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Slow soliton motion inferred from E.P.R. measurements on $\text{Rb}_2\text{ZnCl}_4 : \text{Mn}^{2+}$ at $T = T_c + \epsilon$

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Résumé. — Nous décrivons les résultats préliminaires d'une étude par R.P.E. de la phase incommensurable de $\text{Rb}_2\text{ZnCl}_4 : \text{Mn}^{2+}$. Nous utilisons une raie de structure fine particulière pour contrôler la densité des domaines commensurables dans la phase incommensurable et pour discriminer le régime de modulation sinusoïdale du régime de soliton. On observe, à $T_c + \epsilon$, des temps d'équilibre très longs, lorsque le cristal est soumis à un saut de température.

Abstract. — We report preliminary results of an E.P.R. investigation on the incommensurate phase of $\text{Rb}_2\text{ZnCl}_4 : \text{Mn}^{2+}$. We use a particular fine structure line to monitor the density of commensurate domains in the incommensurate phase and to discriminate the plane wave modulation regime from the soliton regime. Long equilibrium times are observed at $T_c + \epsilon$, when the crystal is submitted to a thermal jump.

1. Introduction. — Magnetic resonance techniques have been recently used to investigate incommensurate phases [1, 2, 3]. Particularly, a N.M.R. investigation of charge density waves in TaSe_2 [1] has clearly confirmed the existence of discommensurations, i.e. the solution picture. Similar measurements have been extended to the A_2ZnX_4 series [2, 3] in the case of structural incommensurate phases.

In this paper we report a brief description of E.P.R. measurement in $\text{Rb}_2\text{ZnCl}_4 : \text{Mn}^{2+}$. The disadvantage of E.P.R. is the need to introduce a paramagnetic probe in an unstable system.

We emphasize that the experimental results below apply to the particular sample which has been studied. Indeed the lock-in phase transition is very sensitive to impurities and defects. Nevertheless we believe that the Mn^{2+} probe is a rather neutral impurity because it fits the host quite well, from the point of view of the ionic charge, of the ionic radius and of the ground electronic S state.

This paper follows a previous one about the critical exponent β near T_1 [4].

2. Theoretical model [5]. — 2.1 1-D INCOMMENSURATE PHASE. — The displacement field, with respect to the underlying commensurate lattice can be described by : $u_{(z)} = A \cos \phi_{(z)}$.

We define by T_1 the transition temperature from the disordered to the incommensurate phase.

(*) ERA n° 682.

At $T = T_1 - \Delta T$ the plane wave modulation picture holds : $A_{(T)} = A_1 \Delta T^\beta$. $\beta = 0.35 (n=2, d=3)$,
 $\phi = kz, k = \frac{2\pi}{pc} + \delta$.

We define by T_c the commensurate/incommensurate transition temperature.

At $T = T_c + \Delta T$ one assumes that $A_{(T)} = A_c$. Then $\phi_{(z)}$ obeys a Sine-Gordon equation. An analytic expression which accounts for the essential features of the solutions is :

$$\phi_{(z)} = \left\{ \frac{2\pi z}{pc} + \phi_0 \right\} + \frac{4}{p} \left\{ (n-1) \frac{\pi}{2} + \text{arctg} \exp \alpha[z - nb] \right\}.$$

Within this « soliton » picture, low temperature ($T < T_c$) commensurate domains are separated by discommensurations distant by b , centred at $z = nb$. The characteristic length for the discommensuration width is α^{-1} . At $T = T_c$, $b \rightarrow \infty$ and the phase locks at $\frac{2\pi z}{pc} + \phi_0$.

In the particular case of Rb_2ZnCl_4 , $T_1 = 30^\circ\text{C}$, $T_c = -80^\circ\text{C}$, $p = 3$. According to a simple theory the low temperature commensurate phase is stable for $4\alpha > p\pi\delta_0$ with $\delta_0 = 0.015$ [6] and it turns out that the order of magnitude of the soliton width near T_c is 10 units cells. Then the picture of commensurate domain holds in as much as $b \gg 10$. The ratio α^{-1}/b represents the soliton density [7].

Finally we shall assume that the continuous approximation for the displacement field can be used to describe the discrete displacements of the atoms in the lattice.

2.2 E.P.R. LINES IN 1-D INCOMMENSURATE PHASE. — The fine structure lines

$$\left(v = M_S \rightarrow M_{S+1}, -\frac{5}{2} < M_S < +\frac{5}{2} \right)$$

for the Mn^{2+} probe at site i , located at a magnetic field $H_0^v(i)$ above T_i , are shifted by $H_1^v(i)$ in the incommensurate phase.

