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J. Emery, S. Hubert, J.C. Fayet. Influence of the coupling in quadrature of two displacement modes and of the phase of the modulation wave on e.s.r. line shapes and relaxation, in the incommensurate phase of ThBr<sub>4</sub>: Gd<sup>3+</sup>. *Journal de Physique*, 1985, 46 (12), pp.2099-2105. 10.1051/jphys:0198500460120209900 . jpa-00210158

**HAL Id: jpa-00210158**

**<https://hal.science/jpa-00210158>**

Submitted on 4 Feb 2008

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Classification

Physics Abstracts

61.16N — 64.70 — 73.60F

## Influence of the coupling in quadrature of two displacement modes and of the phase of the modulation wave on E.S.R. line shapes and relaxation, in the incommensurate phase of $\text{ThBr}_4 : \text{Gd}^{3+}$

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**Résumé.** — En faisant varier l'orientation du champ magnétique, on obtient divers types de formes de raies de R.P.E. dans la phase incommensurable de  $\text{ThBr}_4 : \text{Gd}^{3+}$ . Ils dépendent de l'importance relative et des différences de phase des contributions linéaires et quadratiques aux déplacements locaux des raies dus à deux modes en quadrature. De plus les fluctuations de phase peuvent avoir des effets importants en moyennant la raie ou en donnant un temps de relaxation  $T_1$  qui dépend de la phase locale. Les fluctuations d'amplitude peuvent également donner une largeur de raie qui dépend de la phase locale.

**Abstract.** — By varying the magnetic field orientation we obtain several types of E.S.R. line shapes in the incommensurate phase of  $\text{ThBr}_4 : \text{Gd}^{3+}$ . They depend on the relative importance and on the phase of linear and quadratic contributions to the local line shifts due to two displacement modes in quadrature. Moreover, phase fluctuations may have drastic effects by averaging the incommensurate-line or by giving rise to a local phase-dependent relaxation time  $T_1$ . Amplitude fluctuations may also contribute to a local phase-dependent line width.

### 1. Introduction.

The analysis of resonance line shapes and relaxation in N.M.R. and N.O.R. measurements of intrinsic nuclear spins, or in E.P.R. measurements of extrinsic probe is an efficient tool to investigate incommensurate phases and to check theories about their static and dynamic properties.

For instance the validity of Mac-Millan's concept of discommensuration was initially established by N.M.R. on TaSe which exhibits a modulation of the charge density [1]. Later, the evolution of N.Q.R., N.M.R. and E.P.R. lines in the structural incommensurate phases of  $\text{Rb}_2\text{ZnCl}_4$  [2, 3],  $\text{Rb}_2\text{ZnBr}_4$  [2] and  $\text{KeSeO}_4$  [4] pointed to a cross over from a plane wave modulation regime near  $T_1$  to a narrow soliton regime near  $T_c$ . The characteristic phason-mode was indirectly observed through  $T_1$  N.M.R. measurements in crystals such as  $\text{Rb}_2\text{ZnCl}_4$  [2] where overdamping prevents direct observation. Particularly, large phase-fluctuations, comparable with a « floating of the static modulation », were inferred from drastic motional averaging effects

on N.M.R. and E.P.R. lines in  $\text{Rb}_2\text{ZnBr}_4$  [5] and  $\text{ThBr}_4$  [6] respectively.

Initially, the magnetic resonance lines were analysed within a simple model in which the spin Hamiltonian for a spin probe was expressed in terms of a power expansion of the « local » displacement associated with a single mode modulation wave [2]. Actually the range of the spin probe is not so small as to involve local effects only. The displacements of neighbouring atoms also contribute to the spin Hamiltonian and their phase differs from the local phase [7].

Moreover, two modes coupled in quadrature are generally responsible for the displacements. These differences of phase can influence the line shape significantly.

In this paper, we discuss the line shapes of a  $\text{Gd}^{3+}$  centre in the incommensurate phase of  $\text{ThBr}_4$  for different orientations of the magnetic field.  $\text{ThBr}_4$  is well suited to the study of « nonlocal » [7] effects since the thorium ions are not displaced by the modulation wave. The plane wave regime approximation is valid at any temperature below  $T_1 \simeq 95$  K, and the eigen vectors of the modulation wave are well known from neutron measurements.  $\text{ThBr}_4$  can be considered as a typical case where the incommensurate

(\*) U.A. n° 807.

phase arises through the coupling in quadrature of two modes of the same symmetry which induces a condensation of one branch at  $q_c = 0.310 c^*$  [8].

