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Critical slowing-down and central peak phenomena near T_1 , in $\text{Rb}_2\text{ZnCl}_4 : \text{Mn}^{2+}$ through E.P.R. measurements

A. Kaziba, M. Pezeril, J. Emery and J. C. Fayet

Laboratoire de Spectroscopie du Solide (*), Faculté des Sciences, 72017 Le Mans Cedex, France

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Résumé. — Nous analysons les élargissements de raies de R.P.E. de la sonde Mn^{2+} au voisinage de T_1 , pour deux orientations voisines du champ magnétique, en termes de mécanismes séculaires et non séculaires. Le ralentissement critique semble marqué au-dessous de ($T_1 + 4$ K) par des phénomènes de pic central.

Abstract. — We analyse the broadening of the E.P.R. lines of the Mn^{2+} probe near T_1 , for two slightly different orientations of the magnetic field, in terms of secular and non-secular mechanisms. The critical slowing-down seems to be marked by central peak phenomena below ($T_1 + 4$ K).

Introduction.

Rb_2ZnCl_4 undergoes the following sequence of phase transitions : paraelectric phase (P) $\xrightarrow{T_1 = 305 \text{ K}}$ incommensurate phase (INC) $\xrightarrow{T_{c1} = 192 \text{ K}}$ commensurate phase (C_1) $\xrightarrow{T_{c2} = 76 \text{ K}}$ commensurate phase (C_2). The space group of the (P) phase, $D_{2h}^{16} P_{nma}$ becomes P_{21cn} in the (C_1) phase where the unit cell is tripled along the a axis. In the (P) phase, disorder involving two orientations of the $(\text{ZnCl}_4)^{2-}$ has been invoked to account for the results of X-rays [1] or neutron diffraction [2].

In spite of numerous studies, the mechanisms responsible for the (P) $\rightarrow$ (INC) phase transition are not completely clear. By Raman scattering a soft-mode is apparent only below ($T_1 - 60$ K) [3], and a broad central peak was observed close to T_1 [4]. It seems that the transition is intermediate between a displacive one and an order-disorder one.

For this material, the local measurements by magnetic resonance are very efficient, since the transition can be observed from all the crystal sites : Cl^- by N.Q.R. [5] Rb^+ by N.M.R. [6] and Zn^{2+} by E.P.R. through the substituted Mn^{2+} probe which correctly fits the host [7]. Particularly, central peak phenomena above T_1 , with very low frequency components, were inferred from the measurements of the ^{87}Rb T_1 , T_2 and T_{ρ_1} relaxation times [8]. Below T_1 , the quadrupolar splitting of the N.M.R. line was analysed in terms of modulated rotations around the a and c axes of the $(\text{ZnCl}_4)^{2-}$ tetrahedra and in terms of the translation of atoms along b according to the Σ_2 symmetry of the displacement modes.

In this paper we consider only the critical slowing-down, above T_1 , through an E.P.R. study

(*) U.A. n° 807.

with the Mn^{2+} probe. The frequency scale of the E.P.R. probe is intermediate between the N.M.R. one and the resolving power of scattering techniques.

Fig. 1. — The $M_s = \frac{3}{2} \rightarrow \frac{5}{2}$ E.P.R. spectra and the result of their deconvolution by the high temperature hyperfine structure.

(a) : $\mathbf{H} // \mathbf{a}$ at $T_1 + 0.1$ K ; (b) : $\angle (\mathbf{H}, \mathbf{a}) = 4^\circ 20'$ at $T_1 + 0.2$ K.

Fig. 2. — Temperature dependence of the line broadening for $\mathbf{H} // \mathbf{a}$.

■ : $M_s = \frac{3}{2} \rightarrow \frac{5}{2}$; $\triangle$: $M_s = \frac{1}{2} \rightarrow \frac{3}{2}$; — : theoretical law (see text : Eqs. (2) and (4)).

