k_BT}(\chi_0)^2 + g_J^4\mu_B^4 \sum_{i,k} f_i \left[ -4 \sum_{\substack{j,j',j'' \\ j\neq i,l \\ j'\neq i,l' \\ j''\neq i,l''}} \frac{J_{ik,jl}J_{jl,j'l'}J_{j'l',j''l''}J_{j''l'',ik}}{(E_i-E_j)(E_i-E_{j'})(E_i-E_{j''})} \right.$$
$$+2\sum_{\substack{j,j' \\ j\neq i,l \\ j'\neq i,l'}} \frac{|J_{ik,jl}|^2|J_{ik,j'l'}|^2 + 2J_{ik,jl}J_{jl,j'l'}J_{j'l',ik}J_{ik,ik}}{(E_i-E_j)(E_i-E_{j'})} \left[\frac{2}{E_i-E_j} + \frac{1}{k_BT}\right]$$
$$-2\sum_{j\neq i,l} \frac{|J_{ik,ik}|^2|J_{ik,jl}|^2}{(E_i-E_j)} \left[\frac{2}{(E_i-E_j)^2} + \frac{2}{(E_i-E_j)k_BT} + \frac{1}{k_B^2T^2}\right]$$
$$\left. + \frac{1}{6k_B^3T^3}|J_{ik,ik}|^4 \right], \tag{A9}$$

where

$$J_{ik,jl} = \langle ik \,|\, J_z \,|\, jl \rangle , \tag{A10}$$

and

$$Q_{ik,jl} = \langle ik \,|\, O_2^0 \,|\, jl \rangle , \tag{A11}$$

are the matrix elements of $J_z$ of $O_2^0$ between the CEF levels. For each CEF sublevel,

$$f_i = \frac{1}{Z_0}e^{-\beta E_i} = \frac{e^{-\beta E_i}}{\sum_{i,k} e^{-\beta E_i}} , \tag{A12}$$

is the Boltzmann population factor.

## APPENDIX B

When the magnetic field is applied along the [100] direction ($x$ axis), the operators involved in the perturbation theory are $J_x$, $O_2^0$, and $O_2^2$. However, it appears much more convenient to perform the calculations with the $z$ axis parallel to **H**. Therefore, a rotation of $\pi/2$ around the $y$ axis may be carried out, transforming $J_x$ into $J_z$, $O_2^0$ into $-\frac{1}{2}(O_2^0-3O_2^2)$ and $O_2^2$ into $\frac{1}{2}(O_2^0+O_2^2)$. In each degenerate CEF level $i$, the rotated eigenvectors $|\,ik\,\rangle'$ have again to be adapted to the new perturbating Hamiltonian, and this condition is easily satisfied in the new coordinate axes by choosing the $|\,ik\,\rangle'$ functions so that $\Delta M_J=2$ in their $|\,J,M_J\,\rangle$ expansion.

The perturbation calculation can then be performed in an analogous way as in Appendix A, except that an additional operator, $O_2^2$, has to be considered leading to new related quadrupolar susceptibilities. Finally an inverse rotation allows to express both quadrupolar susceptibilities $\chi_Q^\alpha$ and $\chi_Q^\epsilon$ in the initial axes system [Eqs. (39) and (45)].

Note that $\chi_\epsilon$ and $\chi_\epsilon^{(2)}$ ($\chi_\gamma$ and $\chi_\gamma^{(2)}$ for tetragonal symmetry) have the same expressions as Eq. (A7) and (A8) except that $O_2^0$ has to be replaced by $O_2^2$ in the quadrupolar matrix element $Q_{ik,jl}$ as well as in $Q_0$.

## APPENDIX C

In tetragonal symmetry, considering a magnetic field along the [110] direction is equivalent to consider the case where **H** is parallel to the $x$ axis after a rotation of $\pi/4$ around the $z$ axis. In this rotation, $O_2^0$ does not change and $O_2^2$ is replaced by $-2P_{xy}$, $P_{xy}$ by $\frac{1}{2}O_2^2$, $O_4^4$ by $-O_4^4$ and $O_6^4$ by $-O_6^4$. The same calculation as previously may be performed (Appendix B), but the quadrupolar parameter $G^\delta$ is now involved instead of $G^\gamma$. Returning to the initial axes system by an inverse rotation then provides the final expressions for $\chi_M^{(3)}$ and $\chi_Q^\delta$ [Eqs. (47) and (49)].

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[1] M. Giraud, P. Morin, and D. Schmitt, J. Magn. Magn. Mater. 52, 41 (1985) and references therein.

[2] J. Kotzler, Z. Phys. B55, 119 (1984).

[3] P. M. Levy, J. Phys. C6, 3545 (1973).

[4] P. Morin, D. Schmitt, and E. de Lacheisserie, Phys. Rev. B 21, 1742 (1980).

[5] P. Morin and D. Schmitt, Phys. Rev. B 23, 5936 (1981).

[6] J. Kotzler and G. Raffius, Z. Phys. B38, 139 (1980).

[7] H. U. Häfner, D. Davidov, and G. J. Nieuwenhuys, J. Magn. Magn. Mater. 38, 45 (1983).

[8] G. Creuzet and I. A. Campbell, Phys. Rev. B23, 3375 (1981).

[9] P. M. Levy, P. Morin, and D. Schmitt, Phys. Rev. Lett. 42, 1417 (1979).

[10] P. Pureur, G. Creuzet, and A. Fert, J. Magn. Magn. Mater. 53, 121 (1985).

[11] P. Hendy, K. M. Al-Rawi, E. W. Lee, and D. Melville, J. Phys. F 9, 2121 (1979).

[12] V. M. T. S. Barthem, G. Creuzet, D. Gignoux, A. Naït-Saada,

and D. Schmitt, Phys. Rev. B **37**, 1733 (1988).

[13] P. Morin and D. Schmitt, Phys. Rev. B **27**, 4412 (1983).

[14] M. T. Hutchings, Solid State Phys. **16**, 227 (1964).

[15] D. Givord, P. Morin, and D. Schmitt, J. Magn. Magn. Mater. **40**, 121 (1983).

[16] R. Aleonard and P. Morin, Phys. Rev. B **19**, 3868 (1979).

[17] E. de Lacheisserie, Ann. Phys. **5**, 267 (1970). Note that the classical expressions in this reference have been adapted to the quantum treatment used here.

[18] K. Andres, S. Darack and H. R. Ott, Phys. Rev. B **19**, 5475 (1979).

[19] B. Lüthi and H. R. Ott, Solid State Commun. **33**, 717 (1980).

[20] G. A. Gehring and K. A. Gehring, Rep. Prog. Phys. **38**, 1 (1975).

[21] R. R. Birss, in *Symmetry and Magnetism,* edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1964).

[22] Y. L. Wang, Phys. Lett. **35A**, 383 (1971); P. Boutron, Phys. Rev. B **7**, 3226 (1973).

[23] V. M. T. S. Barthem, G. Creuzet, D. Gignoux, and D. Schmitt (unpublished).

[24] R. L. Melcher, in *Physical Acoustics Vol. XII,* edited by W. P. Mason and R. N. Thurston (Academic, New York, 1976).

[25] P. Morin, J. Rouchy, and E. du Tremolet de Lacheisserie, Phys. Rev. B **16**, 3182 (1977).

[26] P. Morin and S. J. Williamson, Phys. Rev. B **29**, 1425 (1984).