## 2. Theoretical framework.

Let us consider, according to Heine [9], a displacement field arising from a plane wave modulation with a wave vector  $\mathbf{q}_s$  along  $\mathbf{c}$  :

$$\eta_{ik}^i = A(T_1 - T)^\beta (\alpha_k^i \cos(\varphi_l + \phi_k) + \beta_k^i \sin(\varphi_l + \phi_k))$$

with  $i = x, y, z$  and  $\beta = 0.35$  the theoretical exponent for  $d = 3$  and  $n = 2$ ,  $l$  represents a particular atom,  $\varphi_l = q_s z_l + \varphi_0$  is its local phase and  $k$  represents either  $l$  or a surrounding atom such that  $\phi_k = \varphi_k - \varphi_l$ .  $A$  is an amplitude parameter,  $\alpha_k^i, \beta_k^i$  depend on the eigen vectors of two modes coupled in quadrature. This coupling is a basic process for the occurrence of an incommensurate phase [9].

In  $\text{ThBr}_4$  this displacement field takes a very simple form which is such that the displacements of the bromines surrounding  $\text{Th}^{4+}$  at site  $l$ , can be reduced to a global rotation and a global twist which combine in quadrature [8]. The  $\text{Th}^{4+}$  ions are not displaced ( $\beta_l = \alpha_l = 0$ ) and

$$\begin{aligned} \alpha_1^x &= \alpha_2^y = -\alpha_2^x = -\alpha_8^y & \beta_1^x &= -\beta_7^y = -\beta_2^x = \beta_8^y \\ \alpha_5^x &= \alpha_3^y = -\alpha_6^x = -\alpha_4^y & \beta_5^x &= -\beta_3^y = -\beta_6^x = -\beta_4^y \\ \frac{\alpha_1^x}{\alpha_1^y} &= \frac{\alpha_5^x}{\alpha_5^y} = \text{tg } \varphi(R) & \beta_1^{(x)} &= -\alpha_5^{(s)} \\ & & \beta_5^{(x)} &= \alpha_1^x. \end{aligned}$$

Generally, local ( $k = l$ ) and non local ( $k \neq l$ ) atomic displacements within the range of the spin probe at site  $l$  contribute to modifications of the local parameters  $B_n^m$  of the local spin-crystal field interaction. One can always write :

$$\begin{aligned} \Delta B_n^m &= (\Delta B_n^m)_1 + (\Delta B_n^m)_2 \\ (\Delta B_n^m)_1 &= A(T - T_1)^\beta \mathcal{B}_n^m(1) \cos(\varphi_l + \phi_n^m(1)) \\ (\Delta B_n^m)_2 &= A^2 |T - T_1|^{2\beta} \mathcal{B}_n^m(2) \cos 2(\varphi_l + \phi_n^m(2)). \end{aligned}$$

The  $\mathcal{B}_n^m(1)$  and  $\mathcal{B}_n^m(2)$  respectively involve first and second derivatives of the parameters with respect to the atomic displacements, and represent linear and quadratic terms with respect to the critical amplitude of the modulation wave. We have limited the power expansion to second order. It turns out that the non local contributions and the coupling in quadrature of two modes induce phase parameters  $\phi_n^m(1)$ ,  $\phi_n^m(2)$  which depend on the details of the spin-lattice interaction.

The associated local line shifts with respect to the line position  $H_0$  in the normal phase, corresponding to a transition  $|1\rangle \rightarrow |2\rangle$ , can be expressed analytically within the frame work of perturbation theory. One obtains :

**2.1 LINEAR TERMS.** — These involve diagonal matrix elements :  $O_n^m$ , and linear parameter modifications :  $(\Delta B_n^m)_1$  :

$$\sum_{n,m} (\langle 1 | O_n^m | 1 \rangle - \langle 2 | O_n^m | 2 \rangle) (\Delta B_n^m)_1.$$

Collecting all contributions one may write :

$$\Delta H_1(\varphi_l) = A(T_1 - T)^\beta h_1 \cos(\varphi_l + \phi_1).$$

$h_1$  and  $\phi_1$  depend on the magnetic field orientation.  $\phi_1 = 0$  when local effects and a single mode dominate the local line shift.

**2.2 QUADRATIC TERMS.** — These involve two mechanisms : second order perturbations by the  $(\Delta B_n^m)_1 O_n^m$ , associated with non diagonal matrix elements and first order perturbations by the  $(\Delta B_n^m)_2 O_n^m$ , associated with diagonal matrix elements.

It is worthwhile to emphasize an important difference with N.M.R. measurements [7]. A typical separation for Zeeman levels is in the range  $10^7$ - $10^8$  Hz and typical matrix elements associated with  $(\Delta B_n^m)_1$  are of the order of  $10^4$  Hz. It turns out that quadratic line shifts through second order perturbations are three or four orders of magnitude lower than linear shifts. The situation is reversed in E.P.R. The typical separation between E.P.R. spin levels is  $10^{10}$  Hz (X Band) and typical matrix elements associated with  $(\Delta B_n^m)_1$  are in the range  $10^8$ - $10^9$  Hz (Fig. 3). It turns out that quadratic line shifts through second order perturbations may have, in favourable cases, the same order of magnitude as the linear ones.