1. Experimental results.

We have studied the hyperfine sextuplet corresponding to the high magnetic field fine structure transition $M_s = \frac{3}{2} \rightarrow \frac{5}{2}$ for $\mathbf{H} \parallel \mathbf{a}$ and for $\mathbf{H}$ in the ab -plane with $\langle (\mathbf{H}, \mathbf{a}) = 4^\circ 20'$. In both cases, the magnetic field is not far from the main quadrupolar axis. The hyperfine structure, for both orientations, is not affected by « forbidden » hyperfine lines [7] and the hyperfine splittings are identical. Therefore we can safely consider the hyperfine splittings as a common irrelevant background.

The critical line broadening is represented in figures 1, 2 and 3. In figure 1, we remark that the small tilt of $\mathbf{H}$ ($4^\circ 20'$) induces a drastic effect. The broadening of the individual line was obtained by the deconvolution [10] of the experimental sextuplets, near T_p , by the experimental sextuplet obtained at $(T_1 + 20 \text{ K})$ where the individual lines exhibit the least width.

We may distinguish the following regimes :

a) In the temperature range $(T_1 + 20 \text{ K}) \rightarrow (T_1 + 4 \text{ K})$, one observes a monotonic and identical increase of the broadenings for both orientations (Figs. 2 and 3). The line shape is purely Lorentzian.

Fig. 3. — Temperature dependence of the line broadening for $\langle (\mathbf{H}, \mathbf{a}) = 4^\circ 20'$.

■ : Experimental results for $M_s = \frac{3}{2} \rightarrow \frac{5}{2}$; — : theoretical law.

Insert : Sketch of the spectral densities in the following regimes :

1 — Fast fluctuation regime (1) ($I_1(w_0) \simeq I_1(0)$).

2-3 — Slowing-down below $T_1 + 4 \text{ K}$: $I_1(w_0)$ is responsible for the observed line broadening for $\mathbf{H} \parallel \mathbf{a}$ (2) and central components account for the divergence of the line broadening for $\langle (\mathbf{H}, \mathbf{a}) = 4^\circ 20'$ (3).

b) Below $(T_1 + 4 \text{ K})$ the broadening exhibits a saturation for $\mathbf{H} \parallel \mathbf{a}$ (Fig. 2) and oppositely a sharp increase for $\langle \mathbf{H}, \mathbf{a} \rangle = 4^\circ 20'$, particularly below $(T_1 + 3 \text{ K})$ (Fig. 3). Close to T_1 , the line shape has a marked Gaussian character.

c) The centre of the sextuplet is linearly shifted to high magnetic fields by cooling from $(T_1 + 20 \text{ K})$ to $(T_1 + 8 \text{ K})$ (Fig. 4). Between $(T_1 + 8 \text{ K})$ and T_1 its position is stationary.

T_1 was estimated from the appearance of « forbidden » hyperfine lines in the $M_s = -1/2 \rightarrow 1/2$ sextuplet for $\mathbf{H} \parallel \mathbf{b}$ which indicates a symmetry breaking of the point symmetry of the Zn^{2+} site [17], and was refined by observing the sharp increase of these lines at T_1 for $\mathbf{H} \parallel \mathbf{a}$.

Fig. 4. — Temperature dependence of the centre of the $M_s = \frac{3}{2} \rightarrow \frac{5}{2}$ sextuplet.

— Above $T_1 + 8 \text{ K}$: thermal drift due to lattice contraction.

— Below $T_1 + 8 \text{ K}$: the thermal drift is compensated by an increase of the mean square amplitude of fluctuations.

2. Theory.

The influence of the order parameter fluctuations in approaching T_1 from above, can be described by :

$$H(t) = H_0 + \rho(t) H_1 + \rho^2(t) H_2 \quad (1a)$$

$$= \{ H_0 + \langle \rho^2 \rangle H_2 \} + \{ \rho(t) H_1 + (\rho^2(t) - \langle \rho^2 \rangle) H_2 \} \quad (1b)$$

where $\langle \rho(t) \rangle = 0$.

