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Evidence for random strain at the cubic site of Yb$^{3+}$ in palladium by Mössbauer spectroscopy on $^{170}$Yb

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Résumé. — Nous avons effectué l'analyse du spectre hyperfin Mössbauer de relaxation lente de l'ion paramagnétique Yb$^{3+}$ dans le palladium à $T = 0.11$ K. Dans cet alliage, les deux états de champ cristallin de Yb$^{3+}$ les plus bas en énergie (état fondamental $\Gamma_7$ et premier état excité $\Gamma_8$) sont quasi dégénérés ($\Delta \approx 2.5$ K). Ceci confère au spectre hyperfin magnétique une grande sensibilité aux distorsions de champ cristallin par rapport à la symétrie cubique, ce qui se traduit par un élargissement statique important des raies. Notre analyse nous a permis d'estimer le produit de la constante magnétoélastique $V$ par l'écart-type $\sigma$ de la distribution des déformations aléatoires : $V \sigma = 0.04$ K. La forme du spectre suggère que les déformations dominantes dans PdYb sont de symétrie $\Gamma_5$. En outre, nous avons mis en évidence des effets plus fins liés à l'interaction hyperfine au second ordre en perturbation.

Abstract. — We have analysed the slow relaxation Mössbauer emission spectrum obtained at $T = 0.11$ K of the paramagnetic ion Yb$^{3+}$ in palladium. In this alloy, the two Yb$^{3+}$ lowest crystal field states (ground state $\Gamma_7$ and first excited state $\Gamma_8$) are quasi-degenerate (separation $\Delta \approx 2.5$ K). In this situation the magnetic hyperfine spectrum is very sensitive to crystal field distortions away from cubic symmetry, which gives rise to an important static broadening of the lines. Our lineshape analysis provides an estimate of the product of the magnetoelastic constant $V$ and the mean square deviation $\sigma$ of the random strain distribution : $V \sigma = 0.04$ K. The spectrum lineshape suggests that the predominant distortions in PdYb have $\Gamma_5$ symmetry. In addition, we put in evidence finer effects related to the hyperfine interaction when treated to second perturbation order.

1. Introduction.

In a previous publication [1], we gave an analysis of the static and dynamic properties of the paramagnetic Yb$^{3+}$ impurity in a cubic metallic host, palladium, based upon the emission Mössbauer spectra on $^{170}$Yb between 0.1 and 2 K. We derived the crystal field level scheme of Yb$^{3+}$ : the ground state is the $\Gamma_7$ doublet and the first excited state is the $\Gamma_8$ quartet lying at an energy of only about 2.5 K above the ground state.

This fortuitous quasi-degeneracy of the two lowest crystal field levels is very unusual, and we showed that it is responsible for the peculiarities we observed in the static and dynamic properties of Yb$^{3+}$ in Pd.

The slow relaxation spectrum emitted by $^{170}$Yb in Pd at 0.11 K shows an important static line broadening that we attributed [1] to the presence of a distribution of crystal field parameters at the site of the Yb$^{3+}$ impurity, caused by the random lattice deformations occurring in the sample. In palladium, these non-cubic crystal field components (which magnitudes are about 0.1 K [2, 3]) appreciably mix the « cubic » ground state $\Gamma_7$ of the Yb$^{3+}$ ion with the low energy excited state $\Gamma_8$, and lead to an exceptionally important deformation of the slow relaxation hyperfine spectrum associated with $\Gamma_7$.

In publication [1] a first analysis of the emission spectrum at $T = 0.11$ K, made with a simplified axial strain model, allowed us to obtain simulated spectra close to the experimental spectrum in the hypothesis when the $\Gamma_8$ quartet (and not the $\Gamma_6$ doublet) is the first excited state with an energy of about 2.5 K.

However, some of the features of the experimental lineshape remained unexplained within the frame of the above model :

i) the value obtained for the Isomer Shift (I.S.) did not match with the values usually observed for $^{170}$Yb$^{3+}$ in metallic hosts [4];

ii) we had to artificially introduce a non-zero mean axial component of the crystal field in order to account for the strong reduction of the $^{170}$Yb$^{3+}$ hyperfine constant with respect to the theoretical value associated with a $\Gamma_7$ state.
In the present paper, we have performed a more refined analysis of the combined effects of the hyperfine interaction and of the crystal field deformations on the slow relaxation Mössbauer spectrum associated with the electronic doublet \( \Gamma_8 \). We introduce quantum mixing of the crystal field states via the hyperfine interaction (whose magnitude is about 0.1 K for a rare earth ion), and we use a decomposition of the magnetoelastic interaction (which couples the Yb magnetic moment \( J \) and the crystal field distortions) according to the irreducible representations \( \Gamma_3 \) and \( \Gamma_5 \) of the cubic group.

With respect to the model calculation of reference [1], the present approach of the problem is more realistic. First, instead of considering only axial deformations, we take correct account of the symmetry properties of random strains at a cubic site. Second, the perturbation treatment is more adequate: while in reference [1], we treated the hyperfine interaction at first order with respect to the crystal field (cubic + deformations), in the present paper, we consider both hyperfine and magnetoelastic interactions up to second order perturbation with respect to the cubic crystal field. We also included the second order corrections due to the strain interaction in the electro-nuclear levels associated with the ground nuclear state, which had erroneously been omitted in reference [1].

Section 2 contains generalities about hyperfine interactions and the magnetoelastic coupling (limited to 2nd order terms in \( J \)). Then, the main features of the Mössbauer lineshape associated with a \( \Gamma_7 \) doublet are described when the two above-mentioned interactions are treated to first order perturbation (section 3), then to second order perturbation (section 4) with respect to the cubic crystal field interaction. Section 5 contains spectral simulations in the presence of a distribution of deformations. We study the influence of the nature of the first excited state (\( \Gamma_8 \) or \( \Gamma_9 \)) and of the type of distortion with respect to cubic symmetry (\( \Gamma_3 \) or \( \Gamma_5 \)) on the lineshape associated with the \( \Gamma_5 \) ground doublet. We apply the results to the analysis of the spectrum of PdYb\(^{3+} \) at \( T = 0.11 \) K; our conclusions support those of publication [1] as concerns the nature of the lowest energy crystal field excited state, namely that it is the \( \Gamma_8 \) quartet. Furthermore, the present analysis overcomes difficulties encountered in the previous model and suggests that the dominant deformations at the Yb\(^{3+} \) site in Pd have \( \Gamma_5 \) symmetry.