In the particular case where a single operator  $O_n^m$  is involved in the line shifts, we cannot discriminate between local and non local effects, nor between single and two mode contributions.

Nevertheless one can write in both cases :

$$\Delta H(\varphi_l) = A^2(T_1 - T)^{2\beta} (h_2' + h_2'' \cos 2(\varphi_l + \phi_2))$$

with  $h_2' = h_2''$  and  $\phi_2 = 0$  for local and single mode contributions.

The experimental line shape is the sum of local lines and is given, in the plane wave modulation-regime, by :

$$F(H - H_0) = \int_0^{2\pi} f\left(\frac{H - H_0 + \Delta H(\varphi_l)}{L}\right) d\varphi_l$$

$$\Delta H(\varphi_l) = \Delta H_1(\varphi_l) + \Delta H_2(\varphi_l).$$

$f$  and  $L$  represent in the static approximation a background line shape and line width respectively. Those sites corresponding to  $\frac{d(\Delta H(\varphi_l))}{d\varphi_l} = 0$  give rise to « singularities » superposed on a continuous absorption line.

When linear terms are dominant ( $\Delta H_2 = 0$ ), one obtains two edge-singularities located at

$H_0 \pm h_1(T_1 - T)^\beta$  and associated with  $(\varphi_l + \phi_1) = 0, \Pi$ . One cannot discriminate between  $\phi_1 = 0$  and  $\phi_1 \neq 0$ , i.e. between local and non local, single mode and two-mode contributions.

When both linear and quadratic terms contribute, one obtains two, three or four singularities, depending on the relative strength of the quadratic term. In principle this sequence can be observed by cooling, since  $\Delta H_2/\Delta H_1$  varies critically as  $(T_1 - T)^\beta$ . The clear mark of non local and two-mode contributions (i.e.  $\phi_1 \neq \phi_2$ ) is the appearance of a fourth singularity.

When linear terms are forbidden by symmetry, one obtains two symmetrical edge singularities associated with  $(\varphi_l + \phi_2) = (0, \Pi); (\pm \Pi/2)$  located at  $H_0 + (h'_2 \pm h''_2)(T_1 - T)^{2\beta}$ . The clear mark of non local and two-mode contributions is the deviation from  $H_0$  of both singularities.

Otherwise,  $h'_2 - h''_2 = 0$ , and the singularity associated with  $\varphi_l = \pm \Pi/2$  is nearly stationary at  $H = H_0$ , apart from an irrelevant and uncritical thermal drift.

A further complication arises from the local line width which may depend on the local phase, through phase and amplitude fluctuations associated with the phason and amplitudon modes. For small fluctuations, with a correlation length larger than the range of the probe one may write :

$$\delta\eta_k^i = \delta A[\alpha_k^i \cos(\varphi_l + \phi_k) + \beta_k^i \sin(\varphi_l + \phi_k)] - \delta\varphi_0 A[\alpha_k^i \sin(\varphi_l + \phi_k) - \beta_k^i \cos(\varphi_l + \phi_k)].$$

The fluctuations of the spin Hamiltonian parameters are given by :

$$\delta(\Delta B_n^m)_1 = \frac{\delta A}{A} B_n^m \cos(\varphi_l + \phi_{1n}^m) - \delta\varphi_0 B_n^m \sin(\varphi_l + \phi_{1n}^m).$$

For the sake of simplicity we shall neglect fluctuations of the quadratic terms  $(\Delta B_n^m)_2$ .

At the limit of fast fluctuations the secular contribution [10] to the line width is given by :

$$\Delta L_s \propto J_1^A(0) \cos^2(\varphi_l + \phi_1) + J_1^P(0) \sin^2(\varphi_l + \phi_1)$$

where  $J_1^A$  (respectively  $J_1^P$ ) is the spectral density of amplitudon (respectively phason).

The non secular contributions are closely related to the relaxation time :  $\Delta L_{n.s} \propto T_1^{-1}$ ; for a detailed study see reference [10]. For our purpose, we shall assume that a single operator  $O_n^m$  and phase fluctuations dominate the relaxation mechanisms. One obtains :

$$\{\Delta L_{n.s}\}_n^m \propto L_{n.s}^P \sin^2(\varphi_l + \phi_{1n}^m).$$

$L_{n.s}^P$  involves the square of non diagonal matrix elements  $\langle i | O_n^m | j \rangle$  and spectral densities  $J^P(\omega_{ij})$ , with  $\omega_{ij}$  typically in the 10 GHz range for X band experiments.

It turns out that  $\Delta L_{n.s}$  is phase dependent and vanishes for  $(\varphi_l + \phi_{1n}^m) = 0, \Pi$ . For those sites,  $T_1$  is long, and in favourable cases, one would observe saturation effects on the incommensurate line at the corresponding values of the resonance field.