Expression (1a) is nothing but a power expansion limited to second order with respect to the amplitude $\rho(t)$ of the fluctuations of the soft coordinates. H_0 represents a background Hamiltonian corresponding to the high temperature phase including any uncritical spin-lattice interaction and a background line width. H_1 and H_2 represent static crystal field-spin operators which depend on the detail of the eigenvector of the soft-mode, i.e. on the detail of the correlated atomic displacements within the range of the probe, and on the microscopic mechanisms of the spin-lattice interac-

tion. An actual case, corresponding to $\text{Rb}_2\text{ZnCl}_4 : \text{Mn}^{2+}$ is given below. In expression (1b), we have separated a static part and a time dependent part in $H(t)$. The static part indicates that the line position is influenced by $\langle \rho^2 \rangle$. The time dependent part influences the line shape and the line width. For the sake of simplicity we shall neglect the second order term contribution to the line widths, involving $(\rho^2(t) - \langle \rho^2 \rangle)$. This approximation is certainly valid for small amplitudes and is well adapted to Rb_2ZnCl_4 . Indeed, overdamping [11] or order-disorder serve to decrease the contribution of the second order terms to the line broadening.

Let us consider a transition $|1\rangle \rightarrow |2\rangle$ between eigenstates of H_0 . Within the framework of the perturbation theory and in the fast fluctuation regime the line shape is Lorentzian and the line width is the sum of two contributions : a secular one which involves diagonal matrix elements : $H_1(1-1)$ and $H_1(2-2)$ and the spectral density $I_1(0)$, a non-secular term which involves transitions $1 \rightarrow i$, $2 \rightarrow i$, i.e. off diagonal matrix elements of H_1 , and the related spectral densities $I_1(w_{1i})$ and $I_1(w_{2i})$.

A fast fluctuation regime means that the characteristic frequency of fluctuations is much larger than the line width which would result from static fluctuations with the same probability distribution.

In Rb_2ZnCl_4 the soft-mode has the Σ_2 symmetry. It turns out that, for $\mathbf{H} \parallel \mathbf{a}$, diagonal matrix elements of H_1 on the basis of H_0 are forbidden by symmetry. Therefore secular broadenings cannot occur for this orientation, at least at first order. On the contrary they can occur for $\langle (\mathbf{H}, \mathbf{a}) = 40^\circ$.

On the other hand, a current theory for overdamped soft-modes gives [12] :

$$I_1(0) = At^{-\nu} \text{Arctg}(Bt^{-\nu}) \quad (2)$$

where t is the reduced temperature, ν the critical exponent for the correlation length ($\xi = k_0^{-1} t^\nu$), the term $B = \frac{q_L \sqrt{\Delta}}{k_0}$, Δ characterizes the anisotropy of the correlations, and q_L is the radius of the sphere of integration for all contributing modes $\left(q_L \cong \frac{a^*}{2}\right)$, where $a^* = \frac{2\pi}{a}$ and a is the lattice parameter.

In the next section we analyse the experimental results reported in section 1 with the help of the simple theoretical model sketched above.

3. Interpretation.

Since the ac -plane is mirror for the Zn^{2+} sites, the fine structure can be represented by the following spin Hamiltonian :

$$H_0 = g\beta HS + \frac{1}{3}(b_2^0 O_2^0 + b_2^2 O_2^2)$$

with the quadrupolar crystal field axis z in the ac -plane and x along the b axis. We have omitted the isotropic hyperfine interaction, the effects of which can be eliminated by the deconvolution procedure [10] and we have neglected other terms which have no significant contribution.

We found : $g = 2.001$, $b_2^0 = -465$, $b_2^2 = -58$ (10^{-4} cm^{-1}) and $\langle (Z, a) = \pm 7^\circ$. The quadrupolar interaction is nearly axial, with the main axis z nearly along a and nearly along the shortest $\text{Cl}_1\text{-Zn}$ bond [2]. This can be understood as a trace of a hypothetical parent $\text{P}_{63/\text{mma}}$ hexagonal phase (three-fold axis along $\text{Cl}_1\text{-Zn}$) actually observed in the related $\beta\text{-K}_2\text{SO}_4$ compounds.