2. Hyperfine interactions and crystal field distortions.

The Kramers ion Yb\(^{3+} \) has a half-integer total angular momentum \( J = 7/2 \) in its ground spin-orbit state. A cubic symmetry crystal field splits this multiplet into two doublets (\( \Gamma_8 \) and \( \Gamma_3 \)) and a quartet (\( \Gamma_9 \)). In palladium, the point group symmetry of a substituted impurity is m3m.

The distortions with respect to cubic symmetry may be analysed considering the deformations of the « molecule » formed by the rare earth ion and its 12 nearest metallic neighbours. Group theory shows that, in the absence of a magnetic field, there exists two sets of deformation modes, which transform respectively according to the \( \Gamma_3 \) and \( \Gamma_5 \) representations of the cubic group, and which are coupled to the ionic angular momentum \( J \) by means of the magnetoelastic constants \( V(\Gamma_3) \) and \( V(\Gamma_5) \) [5-7]. For a Kramers ion, this coupling may be written, up to second order terms in \( J \):

\[
\mathcal{K}^{\text{str}} = V(\Gamma_3) \sum_{j=6,7} O_{3g,j} e_{3g,j} + V(\Gamma_5) \sum_{j=x,y,z} O_{5g,j} e_{5g,j}.
\]

In this expression, the \( \{ e_{3g,j}, e_{5g,j} \} \) tensor is the relative strain tensor, and the operators \( O_{3g,j} \) and \( O_{5g,j} \) are equivalent-operators of second order in \( J \) (see sect. 5). The magnetoelastic constants \( V(\Gamma_3) \) and \( V(\Gamma_5) \) have an order of magnitude of 10 K for rare earth ions [6], and the relevant relative deformations amount to a few \( 10^{-3} \). In a crystal, the values of the strains \( e_{3g,j} \) and \( e_{5g,j} \) are generally distributed at random on the lattice sites. In this paper, we shall use a distribution represented by a symmetrical binomial law (see sect. 5).

The free ion Yb\(^{3+} \) hyperfine interaction in the excited nuclear state of \( ^{170}\text{Yb} \), with nuclear spin \( I_e = 2 \), contains a magnetic and an electric quadrupolar term [8]:

\[
\mathcal{K}^{\text{hf}} = \mathcal{K}^{M} + \mathcal{K}^{Q},
\]

where \( \mathcal{K}^{M} = a_J I \cdot J \) and :

\[
\mathcal{K}^{Q} = b_J \left[ \left( I \cdot J \right)^2 + \frac{3}{2} I \cdot J - J(J+1) \right].
\]

The hyperfine constants \( a_J \) and \( b_J \) for the \( J = 7/2 \) state of \( ^{170}\text{Yb}^{3+} \) are [9, 10] :

\[
a_J = 14.40 \times 10^{-3} \text{ K} \quad \text{(magnetic constant)};
\]

\[
b_J = 0.60 \times 10^{-3} \text{ K} \quad \text{(quadrupolar constant)}.
\]

On the other hand, the hyperfine interaction vanishes in the ground nuclear state with spin \( I_s = 0 \).

The base states of the electro-nuclear system formed in the excited nuclear state are

\[
| J = 7/2, J_z > \otimes | I_e = 2, I_z > .
\]

The coupled electron-nucleus system has Kramers degeneracy, for it is made up of a tensorial product of a half-integer spin (\( J = 7/2 \)) and of an integer spin (\( I_e = 2 \)). The hyperfine and strain interactions \( \mathcal{K}^{\text{hf}} \) and \( \mathcal{K}^{\text{str}} \) are of the same order of magnitude (0.1 K) lead to a quantum mixing of the electro-nuclear states arising from the various crystal field levels. In practice, this mixing is important only for closely spaced electronic states (with energy separation \( \Delta \sim 1 \) K), which is a relatively rare situation in dilute alloys with rare earth Kramers ions.

When the energy $\Delta$ of the nearest excited crystal field level is much greater than about 1 K, the interactions $\mathcal{K}_{\text{str}}$ and $\mathcal{K}_{\text{nucl}}$ produce a very weak mixing of the ground state $\Gamma_7$ with the excited states. At low temperature ($k_B T \ll \Delta$) computation of the hyperfine spectrum is performed by diagonalizing $\mathcal{K}_{\text{nucl}} + \mathcal{K}_{\text{str}}$ inside the 10-fold degenerate multiplet (the index $\pm 2$ represents the two Kramers-conjugate states of the $\Gamma_7$ doublet).

The electric part of $\mathcal{K}_{\text{nucl}}$ is a tensor of rank 2 [8], and thus transforms like $T_3 + F_5$, and so does $\mathcal{K}_{\text{str}}$. It is easy to check that the decomposition of the product of representations $\Gamma_3 \times (\Gamma_3 + F_5)$ does not contain $\Gamma_7$ (and symmetrically for $\Gamma_6$). Therefore, $\mathcal{K}_{\text{nucl}}$ and $\mathcal{K}_{\text{str}}$ have zero matrix elements inside an electro-nuclear multiplet associated with $\Gamma_7$ (or $\Gamma_6$). This fact corresponds to the « isotropy » of the $\Gamma_7$ and $\Gamma_6$ doublets, in contrast to the $\Gamma_8$ quartet, which gives rise to a non-zero quadrupolar hyperfine interaction even at a site with cubic symmetry.

Diagonalizing $\mathcal{H}_{\text{nucl}} = a J \cdot I$ in the subspace $| \Gamma_7 \rangle \otimes | I_e = 2 \rangle$ leads to 10 hyperfine eigenstates 2-fold Kramers degenerate; in cubic symmetry, these 10 states give rise to two multiplets, 4-fold and 6-fold degenerate (called respectively $F_1$ and $F_2$ in [1]), whence the two lines of the slow relaxation spectrum of $^{170}\text{Yb}^{3+}$ associated with the $\Gamma_7$ doublet when $\mathcal{K}_{\text{nucl}} \ll \Delta$. The Mössbauer spectrum of $^{170}\text{Yb}^{3+}$ in Au [11], at low temperature, provides a good example of a lineshape which is well described by a hyperfine interaction treated to first order perturbation: the excited Yb$^{3+}$ crystal field levels in Au lie indeed at energies greater than 80 K above the ground state $\Gamma_7$. This kind of spectrum (see Fig. 1) shows the following characteristics:

i) the centre of gravity $E_G$ of the energies related to the excited nuclear state is not modified, because $E_G = 1/10. a_J \text{Tr}(I \cdot J) = 0$, the trace being restricted to the states in the $| \Gamma_7 \pm 2 \rangle \otimes | I_e = 2 \rangle$ multiplet. The shift in the centre of gravity is simply arising from the difference in the valence and the electronic environment between the studied source alloy and the reference absorber, with also a negligibly small contribution due to the second order Doppler shift. Its value in AuYb$^{3+}$ (0.164 ± 0.040 mm/s [1]) may be considered as a typical Isomer Shift for Yb$^{3+}$ in metallic hosts [4];

ii) the hyperfine constant associated with the $\Gamma_7$ doublet, which is defined as $A = a_J g / g_J = 13.15$ mm/s ($g_J = 8/7$ for $J = 7/2$; $g = 3.43$ for $\Gamma_\gamma$). In compounds with metallic character, there appears an extra hyperfine contribution $\Delta A_{\text{eff}}$ in principle positive in sign, coming from the dynamic polarization of s-type conduction electrons [12-14]. In AuYb$^{3+}$ : $A_{\text{eff}} = A + \Delta A_{\text{eff}} = 13.20 \pm 0.07$ mm/s [11], which demonstrates that $\Delta A_{\text{eff}}$ is very small ($< 0.01 A$).

iii) the static broadenings of the two lines are zero to first order perturbation. In AuYb at low temperature and for low enough impurity concentration (~ 100 ppm), the electronic relaxation is negligible and the broadenings of the two lines are small and have the same magnitude ($\Delta \Gamma \approx 0.6$ mm/s at $T = 0.1$ K).

In contrast to the above, the analysis of the $T = 0.11$ K spectrum in PdYb$^{3+}$ (see Fig. 2) performed in reference [1] yields the following features:

i) the observed I.S. is:

$I.S. (\text{PdYb}) = - 0.28 \pm 0.06$ mm/s (Ref. YbB$_6$),

that is:

$I.S. (\text{PdYb}) = - 0.54 \pm 0.06$ mm/s (Ref. source TmAl$_2$ [4]).

This value may be compared with that observed in AuYb [11]:

$I.S. (\text{AuYb}) = + 0.164 \pm 0.040$ mm/s (Ref. source TmAl$_2$).

Fig. 2. — Emission spectrum at $T = 0.11$ K in PdYb$^{3+}$. The solid line is a fit to 2 Lorentzian shaped lines.
Assuming that the latter value is representative of $^{170}\text{Yb}^{3+}$ in a metallic host, then the centre of gravity of hyperfine energies in PdYb is shifted by $-0.7 \pm 0.1 \text{ mm/s}$;

ii) the mean energy distance between the two spectral lines yields an effective hyperfine constant of 12.40 mm/s, that is 6% lower than the theoretical value in cubic symmetry (13.15 mm/s).

iii) the static broadenings of the two lines are important and very different from each other. The broadening of the line at the higher energy is 6.40 mm/s, that is 7 times bigger than that of the lower energy line.

It appears clearly that one cannot account for these characteristics within the frame of a first order perturbation model. Because the first excited crystal field state is so close from the ground state in PdYb (2.5 K), second and higher order corrections to the electron-nuclear energies, due to the level mixing via hyperfine and random strain interactions, become significant. We shall show in the next sections that the characteristics of the observed Mössbauer emission spectrum of PdYb$^{3+}$ at $T = 0.11 \text{ K}$ can be explained in this manner.

4. Spectroscopic anomalies in the presence of low energy crystal field excitations.

When an excited crystal field state lies close to the ground state, the lineshape must be computed to higher than first order perturbation. The magnetic ($\mathcal{K}^\text{M}$) and quadrupolar ($\mathcal{K}^\text{Q}$) hyperfine interactions, as well as the random strains ($\mathcal{K}^\text{str}$), appreciably couple the ground ($\Gamma_\gamma$) level with the closest crystal field excited state. In this section, we shall consider the perturbation approach, which allows general information to be obtained about the spectroscopic corrections provoked by mixing of the $\Gamma_\gamma$ level with higher levels. However, the perturbation expansions could not be used in the spectral simulations because the perturbation treatment is only valid in a limited range of the perturbation parameter ($< 1/100$), whereas a correct simulation of the experimental spectrum requires strain parameters up to 1/10 of the crystal field energy separation. So we shall also report results of numerical calculations obtained through the diagonalization of the total Hamiltonian of the problem $\mathcal{K}^\text{exc} + \mathcal{K}^\text{hf} + \mathcal{K}^\text{str}$ (where $\mathcal{K}^\text{exc}$ is the cubic crystal field interaction), of dimension $(2J + 1) \times (2J + 1) = 40$, in the presence of a set of relative deformations $(\epsilon_{2s,2p}, \epsilon_{2s,3p}, \epsilon_{2p,3p}, \epsilon_{5s,5p}, \epsilon_{5p,6s})$.

At low temperature ($k_B T \ll \Delta$), when the ground doublet $\Gamma_\gamma$ alone is markedly populated, the Mössbauer transitions take place between the $2 \times (2 I_\gamma + 1) = 10$ ground-electro-nuclear states associated with the excited nuclear state ($I_\alpha = 2$), which we shall call $\psi_{\alpha}$, and the $2 \times (2 I_\gamma + 1) = 2$ ground states associated with the ground nuclear state ($I_\nu = 0$), which we shall call $\psi_{\nu}$.