### 3. Actual case : the Gd<sup>3+</sup> centre in ThBr<sub>4</sub>.

The simple displacement field in ThBr<sub>4</sub> (Fig. 1) permits us to discuss the interaction of the spin probe with the modulation-wave, for a Gd<sup>3+</sup> probe substituted for Th<sup>4+</sup>. We shall assume that the interactions are limited to the Bromine ligands since the superposition model works rather well in this case [11].

In the normal phase, above  $T_c$ , the local symmetry is  $D_{2d}$ . The spin Hamiltonian parameters are  $b_2^0, b_4^0, b_4^4, b_6^0, b_6^4$ , with  $z$  along  $c$  and  $x, y$  along  $a$ . For the high field line  $\Delta M_s = |\frac{5}{2}| \rightarrow |\frac{7}{2}|$  the Zeemann effect is preponderant and we shall consider  $M_s(H)$  as a good quantum number.

In the incommensurate phase, the effects are purely « non local », since Th<sup>4+</sup> is not displaced. However, all the surrounding bromines are displaced in phase for the global rotation and for the global twist. Therefore the spin Hamiltonian is not marked by the trivial phase differences between surrounding atoms but by the fundamental coupling in quadrature of two displacement modes. The single phase to be considered is the « local phase »  $\varphi_l$  at the thorium site.

The parameters  $b_2^0, b_4^0, b_4^4, b_6^0, b_6^4$ , can only exhibit quadratic modifications from symmetry. As seen below, we were unable to detect any significant

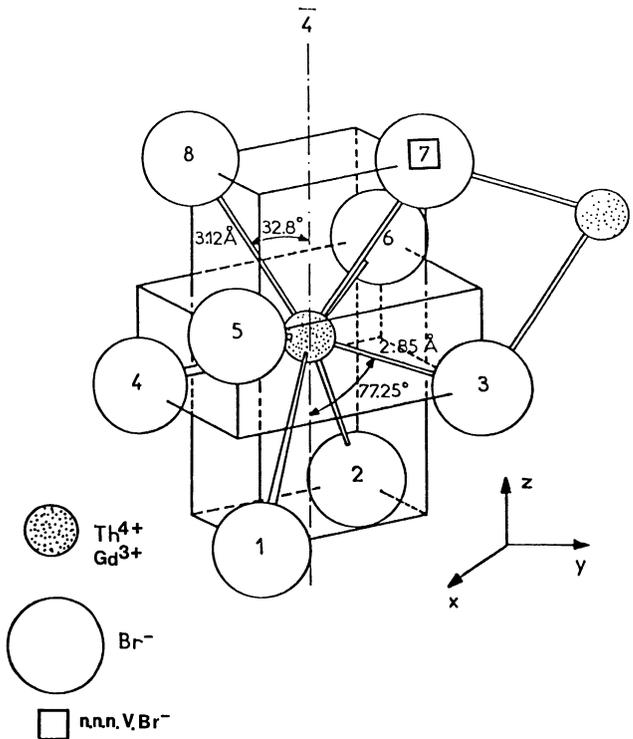


Fig. 1. — The  $D_{2d}$  crystal site of Th<sup>4+</sup> in  $(\beta)$  ThBr<sub>4</sub>. The position of the nnnBr-vacancy is marked by a square.

variation in these parameters arising from the modulation wave. The twist displacement induces a quadrupolar asymmetry  $b_2^2 O_2^2$ , with  $x'$  along (110).  $b_2^2$  is an odd function of the twist amplitude.

For the second order approximation we may consider a linear dependence :

$$\alpha_T \mathcal{B}_2^2 \cos \varphi_1 O_2^2.$$

For  $\mathbf{H} \parallel \mathbf{c}$  the twist can only induce quadratic line-shifts through second order perturbations. For high resonance fields these shifts would be weak since they involve a coupling between levels with a large Zeeman separation ( $\Delta M_H = \pm 2$ ).

For  $\mathbf{H}$  in the (001) plane :  $(\mathbf{H}, \mathbf{a}) = \theta$ , the twist Hamiltonian can be expressed in the magnetic reference frame ( $Z \parallel H$ ,  $x \parallel c$ ) according to :

$$\Delta \mathcal{H}_T = \{ \mathcal{B}_2^2 \alpha_T \cos \varphi_1 \} \left\{ \sin 2\theta \left\{ \frac{O_2^0}{2} - \frac{O_2^2}{2} \right\} + i \frac{\cos 2\theta}{2} \cdot O_2^{-1} \right\}.$$

A similar effect occurs for smaller terms involving  $O_4^2$  and  $O_6^2$ ;

The rotational motion induces a rotation  $\alpha_T$  of the  $xy$  axes. This has no significant effect for  $\mathbf{H} \parallel \mathbf{c}$ . For  $\mathbf{H}$  in the (001) plane, the rotation of the  $x, y$  axes corresponds to modification of the spin Hamiltonian in the magnetic reference frame given by :

$$\Delta \mathcal{H}_R = \{ \alpha_R \sin \varphi_1 \mathcal{B}_4^4 \} \left\{ \sin 4\theta \left\{ \frac{1}{4} O_4^0 - \frac{1}{2} O_4^2 + \frac{1}{8} O_4^4 + i \cos 4\theta \left\{ \frac{1}{2} O_4^{-1} - O_4^{-3} \right\} \right\} \right\}$$

to first order with respect to the rotation amplitude  $\alpha_R$ .

