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S. Hubert, J. Emery, J.J. Rousseau, J.C. Fayet. E.P.R. investigation of the incommensurate phase of $\text{ThBr}_4: \text{Gd}^{3+}$, through fourth order spin-crystal field interaction. Journal de Physique Lettres, 1982, 43 (22), pp.815-821. 10.1051/jphyslet:019820043022081500 . jpa-00232130

HAL Id: jpa-00232130

<https://hal.science/jpa-00232130>

Submitted on 1 Jan 1982

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Classification

Physics Abstracts

61.16N — 64.70 — 73.60F

E.P.R. investigation of the incommensurate phase of $\text{ThBr}_4 : \text{Gd}^{3+}$, through fourth order spin-crystal field interaction

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(Reçu le 23 juin 1982, révisé le 23 septembre, accepté le 1^{er} octobre 1982)

Résumé. — La forme de la raie de R.P.E. $\Delta M_S : |\frac{5}{2}| \rightarrow |\frac{7}{2}|$ pour le centre Gd^{3+} -n.n.n. $V_{(\text{Br}^-)}$ peut être interprétée de façon cohérente en supposant une rotation modulée autour de *c* des liaisons Th-Br comme composante essentielle du champ de déplacement dans la phase incommensurable. La sensibilité de la sonde Gd^{3+} provient de la grande valeur du paramètre du quatrième ordre b_4^4 de l'Hamiltonien de spin, liée à la configuration aplatie du tétraèdre de Br^- plus proches voisins. Nous donnons des résultats préliminaires et les grandes lignes de développements possibles de la présente étude.

Abstract. — The shape of the E.P.R. line $\Delta M_S : |\frac{5}{2}| \rightarrow |\frac{7}{2}|$ for the Gd^{3+} -n.n.n. $V_{(\text{Br}^-)}$ centre, can be consistently interpreted by assuming a modulated rotation around the *c* crystal axis of the Th-Br bonds as an essential component of the displacement field in the incommensurate phase. The sensitivity of the local Gd^{3+} probe arises from the high value of the fourth order parameter b_4^4 linked to the flat configuration of the n.n. Br^- tetrahedron. We report preliminary results and we outline possible developments of the present investigation.

1. Introduction. — Recently, Blinc *et al.* [1] have developed computer reconstructions of the particular shape of N.M.R., N.Q.R., E.P.R. lines in incommensurate phases, a simple model. We shall use their results for one dimensionally modulated systems.

Briefly, these authors assume that the local line shifts, ΔH or $\Delta\omega$, mirror the amplitude *u* of the local atomic displacements through a polynomial law : $\Delta(H \text{ or } \omega) = au + bu^2 + \dots$. This law depends on the particular conditions of the spin-crystal field interaction, the simplest case being a linear law. The different modulation regimes of *u* (i.e. plane wave, broad or narrow soliton regimes) are connected to different integration constants of a Sine Gordon equation. The experimental N.M.R. line shapes of ^{87}Rb in Rb_2ZnCl_4 obey this model [1]. For E.P.R. lines in the same crystal doped with Mn^{2+} one may refer to [2, 3].

(+) E.R.A. n° 682.

Recently a phase transition was observed by Raman scattering spectroscopy [4] and nuclear quadrupolar resonance [5] at 94 K for ThBr_4 and 70 K for ThCl_4 . Single crystal neutron diffraction experiments revealed that the low-temperature structure is incommensurate with a modulation along the fourfold axis [6, 7] without any locking until 10 K. At room temperature ThBr_4 has a D_{4h}^{19} tetragonal structure isostructural with ThCl_4 and UCl_4 [8]. In this structure, the Th^{4+} ions are at a site of D_{2d} symmetry and a dopant ion substitutes into this site.

In this paper we have used Gd^{3+} substituted for Th^{4+} as an E.P.R. probe of the lattice properties. We shall emphasize that we have considered the short range fourth order spin-crystal field interaction as previously done for $\text{RbCdF}_3 : \text{Gd}^{3+}$ below T_c [9]. Therefore, the condition of validity of the model developed by Blinc, i.e. the short range character of the spin-probe, is fulfilled; indeed one may question this point when one uses, as usual, the quadrupolar spin-crystal field interaction.

2. Experimental. — The single crystals doped with 0.05 % of Gd^{3+} [10], grown by one of us (S. H.), were cooled by a regulated helium gas flow, with a temperature stability ± 0.05 K in the course of the experiment. We have neglected any temperature difference between the sensor and the sample. Nevertheless we assumed that this difference remained constant within a temperature range of few K around T_c .

3. Tetragonal phase. — In the doped sample, Gd^{3+} substitutes for Th^{4+} and charge compensation occurs through Br^- vacancies. In freshly grown crystals, three types of paramagnetic centres were observed : a D_{2d} centre and two orthorhombic ones [11].