The states $\psi_{\nu}$ are the ground eigenfunctions of the interaction $\mathcal{K}^\text{exc} + \mathcal{K}^\text{hf} + \mathcal{K}^\text{str}$, and are mixtures of the base functions $|F_\nu \rangle |I_\nu = 2, m_\nu \rangle$ ($\alpha = 6, 7, 8$) where the main contribution comes from states $|I_\nu = 2, m_\nu \rangle$. When the interaction $\mathcal{K}^\text{str} + \mathcal{K}^\text{nuc}$ is treated to second order perturbation, one gets energy terms in $\mathcal{K}^\text{str}^2$, in $\mathcal{K}^\text{nuc}^2$, and cross terms $\mathcal{K}^\text{str} \times \mathcal{K}^\text{str}$, the degeneracy of the $F_1$ and $F_2$ multiplets is then lifted respectively into 2 and 3 Kramers doublets (see Fig. 3). By contrast, the degeneracy of the 2 $\psi_{\nu}$ Kramers conjugate states, ground eigenfunctions of $\mathcal{K}^\text{exc} + \mathcal{K}^\text{str}$ is not lifted by this purely electrostatic interaction. These ground state levels are however shifted in energy by a term in $\mathcal{K}^\text{str}$, but this shift is identical with that of the $\psi_{\nu}$ states arising from the term in $\mathcal{K}^\text{str}$. This occurs because $\mathcal{K}^\text{str}$ acts solely upon the electronic variables $|I_\alpha \rangle$. The second order corrections to the transition energies $E(\psi_{\nu}) - E(\psi_{\nu})$ thus come only from the terms in $\mathcal{K}^\text{str}^2$ and the cross terms $\mathcal{K}^\text{str} \times \mathcal{K}^\text{str}$. These are inversely proportional to the energy distance $\Delta$ to crystal field excited states, and they split the two lines arising from the 2 multiplets $F_1$ and $F_2$. They lead to spectroscopic anomalies which will be the more important, the closer the first excited level to the ground state.

To begin with, we investigated two important properties of the matrix elements of the hyperfine interaction:

a) the ground state $\Gamma_\alpha$ is coupled with $\Gamma_\gamma$ only via $\mathcal{K}^\text{str}$, whereas it is coupled to $\Gamma_\nu$ by $\mathcal{K}^\text{str}$ and $\mathcal{K}^\text{nuc}$. As $\mathcal{K}^\text{str} \gg \mathcal{K}^\text{nuc}$ for $^{170}\text{Yb}^{3+}$, the matrix elements $\langle \Gamma_\gamma | \mathcal{K}^\text{str} | \Gamma_\nu \rangle$ are an order of magnitude smaller than the elements $\langle \Gamma_\gamma | \mathcal{K}^\text{nuc} | \Gamma_\nu \rangle$.

Fig. 3. — Electro-nuclear states at different perturbation orders. The figure is not to scale. The excited ($I_\alpha = 2$) and ground ($I_\nu = 0$) nuclear states are separated by an energy of 84.3 keV. The energy separation $\Delta$ between the 2 crystal field states $\Gamma_\gamma$ and $\Gamma_\nu$ is 2.5 K ($\approx 0.21$ meV); the energy splitting $\Delta_{\text{str}}$ between the 2 hyperfine multiplets $F_1$ and $F_2$ is about 0.11 K ($\approx 9.5$ μeV). The vertical lines represent the Mössbauer transitions observed at low temperature. $\mathcal{K}^\text{nuc}$ is the nuclear interaction; see text for explanation of the other symbols.
b) we computed the matrix elements of $H_{hf}$ between the eigenstates of the multiplets $F_1$ and $F_2$ and the states $|I_\sigma \rangle |I_\tau = 2 \rangle$: we find that elements $\langle F_1 \mid H_{hf} \mid F_2, I_\tau = 2 \rangle$ contain contributions of the same magnitude, but of opposite signs, from terms in $K_{hf}$ and $K_{Q2}$, whereas for elements $\langle F_2 \mid H_{hf} \mid F_1, I_\tau = 2 \rangle$ the 2 contributions have the same sign. The elements involving $F_2$ are therefore one order of magnitude bigger than the elements involving $F_1$; one can say that $F_1$ is very weakly coupled to the states $|I_\sigma \rangle |I_\tau = 2 \rangle$. One can see on figure 4 the drastic effect this property induces on the electro-nuclear energies (in the absence of strain). The line arising from multiplet $F_1$ remains stationary, while the line arising from $F_2$ splits markedly and shifts to lower energies for $L_1$ values below 5 K.

In addition, our perturbation calculations (see Appendix) yielded a property of the cross term:

c) the centres of gravity of the lines arising from $F_1$ and $F_2$ do not depend on terms in $K_{hf} \times K_{str}$ but solely on terms in $K_{hf}$.

Let us examine now the effect of these $K_{hf}^2$ and $K_{hf} \times K_{str}$ terms on the hyperfine spectrum:

i) Spectrum centre of gravity. — The term in $K_{hf}^2$ leads to an overall negative energy shift of the $|I_\sigma \rangle$ levels associated with the nuclear excited state, in agreement with the well known result of perturbation theory (see Fig. 4). As there is no hyperfine interaction in the ground nuclear state, and as according to property c) above, the contribution of cross terms in $K_{hf} \times K_{str}$ to the shift of the centre of gravity is zero, a decrease occurs in the energy of the Mössbauer transition, that is there appears a negative apparent Isomer Shift for the Mössbauer spectrum observed in the ground doublet $I_\sigma$. This apparent I.S. is in second order perturbation entirely due to hyperfine mixing. Now, exact diagonalization of the Hamiltonian $H_{hf} + K_{str}$ inside the whole multiplet $|J = J_{\sigma} \rangle |I_\tau = 2 \rangle$ indeed shows that the shift of the centre of gravity of the spectrum is well represented by the following law, when the crystal field energies $\Delta (I_{\sigma})$ and $\Delta (I_{\tau})$ are greater than 1 K:

$$E_\sigma (\text{in mm/s}) = - 0.23/\Delta (I_{\sigma}) - 1.58/\Delta (I_{\tau})$$

$$(\Delta (I_\tau) \text{ in K})$$

With the values used in reference [1]: $\Delta (I_{\tau}) = 25$ K and $\Delta (I_{\sigma}) = 70$ K, one obtains a calculated shift of $-0.63$ mm/s, which is compatible with the experimental value $-0.7 \pm 0.1$ mm/s. The existence of an apparent I.S. is the consequence of a thermal population effect: we only observe the hyperfine spectrum arising from the ground multiplet $|J = J_{\tau} \rangle |I_\tau = 2 \rangle$. At higher temperature, no shift occurs in the centre of gravity of the spectrum because the excited $I_{\tau}$ and $I_\sigma$ levels are now populated [$\text{Tr} (K_{hf}) = 0$ in the electro-nuclear space $|J = J_{\tau} \rangle \otimes |I_\tau >$].