Therefore, one may expect the following scheme for a  $\text{Gd}^{3+}$  probe :

**3.1  $\mathbf{H} \parallel (001)$  AND  $\mathbf{H} \parallel (100)$ .** — Quadratic terms only are allowed by symmetry. For  $\mathbf{H} \parallel (100)$  ( $\theta = 0$ ) they arise both from the twist and from the rotation, through second order perturbations by the terms  $O_2^{-1}$  (twist),  $O_4^{-1}$  and  $O_4^{-3}$  (rotation).

**3.2  $\mathbf{H} \parallel (110)$ .** — ( $\theta = 45^\circ$ ) : a linear shift arises from the twist which has its maximum effect ( $\sin 2\theta = 1$ ). Quadratic shifts arise both from the twist ( $O_2^2$ ) and from the rotation  $|O_4^{-1}, O_4^{-3}|$ .

**3.3  $\theta \simeq 22.5^\circ$ .** — Linear shifts arise both from the twist and from the rotation which has its maximum effect ( $\sin 4\theta = 1$ ). Quadratic shifts arise from the two displacements. All terms of the spin Hamiltonian are involved.

Unhappily we were unable at the present time to get tractable signals from the  $\text{D}_2^d \text{Gd}^{3+}$  centre, except for  $\mathbf{H} \parallel \mathbf{c}$ . Indeed, the more intense lines in the doped crystals arise from  $\text{Gd}^{3+}$  compensated by a  $\text{Br}^-$

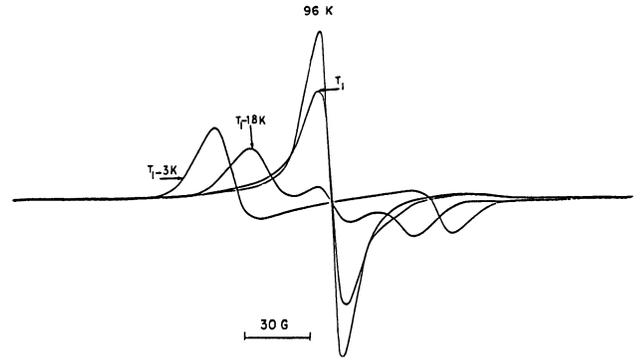


Fig. 2. — Experimental spectra near  $T_1$ . One notices at  $T_1 - 1.8$  K a coexistence of « in commensurate » singularities with a « normal like » line.

vacancy in the second ligand shell (Fig. 1). The charge compensation breaks the local symmetry and induces supplementary terms in the spin Hamiltonian. Nevertheless, by assuming a limited perturbation from the second shell vacancy, the discussion about the  $\text{D}_{2d}$  centre will be used as a qualitative guide to analyse the experimental results on the charge-compensated defect.

#### 4. Experimental results.

**4.1 TEMPERATURE RANGE  $|T_1, T_1 - 3 \text{ K}|$ .** — In this temperature range the theoretical model sketched in section 1 does not apply. Indeed, for most orientations of  $\mathbf{H}$  in the (001) plane, we observe the coexistence of edge singularities and of a « normal-like » line (Fig. 2) [5, 6]. The intensity of this line rapidly decreases and below  $(T_1 - 3)$  K one obtains a fully incommensurate-line.

The « normal-like » line arises from large phase fluctuations which average the local line shift. They may occur in regions of the crystal sufficiently free from pinning defects. By cooling, the interaction of the modulation wave with defects critically increases with the amplitude. As the number of effective pinning defects increases very large phase fluctuations can no longer occur [5] at a few degrees below  $T_1$ . Then the incommensurate phase can be described in terms of a pinned modulation wave, with some gap at the phason mode and a small fluctuation amplitude, to which the theoretical models apply. A temperature gradient or a distribution of the critical temperature in the sample could account for the coexistence of commensurate and incommensurate domains. This cannot occur presently. Indeed the edge singularities would be smoothed by the temperature distribution. On the other hand, a variation of  $T$  or of  $T_1$  of 3 K in the bulk is excluded for the very small sample which was used.

**4.2  $T < T_1 - 3 \text{ K}$ .** —  $\mathbf{H} \parallel \mathbf{c}$  : no significant effect of the transition is apparent on the  $\text{Gd}^{3+}$  E.P.R. lines, both for the  $\text{D}_2^d$  site and for the charge compensated centre.