3.1 D_{2d} CENTRE. — The Gd^{3+} ion with distant Br^- vacancies gives rise to a D_{2d} centre (Fig. 1). The corresponding spin Hamiltonian parameters have been previously determined : $b_0^0 = 460$; $b_4^0 = 10.0$; $b_4^4 = 123.0$; $b_6^0 = 1$; $b_6^4 = 3$, in 10^{-4} cm^{-1} [11] (note the large value of b_4^4). Using the superposition model [12] as a first approximation for the fourth order parameters we find :

$$b_4^0 = \frac{1}{2} \bar{b}_4 (35 \cos^4 \alpha - 30 \cos^2 \alpha + 3); \quad b_4^4 = \frac{35}{2} \bar{b}_4 \sin^4 \alpha$$

$\bar{b}_4$ is a parameter which characterizes the Gd^{3+} -n.n. Br^- bonds (n.n. for nearest neighbour),

Fig. 1. — The D_{2d} crystal site of Th^{4+} in ThBr_4 . The spin Hamiltonian axis (x, y, z) of $\text{Gd}^{3+}(D_{2d})$ are along the crystal axes.

and $\alpha = 77^\circ 30'$ is the angle of the bonds with the spin Hamiltonian axis, i.e. with the crystal axis $\mathbf{c}$. The flat configuration of the n.n. Br^- tetrahedron ($\alpha \gg 55^\circ$) accounts for the large value of b_4^4 and the calculated value of $b_4^4/b_4^0 \simeq 20$ has a correct order of magnitude.

The consequence is a marked anisotropy of the high field line $|\frac{5}{2}| \rightarrow |\frac{7}{2}|$ when H is rotated in the (001) plane. Indeed this anisotropy is given to first order, by $H(A, \theta) = H_0 + Ab_4^4 \cos 4\theta$ with $\theta = (\mathbf{a}, \mathbf{H})$ and $\mathbf{x} = \mathbf{a}$. The contribution of b_6^4 is neglected and A is a constant.

Imagine a situation in which the local surroundings of the Gd^{3+} ion rotates by ε around $\mathbf{c}$. The essential effect would be a tilt by ε of the $\mathbf{x}$ spin Hamiltonian axis and a shift of the line by :

$$\Delta H(\varepsilon) \sim b_4^4 \{ \cos [4(\theta + \varepsilon)] - \cos [4\theta] \}.$$

For $\theta = 22^\circ 30'$ the shift is maximum and linear in ε up to $O(\varepsilon^3)$. For $\theta = 0, \pi/4$, the shift is minimum and quadratic in ε . For a physical illustration of this situation one may refer to the E.P.R. spectra of $\text{RbCdF}_3 : \text{Gd}^{3+} - \text{V}_{(\text{Cd}^{2+})}$ below T_c [9].

3.2 THE Gd^{3+} -n.n.n. $\text{V}_{(\text{Br}^-)}$ CENTRE. — The most intense lines in the sample under investigation were attributed to Gd^{3+} ions associated to n.n.n. Br^- vacancies (n.n.n. for next n.n.). Indeed, the main features of these lines are not very different from the lines of the D_{2d} centre. This observation excludes charge compensation at a n.n. Br^- site which would produce important modifications of the spin Hamiltonian parameters and axes. Nevertheless the symmetry of the centre is lowered from D_{2d} to C_s , and a D_{2d} site gives rise to four centres, depending on the location of the n.n.n. vacancy at sites 1, 2, 3 or 4 (Fig. 1).

When H rotates in the (001) plane, these centres give rise to a doublet with a component corresponding to $\text{V}_{(\text{Br}^-)}$ at sites 1 and 2, and the other one corresponding to $\text{V}_{(\text{Br}^-)}$ at sites 3 and 4. The two components merge into a single line for $\mathbf{H} \parallel [110]$. The essential point is that the anisotropy of the lines $|\frac{5}{2}| \rightarrow |\frac{7}{2}|$ nearly vary as $\cos 4\theta$ which demonstrates a small tilt of the spin Hamiltonian axes away from the crystal axes, and a small contribution of the orthorhombic terms. In other words, the fourth order terms have a dominant contribution and nearly act in the same way as for the D_{2d} centre. Moreover, for $\theta = (\mathbf{a}, \mathbf{H}) = 22^\circ 30'$ the lines of the doublet are separated by about 300 gauss near T_1 in the tetragonal phase. This large separation prevents line overlap when the lines are shifted and when the line shape is modified (see Fig. 2b) in the incommensurate phase below T_1 .