Such a shift of the centre of gravity, provoked by second order hyperfine mixing, has already been observed in Mössbauer absorption spectra on $^{169}$Tm in the compounds TmCl$_3$, 6 H$_2$O [15] and TmFe$_2$Si$_2$ [16]. In these compounds, the Tm$^{3+}$ Van Vleck ion has two non-magnetic ground electronic singlets very close in energy ($\Delta \approx 1$ K). Hyperfine mixing gives rise to a « pseudo-quadrupolar » shift of the spectrum associated with each electronic level. In contrast with the situation in PdYb, electronic relaxation is fast at low temperature in these Tm compounds; the centre of gravity of the spectrum is then a thermal average over crystal field levels, which is temperature dependent.

ii) Effective hyperfine constant. — If one examines the energy corrections caused by the term in $K_{hf}^2$ in each multiplet $F_1$ or $F_2$, property b) of the matrix elements of $K_{hf}$ implies that the mean negative shift of the lines arising from $F_2$ is bigger than that of $F_1$ (see Fig. 4). The hyperfine mixing thus reduces the hyperfine splitting below the value $\Delta_{hf} = 0.108$ K obtained without mixing.

Our computer calculations yield the following variation for the effective hyperfine constant due to terms in $K_{hf}^2$:

$$A_{eff} (\text{mm/s}) = A - 0.076/\Delta (I_{\sigma}) - 1.020/\Delta (I_{\tau})$$

$$(\text{A in K})$$

Using the above-quoted values for $\Delta (I_{\sigma})$ and $\Delta (I_{\tau})$, one gets an effective hyperfine constant $A_{eff} = 12.76$ mm/s, showing a $3\%$ reduction with respect to the cubic theoretical value $A = 13.15$ mm/s.

Fig. 4. — Hyperfine transition energies associated with the $I_\tau$ doublet as a function of the energy distance $\Delta$ to the $I_\sigma$ quartet. The energies were obtained by diagonalization of the interaction $K_{hf} + K_{str}$, the $I_\tau$ doublet lying at a fixed energy of 70 K. The asymptotical dash-dotted lines are the energy values calculated to first order perturbation. a) Transitions arising from the $F_1$ multiplet; b) transitions arising from the $F_1$ multiplet; c) centre of gravity of the 2 multiplets.
According to property c), the cross strain terms do not lead to any second order reduction of the effective hyperfine constant associated with $\Gamma_\gamma$. As it is known that the presence of a deformation with respect to cubic symmetry leads to a second order reduction of the mean spectroscopic $g$-value of $\Gamma_\gamma$, in some cases (for an elongation or compression strain along a 3-fold cubic axis [17] or along a 4-fold cubic axis [1, Appendix 1], one could think that the same property would hold for the hyperfine constant. In fact, our exact calculations have shown that the strain terms actually provoke a reduction of the effective hyperfine constant, but only in higher than second order. For a reasonable value of the strain parameters (see Sect. 5), it amounts to about 1% of the cubic $A$ value. The experimental reduction of the hyperfine constant in PdYb$^{3+}$ (6%) must therefore contain a small extra contribution which may be thought to arise from conduction electron polarization, although recent theoretical estimates predict an enhancement of the effective hyperfine constant for rare earth impurities in d-band hosts [18].

iii) Line broadenings. — The degeneracy lifting caused by second order terms leads to a broadening of the two lines arising from the $F_1$ and $F_2$ multiplets. The $\mathcal{X}_{\text{str}}$ term leads to a splitting which is much more important for the line arising from $F_2$ (see Fig. 4), however the resulting broadening is smaller than that observed experimentally. The cross terms in $\mathcal{X}_{\text{hf}} \times \mathcal{X}_{\text{str}}$ have a similar effect (see also Ref. [9]) but may now yield a splitting of the same magnitude as that observed experimentally. However, our spectral simulations showed that it is impossible to reproduce the experimental lineshape with a single set of relative deformations, and that in fact it is necessary to introduce a continuous distribution of these parameters (see Sect. 5).

From these considerations, one can draw the following conclusions:

i) the presence of an excited $\Gamma_6$ state has very little influence on the spectral shape associated with $\Gamma_\gamma$;

ii) the apparent negative Isomer Shift is almost entirely due to the mixing by the hyperfine interaction (diagonalization of the complete Hamiltonian in the whole electron-nuclear multiplicity shows that the presence of a $\mathcal{X}_{\text{str}}$ of reasonable magnitude does not modify the centre of gravity of the spectrum by more than 8%). Considering the quartet $\Gamma_8$ alone at an energy $\Delta$ above the ground state, one can estimate the range of $\Delta$ values which are compatible with the experimental difference (0.7 ± 0.1 mm/s) observed with respect to the L.S. in AuYb; one gets from the equation yielding $E_\text{G} = 1.58/\Delta = -0.7 ± 0.1$ (x in K), thus: $2.0$ K < $\Delta$ < $2.6$ K. This range of values for $\Delta$ agrees well with the value (2.5 K) derived from the totally independent method based on our measurements of the localized magnetic moment relaxation rates as described in reference [1];

iii) the mean energy separation between the two lines arising from the hyperfine multiplets $F_1$ and $F_2$ is reduced by mixing via $\mathcal{X}_{\text{hf}}$ at second order and via $\mathcal{X}_{\text{str}}$ at higher orders.

The second order corrections in $\mathcal{X}_{\text{hf}} + \mathcal{X}_{\text{str}}$ in the presence of an excited $\Gamma_8$ state at an energy of about 2.5 K, thus account qualitatively for the main features of the slow relaxation hyperfine spectrum of Yb$^{3+}$ in Pd. As was said in the introduction, the present model shows several improvements with respect to that of reference [1]: we consider deformations both of $\Gamma_3$ type and of $\Gamma_5$ type (shear), whereas the calculation in reference [1] assumed only axial $J_{3g,\delta}$ strains; the second order terms in $\mathcal{X}_{\text{str}}$, which were lacking from our previous calculation, are now present and account for the shift of the spectrum centre of gravity.

But we saw that one cannot reproduce the observed lineshape with a single set of strain variables. So, in the next section, we shall examine the influence of a distribution of distortions with respect to cubic symmetry on the Yb$^{3+}$ slow relaxation spectrum associated with $\Gamma_\gamma$. Note that, now, the number of distributed variables is 5, which increases greatly the computer time necessary to synthesize a spectrum with respect to the model of reference [1], where $\varepsilon_{3g,\theta}$ was the only distributed parameter.

5. Analysis of random crystal field strains in PdYb$^{3+}$.

5.1 SPECTRAL SIMULATIONS. — The crystal field interaction describing random distortions with respect to cubic symmetry has been discussed in section 2. We recall here that it is written:

$\mathcal{X}_{\text{str}} = V(\Gamma_3) - V(\Gamma_3) - V(\Gamma_5) + V(\Gamma_5) + V(\Gamma_5) + V(\Gamma_5) + V(\Gamma_5) + V(\Gamma_5)$.