We assume $H_1(i) = h_1 u_{(zi)}$, i.e. a shift proportional to the local amplitude of the displacement field.

Indeed, the line shifts are essentially influenced by the local distortions of the $[\text{MnCl}_4]_{(i)}^-$ tetrahedra, which modify the electric field gradient parameters b_2^m [8].

The distortion of the tetrahedral unit centred at z_i can be represented by $\{D_{(zi)}\} = \{D\} u_{(zi)}$ where $\{D\}$ is a set of displacements related to the symmetry of the mode which condenses at $q = k$. At first order approximation the variations of the b_2^m are linear in $u_{(zi)}$ and therefore $H_1^v(i)$ should be linear in $u_{(zi)}$, from a first order perturbation treatment of the spin Hamiltonian.

3. Experimental results and discussion. — **3.1 COMMENSURATE PHASES.** — In figure 1, we have represented the hyperfine structure of the fine structure line

$$v = \left| \pm \frac{3}{5} \right| \leftrightarrow \left| \pm \frac{5}{2} \right|, \quad H_0^v \simeq 0.12 \text{ T}.$$

The magnetic field is along the c axis of the Pmcn high temperature lattice. The single sextuplet (Fig. 1a) observed at $T = T_1 + \varepsilon$, is split into three overlapping sextuplets at $T = T_c - \varepsilon$ (Fig. 1b), in accordance with the lock of the phase at

$$\phi_i = \phi_0, \quad \phi_0 + \frac{2\pi}{3}, \quad \phi_0 + \frac{4\pi}{3}.$$

Fig. 1. — Typical E.P.R. line shapes for the transition $\Delta M_s = \pm \frac{5}{2} \leftrightarrow \pm \frac{3}{2}$.

a)-b) Commensurate phases

a) $T = T_1 + \varepsilon$: a single hyperfine sextuplet is observed.

b) $T = T_c - \varepsilon$: three hyperfine sextuplets (λ, ϕ, π) corresponding to $k = \frac{2\pi}{c}$ are observed. They partially overlap.

$$\lambda \rightarrow \phi_0; \quad \phi \rightarrow \phi_0 + \frac{2\pi}{3}; \quad \pi \rightarrow \phi_0 + \frac{4\pi}{3}.$$

c)-d) Incommensurate phase

c) Plane wave modulation limit. Edge singularities for $M_l = \pm \frac{5}{2}$ are indicated by arrows.

d) Soliton limit : the line ϕ denotes commensurate domains.

Within the model above one finds $\phi_0 = 20^\circ \pm 1$, from the distances between the sextuplets. The well resolved and narrow line corresponding to $|M_l| = \frac{5}{2}$ located on the low field side of the central sextuplet ($\phi_i = 258^\circ$), has been blackened in figure 1b. This line will be used later to indicate the existence of broad, low temperature commensurate domains in the sample.

Amplitude fluctuations δA and phase fluctuations $\delta \phi$ act on the line width of commensurate domains through :

$$\delta H_i^y = h_1^y | \cos \phi_i \delta A | + | \sin \phi_i \delta \phi |.$$

Then spatial amplitude fluctuations can account for the different line widths of the three

sextuplets (Fig. 1b). Indeed the line widths vary as $|\cos \phi_i|$

$$\delta H_{(\phi=\phi_0)} > \delta H_{(\phi=\phi_0+\frac{2\pi}{3})} > \delta H_{(\phi=\phi_0+\frac{4\pi}{3})}$$

$$|\cos \phi_0| > \left| \cos \phi_0 + \frac{2\pi}{3} \right| > \left| \cos \phi_0 + \frac{4\pi}{3} \right|.$$

3.2 INCOMMENSURATE PHASES. — 3.2.1 *Plane wave modulation limit.* — At $T = T_1 - \Delta T$, down to $T \simeq T_C + 5$ K, the hyperfine structure is characterized by two broad overlapping sextuplets (Fig. 1c). Within the plane wave modulation model, the spectral density for the E.P.R. fine structure line should be marked by two edge singularities at $H_1^* = \pm h_1 A_1 \Delta T^\beta$ emerging from a continuous background [13, 4]. In principle the distance between the edge singularities near T_1 permits to measure the critical exponent β . Nevertheless, in the particular case of the Mn^{2+} probe, a more precise but sophisticated method using the « forbidden » hyperfine lines for $H//a$ [4] has been developed. We have found $\beta = 0.36 \pm 0.04$ in accordance with theory and with measurements [9, 10] by neutron scattering and ultrasonic techniques.