In the following we shall mainly use the Gd^{3+} -n.n.n. $\text{V}_{(\text{Br}^-)}$ centre to investigate the incom-

Fig. 2a. — $\theta = 22^\circ 30'$. Line shape above and near $T_1 \simeq 94$ K. On cooling in the range $T_1 + \varepsilon < 96$ K the line becomes markedly Lorentzian.

Fig. 2b. — « Edge singularities » for $\theta = 22^\circ 30'$.

$$\begin{aligned} T(1) &= 79.4 \text{ K}; & T(2) &= 84 \text{ K}; & T(3) &= 85 \text{ K}; & T(4) &= 86 \text{ K}; \\ T(5) &= 87 \text{ K}; & T(6) &= 90 \text{ K}; & T(7) &= 91.8 \text{ K}; & T(8) &= 93 \text{ K}. \end{aligned}$$

The arrows denote « Shoulders » which appear on cooling.

Fig. 2c. — Structure of the low field « edge singularity » at low temperature :

$$T(1) = 50 \text{ K}; \quad T(2) = 55 \text{ K}.$$

The lines of the structure are nearly symmetrical i.e. « commensurate-like ».

mensurate phase : indeed the D_{2d} and the Gd^{3+} -n.n. $V_{(Br^-)}$ lines in the (001) plane exhibit too small an intensity to be easily tractable.

4. Incommensurate phase. — For $H \parallel c$, the lines of both centres, D_{2d} and Gd^{3+} -n.n. $V_{(Br^-)}$, exhibit no significant modification by cooling below T_1 . A displacement field mainly characterized by a rotation around c of the local surroundings, of the Gd^{3+} probe and particularly of the n.n.n. Br^- tetrahedron, can account for this result.

For H in the (001) plane, an important change of the lines $|\frac{5}{2}| \rightarrow |\frac{7}{2}|$ of the Gd^{3+} -n.n. $V_{(Br^-)}$ centre (see Fig. 2 for $\theta = 22^\circ 30'$ and Fig. 3 for $\theta = 0^\circ$) is observed when one undergoes the phase transition.

4.1 $\theta = (\mathbf{a}, \mathbf{H}) = 22^\circ 30'$ (Figs. 2). — 4.1.1 *Pretransitional behaviour* (Fig. 2a). — When one approaches T_1 from above, the line exhibits a marked broadening. The line shape, which is nearly Gaussian at room temperature, probably through the unresolved s.h.f. interaction with the Br nuclei becomes markedly Lorentzian. Rotational fluctuations around $\mathbf{c}$, with increasing amplitude near T_1 , can account for the broadening, and a fast motion regime can account for the Lorentzian component of the line shape.

In a temperature range of a few 0.1 K around 94 K, the spectrum is characterized by two « edge singularities » accompanied by a central line corresponding to the high-temperature line which vanishes on cooling (Fig. 2a). A distribution of T_1 in the bulk of the sample can trivially account for this observation. Nevertheless, depending on the spectral density $J(\omega, T)$ of the rotational fluctuations, slow frequencies can give rise to a nearly static spectrum with two « edge singularities », while fast frequencies can give rise to a motional narrowing characterized by a central line. The intrinsic or extrinsic character of this observation is a point worth clarifying.

4.1.2 *Incommensurate phase near T_1* $T_1 - 7 < T < T_1 - \varepsilon$. — The high-temperature line is modified into two sharp « edge singularities » separated by a continuous absorption background. Assume a local rotation by ε of the fourth order around the x axis. From the discussion above, the line is displaced by $\Delta H_{(e)} \sim b_4^4 \varepsilon$. This linear dependence accounts for the line shape, in the plane wave modulation regime $\varepsilon(z) = \varepsilon_A \cos(kz + \varphi_0)$. Moreover, the highest sensitivity of the spectra to the phase change consistently occurs for $\theta = 22^\circ 5$. Small quadratic contributions to the displacement of the line arising from the actual orthorhombic symmetry of the centre can

Fig. 3a. — Line shape for $\theta = 0^\circ$ near $T_1 = 94$ K.

$$T(1) = 95 \text{ K}; \quad T(2) = 94.7 \text{ K}; \quad T(3) = 93.9 \text{ K}; \quad T(4) = 93.5 \text{ K}.$$

Fig. 3b. — Line shape for $\theta = 0^\circ$ in the incommensurate phase. Note the three singularities, and a much lower splitting as for $\theta = 22^\circ 30'$.

$$T(1) = 91.2 \text{ K}; \quad T(2) = 90.3 \text{ K}; \quad T(3) = 88.4 \text{ K}; \quad T(4) = 85.8 \text{ K}.$$

account for the asymmetry of the « edge singularities » (see Fig. 4 in Ref. [1]). Nevertheless we cannot exclude an eventual contribution of broad solitons (see Fig. 7 in Ref. [1]).