According to the discussion about the  $D_{2d}$  centre, it turns out that the quadratic variations ( $\Delta B_n^m$ ) associated with the diagonal operators  $O_2^0$  and  $O_4^0$  in the magnetic reference frame are very weak, consistent with atomic displacements of small amplitude in the (001) plane. Anyway the rotational motion around  $c$  cannot influence greatly the spectrum for  $\mathbf{H} \parallel c$ . The linear variations of the parameters associated with the twist motions concern  $(O_2^2)'$  and  $(O_4^2)'$  which are second order effects. Their matrix elements for the  $\Delta M_s = \frac{5}{2} \rightarrow \frac{7}{2}$  transition are such that they tend to compensate.

For  $\mathbf{H} \parallel c$  the compensated defects have exactly the same behaviour as the  $D_{2d}$  centre.

$\mathbf{H} \parallel (110)$  : For this orientation we obtain the best sensitivity to the phase change, i.e. the largest splitting of the singularities which deviate symmetrically from the line position  $H_0$  in the normal phase. We conclude that for this orientation, linear terms are dominant. The theoretical model permits us to obtain an accurate computer reconstruction of the line shape (Fig. 3), and the critical variation of the distance between singularities ( $\varphi = 0, \Pi$ ) :  $\Delta H \propto (T_1 - T)^\beta$  is well verified :  $\beta = 0.35 \pm 0.2$ .

The reconstruction is significantly improved (Fig. 3) by introducing a phase dependent line width according to :

$$L(\varphi) = L_0 + L_A \cos^2 \varphi + L_P \sin^2 \varphi .$$

The fit indicates a rapid decrease in  $L_A$  by cooling while  $L_0$  and  $L_P$  are stationary. This model may correspond to a line width dominated by secular mechanisms, and the decrease in  $L_A$  may be associated with the increasing gap of the amplitudon mode.

We were unable to observe the behaviour of the weak  $D_{2d}$  lines, but we suppose the behaviour to be similar. For this orientation, the twist motion induces a linear shift and has its maximum effect which obscures all other contributions. Therefore, we conclude that the observed spectrum corresponds to the simplest case : *local and single mode* effects.

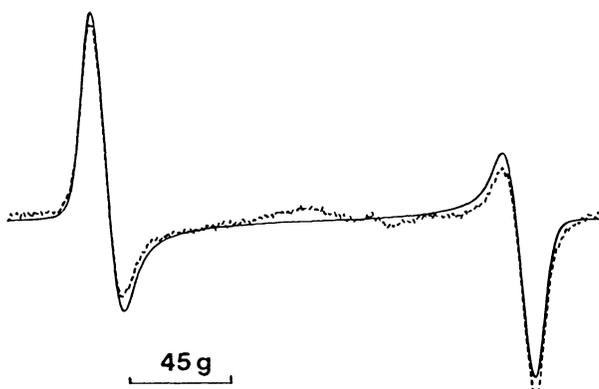


Fig. 3. — Experimental spectrum (dashed line) and theoretical spectrum (full line) with  $\mathbf{H} \parallel |110|$ , with  $T = T_1 - 10$  K. The splitting between singularities is about 180 G.

$\theta = 22.5^\circ$  : The sequence of spectra (Fig. 4) at decreasing temperature with 2, 3, 4 singularities indicates that for this orientation we obtain the more complicated situation, where linear and quadratic contributions are involved with different phase parameters  $\phi_1$  and  $\phi_2$ . We obtained an excellent computer reconstruction (Fig. 4) by using the theoretical model and by introducing a phase dependent line width, not detailed here [11].