The operators $O(\Gamma_i)$ are polynomials of second order in the $\mathcal{J}$ components:

$O(\Gamma_{3g,\theta}) = 3 J_x^2 - J(J + 1)$

$O(\Gamma_{3g,\theta}) = 3 (J_y^2 - J_z^2)$

$O(\Gamma_{5g}) = (J_x J_y + J_y J_z)/2$

$O(\Gamma_{5g}) = (J_x J_y + J_y J_z)/2$

and the quantities $\varepsilon_i$ are the normal displacements [6], which are distributed at random in the solid.

We assume that the relative strain distribution follows a symmetrical binomial law:

$P(k) = 1/2^n \binom{n}{k} \frac{1}{2^n} n! \frac{1}{k!(n-k)!}$

$k$ being a discrete variable which represents the parameter $\varepsilon_i(k = 0, 1, ..., n)$, and $n + 1$ being the number of points in the binomial law. It is known that such a law tends towards a Gaussian law when $n$ becomes large. This binomial law is centred at the origin and has a mean square deviation $\sigma$. The link between the discrete variable $k$ and the $\varepsilon_i$ values is:
$e_i = \sigma_i \sqrt{n_i (2k - n_i)}$; to the variable $e_i$ is associated the probability $P[k(e_i)]$.

The 5 variables $e_i$ are independently distributed; nevertheless, in order to maintain the global cubic symmetry of each site, the mean square deviations of the $e_{3g,4}$ and $e_{3g,5}$ distributions must be identical (we shall call them $\sigma_3$); the same applies to the mean square deviations of the 3 $e_{5g,7}$ parameters, which we shall call $\sigma_5$.

We performed spectral simulations assuming distributions of the relative deformations $e_i$. The 10 ground eigenvalues of the matrix $\mathcal{K}^* = \mathcal{K}_{cc} + \mathcal{K}_{hf} + \mathcal{K}_{str}$, as well as the 2 ground eigenvalues of the interaction $\mathcal{X} = \mathcal{X}_{cc} + \mathcal{X}_{str}$, are calculated numerically for each set of values of $e_{3g,6}$, $e_{3g,7}$, $e_{5g,7}$, $e_{5g,8}$, $e_{5g,9}$ (see Appendix). Then the transition energies are calculated, and we obtain an elementary spectrum by setting Lorentzian-shaped lines at these energies, all with the same width. The final lineshape is obtained by superposing the elementary spectra, each with a weight equal to the product of the 5 probabilities $P[k(e_i)]$. The final lineshape depends only on the 4 electronic parameters $A(\delta_6)$, $A(\delta_8)$, and $V(\delta_3)$. $\sigma_3$, and on the 2 hyperfine parameters: the Isomer Shift [assumed to be equal to that in AuYb (see Sect. 3)] and the linewidth. This last parameter has been fixed to 2.8 mm/s [1]: the natural linewidth of the transition is 2 mm/s, a broadening of 0.7 mm/s comes from the reference absorber we used, and a weak dynamical contribution estimated to be 0.1 mm/s.

If one assumes values for the energy distances $\Delta(\Gamma_6)$ and $\Delta(\Gamma_8)$, the fitting of the experimental spectrum allows in principle the quantities $V(\Gamma_3)$, $\sigma_3$, and $V(\Gamma_5)$, $\sigma_5$ to be obtained. In fact, it was not possible to follow this fitting procedure because the computation time involved would have been too long. Indeed, in order to obtain a good approximation of a continuous distribution, the number of points $N$ of the binomial law must be chosen greater than 20. But the number of iterations to be performed in a spectrum computation is $N^3$ in the presence of deformations of the two types $\Gamma_3$ and $\Gamma_5$, $N^3$ in the presence of deformations of $\Gamma_3$ type only, and $N^2$ with $\Gamma_5$-like distortions alone. In a reasonably long lapse of time, we could only perform spectral simulations in the presence of only one type of deformation. We then tried to obtain the best reproduction of the spectral shape and of the experimental broadening. The reduced number of iterations ($N^2$ or $N^3$) allowed us to get simulated spectra of good quality with $N = 20$ for $\Gamma_3$-like deformations and $N = 12$ for $\Gamma_5$-like distortions.

5.2 RESULTS AND DISCUSSION. — Our simulations support the conclusions that we obtained in section 4. The presence of a low lying $\Gamma_6$ state would deform the spectral shape much less than is experimentally observed. This allows the hypothesis of a $\Gamma_6$ doublet as lowest excited state to be definitely eliminated: when $\Delta(\Gamma_6) > 1$ K, the line broadenings remain very small (for reasonable values of the $V$ and $\sigma$ parameters), and when $\Delta(\Gamma_6) < 1$ K, the shape of the spectrum deviates markedly from that of the hyperfine spectrum associated with $\Gamma_7$. It is thus impossible to reproduce the experimental spectrum with the $\Gamma_6$ doublet close to the $\Gamma_7$ ground state.

In contrast, mixing with the $\Gamma_8$ state influences the spectral shape in a much more drastic way: one observes an important broadening of the line arising from $\Gamma_2$, while the line arising from $\Gamma_1$ is not significantly broadened. The theoretical spectra displayed on figures 5 and 6 approximately reproduce the experimental broadenings. They have been calculated assuming $\Delta(\Gamma_8) = 2.5$ K and $\Delta(\Gamma_8) = 70$ K. The structure on the right hand line is present because we used a discrete distribution of strain parameters with a relatively small number of points. Increasing this...
number makes the structure progressively disappear, but the computation time then becomes unreasonably long.

The spectrum in figure 5 is a simulation in the presence of distortions with $\Gamma_3$ symmetry, with $V(\Gamma_3), \sigma_3 = 0.05$ K. The spectrum in figure 6 is a simulation in the presence of deformations with $\Gamma_5$ symmetry, with $V(\Gamma_5), \sigma_5 = 0.04$ K. It can be seen that the line arising from the $F_2$ multiplet on figure 5 is more asymmetric than the same line on figure 6, whereas the experimental line is symmetric to a good approximation (see Fig. 2). The differential broadening of the 2 lines is less important for the spectrum on figure 5 than for that on figure 6. By comparison, the experimental spectrum seems closer to the spectrum on figure 6, that is, our results seem to point to the fact that the predominant distortions from cubic symmetry on the Yb$^{3+}$ site in Pd are of $\Gamma_5$ symmetry.