The rather unusually large line width in the (P) phase is consistent with the disorder evidenced by X-rays [1] and neutron diffraction [2].

For $\mathbf{H} \parallel \mathbf{a}$, or $\mathbf{H}$ not too far from $\mathbf{a}$, we shall consider that the effective ordering coordinate can be reduced to the angle of rotation $\rho_c(t)$ of the quadrupolar crystal field axis z around c .

First of all, this simple model gives a satisfactory and consistent explanation of the results of E.P.R. investigations in the vicinity of T_1 [7]. Second, the model agrees with the symmetry and with the atomic displacements below T_1 : rotation around c of the $(\text{ZnCl}_4)^{2-}$ and translation along b of the Cl_1 atom, i.e. nearly a rotation around c of the $\text{Zn}-\text{Cl}_1$ bond to which the quadrupolar axis seems to stick. Thirdly, rotations around a of the $(\text{ZnCl}_4)^{2-}$ cannot much affect the E.P.R. spectra for $\mathbf{H} \parallel \mathbf{a}$. Therefore, we shall set :

$$H(t) = g\beta HS + R_{\rho_c(t)}(H_0 - g\beta HS) R_{\rho_c(t)}^+ \quad \text{where} \quad R_{\rho_c} = e^{-i\rho_c S_c}. \quad (3)$$

The transformation of spin operators by rotations is conventional and enables us to calculate the line width [11] in the fast motion regime, according to the model in section 2.

We found for $\mathbf{H} \parallel \mathbf{a}$ and $\angle(\mathbf{H}, \mathbf{a}) = 4^\circ 20'$:

$$\begin{aligned} \Delta H_{\parallel} &\simeq I_1(w_0) \quad (0.1 \text{ cm}^{-2}) \\ \Delta H_d &\simeq (I_1(w_0) + 10^{-2} I_1(0)) \quad (0.1 \text{ cm}^{-2}). \end{aligned} \quad (4)$$

We have only retained the orders of magnitude of the secular and non-secular contributions. $w_0 \simeq 10^{10}$ Hz corresponds to X-band measurements and represents the mean splitting between spin levels involved in the non-secular mechanisms. Indeed, the Zeeman effect is predominant for the high magnetic field line considered here. Consistently with symmetry and with first order approximation, the line broadening is purely non-secular for $\mathbf{H} \parallel \mathbf{a}$. Experimentally, for this orientation, we observed a nearly identical broadening (Fig. 2) for $M_s = 1/2 \rightarrow 3/2$ and $M_s = 3/2 \rightarrow 5/2$ and a substantial broadening for $M_s = -1/2 \rightarrow 1/2$. This result excludes large contributions of secular mechanisms which would arise from second order terms. Nevertheless a weak but significant difference is apparent below $(T_1 + 4 \text{ K})$. In this temperature range we cannot exclude a residual contribution of secular mechanisms, arising through second order terms.

For $\angle(\mathbf{H}, \mathbf{a}) = 4^\circ 20'$, the essential difference is the secular term. In spite of the coefficient (10^{-2}) associated to the small tilt ($4^\circ 20'$) this term has a drastic effect below $(T_1 + 3 \text{ K})$ (Fig. 3).

Let us assume that the spectral width of fluctuations is much larger than w_0 . Then : $I_1(w_0) \simeq I_1(0)$ (insert in Fig. 3) and $\Delta H_{\parallel} \simeq \Delta H_d(4^\circ 20') \simeq I_1(0) (0.1 \text{ cm}^{-2})$ from (4).