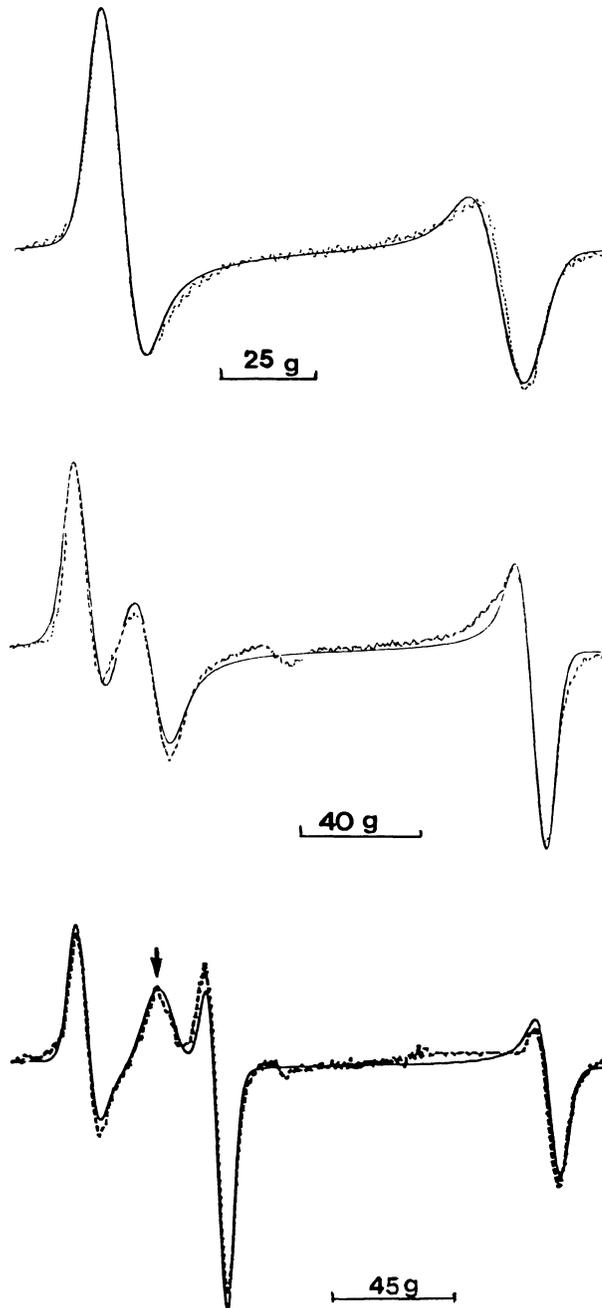


Fig. 4. — Experimental spectrum (dashed line) and theoretical spectrum (full line) with  $\mathbf{H} \perp (001)$  and  $(\mathbf{H}, \mathbf{a}) = 22.5^\circ$ . a) at  $T_1 - T = 7$  K; b) at  $T_1 - T = 23$  K; c) at  $T_1 - T = 50$  K. The fourth singularity  $\downarrow$  is the signature of non local effects.

The critical dependence of the linear term is accurately verified, but the agreement is not so good for the quadratic term. Nevertheless the appearance of the fourth singularity at low temperature proves that  $\Delta H_2/\Delta H_1$  increases by cooling. Moreover, the excellent fit obtained at low temperature needs a small shift of the phase parameter  $\phi_2$ . This does not alter the validity of the theoretical model essentially. Indeed, the irrelevant thermal shift of the background spin Hamiltonian arising from lattice contraction have not been considered.

If one considers the  $D_{2d}$  centre, not observed for this orientation, both the twist and the rotation lead to linear and quadratic line shifts, through different operators. The effect of the vacancy can in no way simplify the situation. Consistently, we have observed a line shape corresponding to the more general case : « non local » and two modes contributions.

$\mathbf{H} \parallel (100)$  : Actually, due to difficulties in handling the hygroscopic crystal, we were unable to take measurements with the certainty that  $\mathbf{H}$  was perfectly aligned along (100). Moreover the vacancy breaks the host point symmetry at the  $Gd^{3+}$  site. For these reasons, we obtained line shapes (Fig. 5) corresponding to the combination of linear and quadratic local line shifts. Nevertheless, the linear line shift, which would vanish for exact orientation and for  $D_{2d}$  symmetry, was lower than for any orientation.

The line represented in figure 5 was accurately reconstructed by setting :

$$\Delta H(\varphi) = h_1 \cos \varphi + h_2 \cos^2(\varphi + \phi_2)$$

with

$$\begin{aligned} h_1 &= -16.41 \\ h_2 &= 7.5 \\ \phi_2 &= 1.44. \end{aligned}$$

The low field singularity corresponds to  $\varphi_0 = 0$  rad, the high field one to  $\varphi'_0 = 3.5$  rad. The larger intensity of the last one is due to the flat dependence of  $\Delta H$  on  $\varphi$  near  $\varphi'_0$ .

We remark that the phase parameter  $\phi_2$  is not far from the particular value  $\pi/2$ , and we may suggest the following scheme to account for this value.

Let us assume that the linear modifications of the Hamiltonian are given by :

$$\Delta \mathcal{H} = \mathcal{K}_1 \cos \varphi + \mathcal{K}_2 \sin \varphi$$

with  $\mathcal{K}_1$  diagonal and  $\mathcal{K}_2$  off diagonal on the basis of  $\mathcal{K}_0$ .  $\mathcal{K}_1$  gives rise to the linear term through first order perturbations and cannot contribute to the longitudinal relaxation.  $\mathcal{K}_2$  gives rise to the quadratic term through second order perturbations, accounts for  $\phi_2 \sim \frac{\pi}{2}$ , and can contribute to the relaxation through fluctuations.