It is of interest to compare these conclusions with those obtained by means of magnetostriction and EPR measurements [6, 7] on rare earth ions doped either in noble metals (Au, Ag) or in binary alloys (LaS, LaSb). In these systems, the width of the EPR line associated with the ground state ($\Gamma_6$ or $\Gamma_7$) of the rare earth ion is mainly due to the mixing by random strains and Zeeman interaction of this ground state with an excited $\Gamma_8$ state lying at about 10 K. Measurement of the linewidth anisotropy with respect to the angle between the external magnetic field and a crystal axis of the single crystal sample allowed the predominant deformation type to be found in each of the studied alloys. In the binary alloys LaS and LaSb, the $\Gamma_3$-like distortions prevail, while in the noble metals Au and Ag the $\Gamma_5$-like deformations seem to dominate.

The crystal structure of palladium being that of the noble metals, our result concerning the predominance of $\Gamma_3$-like distortions in PdYb is not inconsistent with the conclusions derived from EPR measurements. Finally, the order of magnitude of the non-cubic crystal field components $[V(\Gamma_3), \sigma_3 \approx 0.04$ K] we estimated in PdYb is slightly greater than the values given in reference [6] for AgDy $[V(\Gamma_3), \sigma_3 \approx 0.015]$ and AuEr $[V(\Gamma_3), \sigma_3 \approx 0.002]$. It is comparable with the value observed in LaSbDy in reference [7] $[V(\Gamma_3), \sigma_3 \approx 0.03]$. 

6. Conclusion.

In this article, we have investigated the influence of non-cubic crystal field components on the hyperfine slow relaxation spectrum of $^{170}$Yb$^{3+}$ associated with the electronic doublet $\Gamma_7$. We showed that these non-cubic components have a spectacular effect on the spectrum when the first excited crystal field state is the quartet $\Gamma_9$, and when this quartet is close to the ground doublet. We applied this analysis to the interpretation of the Mössbauer emission spectrum recorded in PdYb$^{3+}$ at $T = 0.11$ K. Actually, we treated the more general problem of the mixing of the ground doublet $\Gamma_7$ with the excited states via the combined action of the hyperfine interaction of $^{170}$Yb and the random crystal field distortions with respect to cubic symmetry.

The main results of this paper are the following:

i) the $\Gamma_8$ state is the closest crystal field excited state from the ground $\Gamma_7$ doublet of Yb$^{3+}$ in Pd;

ii) the centre of gravity of the spectrum being shifted towards negative energies by the hyperfine mixing of $\Gamma_7$ and $\Gamma_8$, measurement of its apparent Isomer Shift lead us to an estimation of the energy separation between $\Gamma_7$ and $\Gamma_8$ : $2.0$ K $< \Delta(\Gamma_8) < 2.6$ K. This value agrees fully with that obtained in reference [1] from the measurement of the thermal variation of the paramagnetic relaxation rate of Yb$^{3+}$ in Pd between 0.11 K and 2 K;

iii) the predominant distortions on the Yb$^{3+}$ site in Pd seem to be of $\Gamma_5$ type (shear deformation). The value of the parameter $V(\Gamma_5), \sigma_5$, where $V(\Gamma_5)$ is the magnetoelastic constant and $\sigma_5$ the mean square deviation of the distribution of relative strains, was estimated to be 0.04 K. This value matches with typical strain magnitudes in dilute alloys. As concerns the origin of the observed strains, we can say that most of the defects created by the metallurgical process (rolling of the melted ingot) have been eliminated by a suitable annealing as described in reference [1].

Due to the great dilution of our alloy (100 ppm of rare earth) and to the high purity (5 N) of the palladium wires we used, we think that the observed strains are likely to arise from residual structural defects in the sample.

To our knowledge, the great sensitivity of the Mössbauer slow relaxation spectrum of a magnetic impurity to random distortions of the crystal field has never previously been exploited to study local deformations. In this work, we used the fortuitous closeness of the two lowest crystal field levels of Yb$^{3+}$ in Pd to quantitatively estimate, for the first time, the strain parameters from a magnetic hyperfine spectrum.

In relation to our results, an EPR study of a single crystal of PdYb would be of interest in confirming our conclusions concerning the dominant type of strains in this alloy, as would also the determination of the magnetoelastic constant by means of magnetostriction measurements.

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Appendix.

Computation of Spectroscopic Energy Levels. — Computation of the Mössbauer transition energies requires diagonalization of a matrix of dimension $(2J + 1)(2I_e + 1) = 40$ for the nuclear excited state and of a matrix of dimension $(2J + 1)(2I_g + 1) = 8$.
for the nuclear ground state. The electron-nucleus system, as the electronic system alone, possesses Kramers degeneracy. Let $T$ be the time-reversal operator, $|\Gamma_i\rangle$ an electronic eigenfunction of Yb$^{3+}$ in cubic symmetry and $|m_f\rangle$ a nuclear state of $^{170}$Yb ($I$ is integer). The following relations hold:

\[ T^2 |\Gamma_i\rangle = - |\Gamma_i\rangle \]
\[ T^2 |m_f\rangle = |m_f\rangle , \]

so:

\[ T^2 |\Gamma_i\rangle |m_f\rangle = - |\Gamma_i\rangle |m_f\rangle . \]

The dimension of the Hamiltonian matrices of the problem may then in principle be divided by a factor 2, but this reduction is not straightforward since the $T$ operator has the peculiar property of having no eigenfunctions and of being antilinear. A method for such a reduction has been recently published [19], based on the following fact: if one groups the base states as Kramers-conjugate pairs, the Hamiltonian matrix appears as formed by $2 \times 2$ blocks having the following structure:

<table>
<thead>
<tr>
<th>$\psi_2$</th>
<th>$\bar{\psi}_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\psi_1$</td>
<td>$A$</td>
</tr>
<tr>
<td>$\bar{\psi}_1$</td>
<td>$-B^*$</td>
</tr>
</tbody>
</table>

where $A = \langle \psi_1 | \mathcal{H} | \psi_2 \rangle$ and $B = \langle \psi_1 | \mathcal{H} | \bar{\psi}_2 \rangle$.

It can be shown that there exists an isomorphism between the set of these blocks and the set of quaternions $q = A + jB$, where $j^2 = -1$.