In figures 2 and 3, we have represented the law $I_1(0) = At^{-\nu}$ which is valid for long correlation lengths such that the term $\text{Arctg}(Bt^{-\nu})$ does not differ significantly from $\pi/2$. With respect to this law, one may distinguish the following regimes :

— Between $(T_1 + 4 \text{ K})$ and $(T_1 + 12 \text{ K})$: the experimental line widths for $\mathbf{H} \parallel \mathbf{a}$ and $\angle(\mathbf{H}, \mathbf{a}) = 4^\circ 20'$, verify the law.

— Above $(T_1 + 12 \text{ K})$: the experimental line widths decrease more sharply than given by the law and are systematically smaller, the term $\text{Arctg}(Bt^{-\nu})$ is significantly lower than $\pi/2$ in this temperature range in accordance with the values of the correlation lengths [13].

— Below $(T_1 + 4 \text{ K})$: the experimental line widths exhibit a divergence as the law $I_1(0)$ for $\angle(\mathbf{H}, \mathbf{a}) = 4^\circ 20'$, and saturate for $\mathbf{H} \parallel \mathbf{a}$.

Let us assume that below $(T_1 + 4 \text{ K})$, the slowing-down induces a spectral width not much larger than w_0 . This would induce a saturation (insert in Fig. 3) of the broadening for $\mathbf{H} \parallel \mathbf{a}$ which is actually observed. Nevertheless, this slowing-down does not break the fast motion regime conditions for the secular contribution at least near $(T_1 + 4 \text{ K})$. Indeed, the reference frequency w_s for this broadening corresponds to the « rigid lattice » line width, i.e. typically $w_s \simeq 100 \text{ MHz}$.

Actually, for $\angle(\mathbf{H}, \mathbf{a}) = 4^\circ 20'$, the secular contribution exhibits the same qualitative behaviour as $I_1(0)$ determined from the high temperature regime (Fig. 3), but the order of magnitude is about

two orders larger than that predicted by the theory (4). Therefore we have to invoke « central peak » phenomena (insert in Fig. 3), i.e., phenomena which do not enter the theoretical framework which leads to formula (2). Otherwise our model would be misleading by two orders of magnitude. Of course we cannot say much about the intrinsic or extrinsic character of the phenomena. Probably, the probe which nicely fits the host is not responsible for these phenomena.

For $\langle \mathbf{H}, \mathbf{a} \rangle = 4^\circ 20'$, the marked Gaussian character of the line shape below $(T_1 + 0.2 \text{ K})$, indicates a change over from the fast to the slow motion regime. The Fourier components of the fluctuations, at frequencies lower than the characteristic frequency ω_s , become important. From the observed line width $\Delta H_d(T_1 + 0.15 \text{ K}) = 35 \text{ G}$ and $\Delta H_{\parallel}(T_1 + 0.15 \text{ K}) = 12 \text{ G}$, which represents the non-secular contribution, we may infer central peak components of width lower than 70 MHz.

The shift of the centre of the sextuplet (Fig. 4) can be simply explained. From $(T_1 + 20 \text{ K})$ to $(T_1 + 8 \text{ K})$, the linear drift would be nothing but a trivial effect of the thermal lattice contraction. Below $(T_1 + 8 \text{ K})$, this drift would be compensated by an increase of the mean square amplitude of the fluctuations ρ_c^2 . This compensation is consistent with our rotational model. A tilt of z away from H induces a shift to low fields, from which we can deduce $(\langle \rho_c^2(T_1 + \varepsilon) \rangle)^{1/2} = 1.8^\circ$.

It is worth commenting the value $4^\circ 20'$. We observed that a tilt of the magnetic field by about 5° did not alter the hyperfine structure and induced a neat effect on the broadenings, and therefore was a convenient value. Actually the accurate value we used was $4^\circ 20'$.

4. Conclusion.

All our results are consistent with those of previous studies by X-rays [13] and by N.M.R. [8]. Particularly, important slowing-down effects occur in the temperature range $(T_1 + 3 \text{ K})$ to T_1 as observed by N.M.R. at 90 MHz. We have obtained supplementary information about the behaviour of the spectral densities in the 10^{10} Hz range.

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