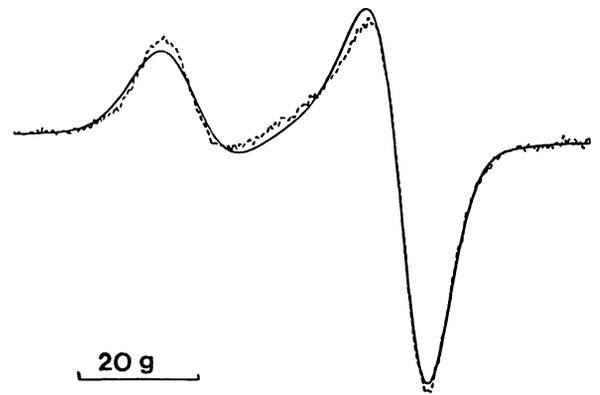


Fig. 5. — Experimental spectrum at low hyperfrequency power (dashed line) and theoretical spectrum (full line) with  $\mathbf{H} \parallel (100)$ .

On the other hand the line clearly exhibits inhomogeneous saturation. The low field singularity does not saturate at all within the available hyperfrequency power, while easy saturation is obtained for values of  $\Delta H(\varphi)$  corresponding to  $\varphi \sim \frac{\pi}{2}$  and  $\frac{3\pi}{2}$  i.e. to the low field tail of the high field singularity (Fig. 6). The same holds at low temperature. Therefore we can attribute this effect to persistent phase fluctuations associated with the low gap phason mode.

The relaxation time is determined by the square of the off diagonal matrix elements of  $\frac{\delta}{\delta \varphi} (\mathcal{K}_2 \sin \varphi)$

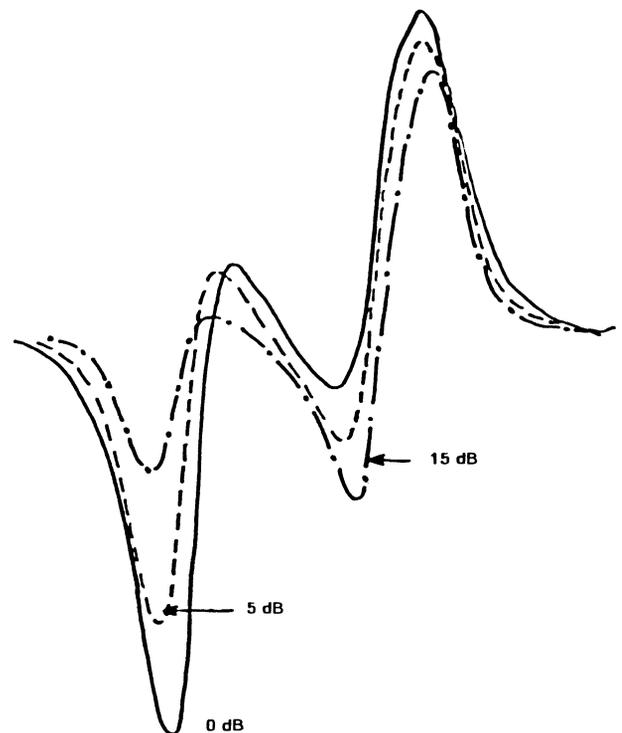


Fig. 6. — Saturation effects for  $\mathbf{H} \parallel (100)$ .

and by the associated spectral densities of phase fluctuations for the frequency  $\omega$  in the 10 GHz range. The relaxation time is long for  $\varphi = \frac{\pi}{2}$  and  $\frac{3\pi}{2}$ , in satisfactory agreement with saturation effects. Similar effects have been observed in N.M.R. in other incommensurate systems [7]. The interest of E.P.R. is to give information on spectral densities in a frequency range intermediate between the range of N.M.R. and the range of scattering experiments.

Of course, we have no means of connecting the variable phase  $\varphi$  to the local phase  $\varphi_l$  of the modulation wave without detailed knowledge of the interaction of the spin probe with the modulation wave. It is worth remarking that  $\mathcal{H}_1$  and  $\mathcal{H}_2$  are in quadrature just as the two displacement modes.

## 5. Conclusion.

By varying the orientation of the magnetic field we have obtained very different line shapes which are in agreement with the theoretical models. We conclude they are valid, as is the plane wave regime approximation in  $\text{ThBr}_4$ . We also may conclude that

the charge-compensated centre used as a probe does not pin the phase of the modulation.

All results are consistent with two displacement-modes in quadrature. In particular, for one orientation of the magnetic field (110) we were able to separate a single mode.

Apart from a short temperature range near  $T_c$  where large phase fluctuations tend to average the incommensurate line, the plane wave modulation is pinned. The contributions of amplitude and phase fluctuations to the line shape and to relaxation give indirect evidence of the amplitudon and phason modes.

A detailed investigation of the spin-lattice interaction for the perturbed vacancy centre is in progress to permit a more quantitative analysis of the present results.

Indeed the symmetry and the nature of operators involved in the modification of the spin Hamiltonian by the modulation wave is a very important point. For instance, the first observation of a sequence with two, three, and four singularities (Figs. 4a, 4b, 4c), predicted by theory, is due to the contribution in that case, of several terms, both for the linear and quadratic line shifts.

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