The problem then reduces to the diagonalization of a selfdual real quaternionic matrix of dimension twice smaller (see Ref. [20] for mathematical definitions). As an example, in table I below is shown the quaternionic matrix corresponding to the ground nuclear level, that is the matrix of the interaction $\mathcal{H}_{ee} + \mathcal{H}_{ur}$ in the base of the eigenfunctions of the cubic crystalline field. Each base state is a Kramers doublet $\{\Gamma_i, \bar{\Gamma}_i\}$; the quantities $A_i = A(\Gamma_i)$ are the eigenenergies of the doublets in the cubic crystal field alone.

In order to perform spectral simulations, we have to repeatedly compute the eigenvalues of these two matrices. So we tried to obtain the analytic expressions of the characteristic polynomial of each of the two quaternionic matrices, using a formal programming language [21]. Since these characteristic polynomials are scalars, they depend only on the scalar quantities built from the $2 + 3$ components of the relative strain tensor which transform like $\Gamma_3$ and $\Gamma_5$. There are five independent scalar expressions that can be built from $\Gamma_3$ and $\Gamma_5$ alone, and they are the following:

\[
\begin{align*}
G_{333} &= V_3^2(e_{3g,i}^2 + e_{3g,a}^2) \\
G_{333} &= V_3^2(e_{3g,i}^2 - 3 e_{3g,a}^2 e_{3g,a}^2) \\
G_{55} &= V_5^2(e_{5g,x}^2 + e_{5g,y}^2 + e_{5g,z}^2) \\
G_{55} &= V_5^2(e_{5g,x}^2 - 2 e_{5g,a}^2 - 2 e_{5g,y}^2 - 2 e_{5g,z}^2) \\
G_{55} &= V_5^2(e_{5g,x}^2 - e_{5g,y}^2 e_{5g,z}^2) .
\end{align*}
\]

We obtained in this way the following polynomial for the 4 eigenvalues of the cubic crystal field in the presence of a set of relative distortions $\{\varepsilon_i\}$:

\[
D = \lambda(\lambda - \Delta_8)^2(\lambda - \Delta_6) - \lambda^2 \left( \frac{1}{2} G_{333} + \frac{63}{2} G_{55} \right) + \lambda \left[ G_{333}(63\Delta_6 + 342\Delta_8) + G_{55} \left( \frac{91}{4}\Delta_6 + \frac{67}{2}\Delta_8 \right) - \right.
\]
\[
- 1728 G_{333} - 216(G_{55} + G_{355}) - 27 \Delta_6 \Delta_8 G_{333} - \left( 16 \Delta_6 \Delta_8 + \frac{35}{4} \Delta_8^2 \right) G_{55} - 162 \Delta_6 G_{333}
\]
\[
+ (6 \Delta_6 + 210 \Delta_8) G_{355} + 216 \Delta_6 G_{555} + \frac{495}{16} (12 G_{333} + G_{555})^2
\]

As to the quaternionic matrix associated with the nuclear excited state, which is of dimension 20, its characteristic polynomial in the 10 variables $\lambda$, $a_3$, $b_3$, $A_6$, $A_8$, $G_{333}$, $G_{555}$, $G_{333}$, $G_{555}$ contains a priori 319 663 terms; therefore, it is nevertheless more advantageous to numerically compute the eigenvalues than to try and establish such a big expression, which has no straightforward compact expression.

We also computed the Mössbauer transition energies up to second perturbation order. However, the expressions obtained could not be used in the spectral simulations because the perturbation treatment is only valid in a limited range of parameters (typically $|V|e| < 0.01 \Delta_8$), whereas a correct simulation of the experimental spectrum requires values of $|V|e|$ up to 0.1 $\Delta_8$.

The second order correction to the energies associated with the ground nuclear state is straightforward.
Table I. — Quaternionic matrix associated with the cubic crystal field interaction and the distortions with respect to cubic symmetry for the Yb$^{3+}$ ion ($J = 7/2$). We only represented the upper-diagonal part, because the matrix is Hermitian. Notations: $V_3 = V(G_3)$; $V_5 = V(G_5)$.

For the labelling on the base states, see for instance reference [22].

One finds:

\[
\delta E_b = -27 \frac{G_{33}}{\Delta_8} - [35(4/\Delta_6) + 16/\Delta_8] G_{55}.
\]

As to the hyperfine energies associated with the 10-fold multiplet $|\Gamma_7\rangle \ | J_e = 2 \rangle$, their expression up to second perturbation order was derived analytically using the above mentioned reduction method. The 10 levels split into 5 Kramers doublets, and the transition energies are obtained by subtraction of the ground nuclear state correction $\delta E_g$. One gets, for the 2 lines arising from the $F_1$ multiplet:

\[
E_1^\pm = -\frac{9}{2} a_j - \frac{1}{\Delta_8} \left( \frac{27}{2} a_j^2 - 567 a_j b_j + 6237 b_j^2 \right) - \frac{3}{4} \frac{969 b_j^3}{\Delta_6} \pm
\]

\[
\pm \sqrt{\frac{54}{5} a_j - \frac{567}{5} b_j} G_{33} \Delta_8^3 + 3 \left[ \frac{24}{5} a_j - \frac{672}{5} b_j \right] \frac{1}{\Delta_8} - \frac{147 b_j^2}{2 \Delta_6} \right]^2 G_{55},
\]

and, for the 3 lines arising from the $F_2$ multiplet:

\[
E_2^\pm = 3 a_j - 21 a_j^2/\Delta_8 + x_i.
\]

In the last expression, the $x_i$ are the roots of the following polynomial:

\[
P = -x^3 + k_1 x^2 + x(k_3 + 21 k_4 G_{33} + 28 k_5 G_{55}) + k_6 + k_7 G_{33} + k_8 G_{55} +
\]

\[
+ 20 k_4 G_{333} + 160 k_5^3 G_{555} + 40 k_4 k_5^2 G_{555},
\]

where the $k_i$ are polynomials in $a_j^2/\Delta_8$, $a_j b_j/\Delta_8$, $b_j^2/\Delta_8$, and $b_j^3/\Delta_8$. One can see that the centre of gravity $E_1$ of the line arising from $F_1$ does not depend on the cross terms in $K_{agt} \times K_{agd}$, nor does the centre of gravity $E_2 = 3 a_j - 21 a_j^2/\Delta_8 + k_1/3$ of the line arising from $F_2$. Thus, up to second perturbation order, the reduction of the hyperfine constant depends only on the hyperfine terms in $K_{agt}^2$ [property c), Sect. 4].
References