The distance between the « edge singularities » permits a study of the temperature dependence of the amplitude ε_A . An exponent law $\varepsilon_A \sim (T - T_1)^\beta$ (Fig. 4) with $\beta = 0.34 \pm 0.02$ holds from T_1 down to $T_1 - 7$. Connected to the high sensitivity of the probe, the question which arises is its ultimate accuracy (through improved temperature regulation) to discriminate between the (X - Y) and Heisenberg values of the critical exponent.

Fig. 4. — Plot of $\varepsilon_A^{1/\beta}$ versus T . ε_A has been monitored by the distance between the maxima of the absorption spectra, i.e. the zero of the derivative which is actually recorded. The temperature scale is our own temperature scale (see text). The curves for $\beta = 0.32$ and $\beta = 0.36$ deviate significantly from a straight line.

The absolute value of ε_A can be directly measured. Indeed, by rotating the crystal by $\pm \varepsilon_A$ around $\mathbf{c}$, the « edge singularities » can be observed, one after another, for the same resonant field. We have found $\varepsilon_{A(T_1 - T = 7)} = 2^\circ 10'$. From the superposition model this value represents the amplitude of the mean rotation angle of the Th-Br bonds.

4.1.3 *Low-temperature phase* $T < T_1 - 7$ (Fig. 2c). — Below $T = T_1 - 7$, the distance between the absorption maxima deviates from an exponent law and simultaneously a shoulder like structure appears on the low-field « edge singularity » (Fig. 2b). By further cooling (Fig. 2c), this structure develops into « commensurate-like » lines, which would correspond to discrete values of the phase of the modulation. Nevertheless the observed spectra cannot be assigned to a narrow soliton regime [1]. A possibility is a pinning of the phase at particular values by the paramagnetic defect which is used as a probe.

4.2 $\theta = (\mathbf{a}, \mathbf{H}) = 0$ (FIGS. 3). — According to the analysis above, the line shift should depend on the square of the amplitude of the local displacement field ε through the fourth order spin-crystal field interaction, and the line splitting should be much weaker, as for $\theta = 22^\circ 30'$. Nevertheless, a linear term in ε , can arise from small orthorhombic terms and from the small tilt of the spin Hamiltonian axes. As shown by Blinc *et al.*, the line shape should be characterized by three

singularities (see Fig. 4 in [1]). This is well verified in figure 3, which is merely shown to illustrate the basic correctness of our straightforward analysis of the E.P.R. spectra.

A more detailed report of this E.P.R. investigation will be given elsewhere.

5. Discussion. — From recent neutron scattering results [7], the Br^- displacements below T_1 can be described as the superposition of a rotational component and a twist component. Noting $\varepsilon_R(\varepsilon_T)$ as the amplitude of the rotation (the twist), one gets :

$$\varepsilon_R = \eta \cos \alpha \cos \phi_l \quad \text{and} \quad \varepsilon_T = \eta \sin \alpha \sin \phi_l.$$

η represents the amplitude of the modulation which is temperature dependent, and ϕ_l is the phase of the modulation wave at the crystal site Th (l). From reference [7], we can evaluate the value of α as being about 25° .

A first order expansion of the local line shift is given by :

$$\Delta H_l = R_\theta \varepsilon_R + T_\theta \varepsilon_T + 0(\varepsilon_R^2, \varepsilon_T^2, \varepsilon_R \varepsilon_T).$$

The parameters R_θ, T_θ depend on the orientation (θ) of the magnetic field in the [001] plane and characterize the individual contribution of the rotation (twist) to the line shift.

Let us assume $R_\theta \gg T_\theta$, i.e. a line shift much more sensitive to the rotation than to the twist. Then we obtain consistency between neutron measurements and E.P.R. results. This assumption is well supported by the high value of b_4^4 which is amplified by the factor of 4 which appears in the angular dependence of $R_\theta \propto d \cos 4\theta / d\theta = -4 \sin 4\theta$. Moreover the amplitude of ε_R is larger by a factor 2 than the amplitude of $\varepsilon_T (\cos \alpha / \sin \alpha \simeq 2)$. Note that our measurement of the amplitude $\varepsilon_R = 3.5 \times 10^{-2}$ radian is in agreement with the value of η measured by neutron scattering (a few percent in units of a). Note also that, neglecting any phase pinning effects, the « edge singularities » at $\theta = 22^\circ 30'$ would correspond to a nearly pure rotation of the ThBr_4 groups i.e. $\phi_l \simeq 0, \pi$.

Of course a more detailed investigation would be necessary to analyse the symmetry lowering effects which arise through the twist of the Br^- anions and through the n.n.n. vacancy and the structure of the « edge singularities » which develop at low temperature.

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