3.2.2 *Soliton picture.* — At $T = T_C + \Delta T$, up to $\Delta T = 5$ K the hyperfine line which is the mark of broad commensurate domains is still present (Fig. 1d). In this temperature range its peak-to-peak width does not vary significantly. The E.P.R. spectrum (Fig. 1d) is constituted by a superposition of a commensurate spectrum (Fig. 1b) and of an edge singularity « spectrum » (Fig. 1c). Indeed the phase varies as $\frac{2\pi z}{pc} + \frac{2}{p} \alpha(z - nb)$ (to first order in $(z - nb)$) in the bulk of the discommensuration, i.e. as in the plane wave modulation picture. From 3.1, the blackened line is very sensitive to phase fluctuations and is smeared out as soon as the phase deviates from the lock-in values.

We have used the height $l_{(T)}$ of the blackened line (Figs. 1b, 1d) to attempt a monitoring of the soliton density through

$$n_s \simeq \frac{l_{(T_C-5)} - l_{(T)}}{l_{(T_C-5)}} \quad T > T_C.$$

Fig. 2. — Dependence on T of the soliton density n_s . The tail of the curve below 193 K reveals a precursive behaviour of n_s .

The height at $(T_C - 5)$ K has been chosen as a reference because it does not exhibit any significant variation below this temperature.

The results are plotted in figure 2. The low temperature tail of the curve could indicate the existence of discommensurations below T_C , either as solitons pinned at defects or as thermal solitons with a sufficiently long life time, or at least indicates a critical behaviour.

Neither a dependence on T as :

$$n_s \sim \ln^{-1} \left| \frac{T_C - T}{T} \right|$$

or a dependence on T as $(T_C - T)^{1/2}$ can account for the behaviour of n_s above T_C . The marked elbow at $T = T_C + 4$ K favours the first law. This result conflicts with recent N.M.R. results [13].

Above $T = T_C + 5$ K, the disappearance of the line ($\phi = 258^\circ$, $M_I = \frac{5}{2}$) can be connected to the disappearance of broad commensurate domains ($b \gg \alpha^{-1}$), and the «soliton» type spectrum (Fig. 1), transforms into the «edge singularity» spectrum smoothly. The width of the spectrum remains constant up to $T = T_C + 15$ K. This observation is consistent with a nearly constant amplitude near T_C , assumption from which one may derive the Sine-Gordon equation.

Thermal hysteresis is observed by cycling T around T_C . Concerning this point, a fast thermal jump near T_C shows that equilibrium times as long as one hour are involved in the diffusion of the discommensuration walls (Fig. 3). Measurements, on other crystals with sensitive probes [11, 12] indicate that the experimental device which has been used has a thermal equilibrium time less than 3 min. At stabilized temperature (± 0.1 K), a measurement can last less than 2 s and can be repeated every 5 s. In comparison with other techniques (N.M.R. on ^{87}Rb , dielectric measurements, diffraction measurements), E.P.R. seems well adapted for an insight on the equilibrium kinetics near the lock-in transition.

Fig. 3. — Evolution of the line ϕ ($M_I = \frac{5}{2}$) at stabilized $T = 193$ K, after a fast thermal jump from 194 to 193 K. One hour separates the outer lines.

4. Conclusion. — We have used the Mn^{2+} probe substituted for Zn^{2+} , to obtain an insight on the local displacement field in the incommensurate phase of Rb_2ZnCl_4 . Our analysis is based on the assumption that the shift of the fine structure lines depends linearly on the two

component order parameter $u(z_i) = A \cos(kz_i + \phi_0)$ and on a simple theoretical model to describe the incommensurate phase. The E.P.R. measurements permit a precise measurement of the critical exponent β near T_b and an easy observation of the plane wave modulation limit near T_l and of the large soliton limit near T_c .

We have attempted to estimate the soliton density with the help of a particular narrow line of the E.P.R. spectrum. We have observed a precursive behaviour of this order parameter for the low commensurate phase $\rightarrow$ incommensurate phase transition.

Lastly, the possibility of doing very fast measurements permits an insight on the equilibrium times with a resolution which can be hardly attained with other techniques.

A more detailed analysis of the experimental results is in progress.

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