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Floating of the modulation wave in incommensurate Rb_2ZnCl_4

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Nuclear-magnetic-resonance measurements in Rb_2ZnCl_4 show that in the vicinity of the paraelectric-incommensurate transition floating of the phase of the pinned incommensurate modulation wave results in a partial motional averaging of the incommensurate line broadening. The root-mean-square phase fluctuations increase from 20° at $T_I - T = 7$ K to 65° at $T_I - T = 0.5$ K.

I. INTRODUCTION

Recent nuclear-magnetic-resonance (NMR) measurements in incommensurate Rb_2ZnBr_4 have shown[1] the coexistence of regions, where the modulation wave is floating with regions where the modulation wave is static, over a 10-K temperature range below the paraelectric-incommensurate transition temperature $T_I = 346$ K. Emery, Hubert, and Fayet[2] have observed a similar behavior by electron-paramagnetic resonance (EPR) in incommensurate $ThBr_4$ in a 2.6-K temperature interval below $T_I = 94$ K. The temperature interval where thermal fluctuations of the phase of the modulation wave become large enough to overcome the pinning energy due to discrete lattice effects and impurities has been recently estimated by Bandour[3] following the work of Overhauser[4] and Axe.[5]

It should be noted that, in spite of the fact that in the absence of impurity and discrete lattice effects the phase of the modulation wave is not fixed relative to the crystal lattice in incommensurate structures, most NMR studies have been analyzed[6] so far with the assumption that the modulation wave is static and pinned over the whole incommensurate phase. Only recently the effects of phase fluctuations on the NMR line shape have been systematically analyzed.[7] In this Rapid Communication we report the results of an investigation of the effect of phase fluctuations of the modulation wave on the NMR line shape in a Rb_2ZnCl_4 crystal grown in the incommensurate phase. We show that though the phase fluctuations are here not so large as to produce a "sharp" motionally averaged line seen in Rb_2ZnBr_4 (Ref. 1) and ThBr (Ref. 2) they are large enough to reduce the effective amplitude of the modulation wave from the static value A to

$$\tilde{A} = A \exp(-\tfrac{1}{2}\langle\phi^2\rangle) \ , \tag{1}$$

where $\langle\phi^2\rangle$ is the mean-square fluctuation in the phase which diverges as T_I is approached from below. The renormalization of the modulation amplitude results in an anomalous temperature dependence of the frequency splitting $\Delta\nu$ between the two incommensurate edge singularities in the NMR spectrum below T_I and an increase in the apparent critical exponent β_{eff} close to T_I. Similar results have been obtained also for crystals with higher T_I grown in paraelectric phase. We believe that similar effects are present in other incommensurate systems too but have been so far overlooked.

II. THEORY

Let us consider the simplest case when the modulation is one dimensional:

$$u_j = A_j \cos\phi(x_j,t) = A \cos\left[\tilde{\phi}(x_j) + \sum_k \phi_k(x_j,t)\right] \ , \tag{2a}$$

where the ϕ_k represent the phase fluctuations with wave vector k. In the high-temperature part of the incommensurate phase the plane-wave modulation limit is appropriate so that we have

$$u(x,t) = A \cos\left[k_I x + \phi_0 + \sum_k \phi_k(x,t)\right] \ , \tag{2b}$$

where k_I is the incommensurate modulation wave vector, and ϕ_0 is the initial phase which is determined by the position of the nucleus in the paraelectric unit cell. The nuclear magnetic resonance frequency ν is assumed to be a simple linear function of the nuclear displacement $u(x,t)$:

$$\nu(x,t) = \nu_0 + a_1 u(x,t) \ . \tag{3}$$

Here we assumed that displacements of all nuclei which contribute to the electric field gradient (EFG) tensor at x are in phase. ν_0 is the resonant frequency in the paraelectric phase, and a_1 is an expansion coefficient which depends on the symmetry of a given nuclear site. Inserting (2) into (3) we find[7] the adiabatic magnetic resonance line shape as

$$f(\nu) = \int_{-\infty}^{+\infty} e^{-i2\pi\nu t''} \times \left\langle\left\langle \exp i2\pi \int_t^{t+t''} \nu(x,t')dt' \right\rangle_x\right\rangle_t dt'' \ . \tag{4}$$

Here the $\langle\,\rangle_t$ indicates a time average and $\langle\,\rangle_x$ an average over all nuclear positions which are equivalent in the paraelectric phase.

Expression (4) has been evaluated by us[1,7] for several specific models of the motion of the modulation wave. Here we assume that the phase fluctuations ϕ_k of the modulation wave are standing waves within a coherence volume $\bar{l}^3$ which is much smaller than the volume of the crystal so that $k_{\min} \lesssim \pi/\bar{l}$. We wish to point out that the details of the motion of the modulation wave are not important if thermal fluctuations $\phi_k(x,t)$ are fast as compared with $\nu_1 = a_1 A$. So we assume a stationary Gaussian distribution of the phase $\phi=\sum_k \phi_k(x,t)$ for each coherence volume:

$$P(\phi)=\frac{1}{(2\pi\sigma^2)^{1/2}}\exp(-\phi^2/2\delta^2) \; , \tag{5}$$

where $\sigma^2=\langle\phi^2\rangle$.

In the limit of fast motion the time averaging in (4) is substituted by the averaging of the $\nu(x,t)$ over the Gaussian distribution (5):

$$\left\langle \exp\left[i2\pi\int_t^{t+t''}\nu(x,t')dt'\right]\right\rangle_t = \exp(i2\pi\nu_0 t'')\exp\left[i2\pi\nu_1 t''\int_0^\infty P(\phi)\cos(k_I x+\phi_0+\phi)d\phi\right] \; . \tag{6}$$

One finally obtains the magnetic resonance line shape as

$$f(\nu)=\frac{1}{\pi[\nu_1^2 e^{-\sigma^2}-(\nu-\nu_0)^2]^{1/2}} \; . \tag{7}$$

Expression (7) reduces to the well-known incommensurate static frequency distribution characterized by two edge singularities if phase fluctuations are negligible so that $\sigma^2=\langle\phi^2\rangle\rightarrow 0$. In the opposite limit of large phase fluctuations, $\sigma^2=\langle\phi^2\rangle\rightarrow\infty$, the incommensurate broadening is motionally averaged and one finds just an unperturbed sharp line at ν_0:$f(\nu)\alpha\delta(\nu-\nu_0)$. In the intermediate case of small but nonzero phase fluctuations we have a partial motional averaging. The splitting between the two edge singularities

$$\Delta\nu=\nu-\nu_0=\pm\nu_1 e^{-\sigma^2/2} \tag{8}$$

is reduced by $e^{\sigma^2/2}$ as compared with the static case but the shape of the spectrum is not changed. The reduction of the splitting reflects the reduction of the effective amplitude of the modulation wave from the static value as given by expression (1).

Since we assumed a diffusive motion of the modulation wave the obtained result—Eq. (7)—is of course very different from the one obtained for a uniform sliding of the modulation wave.[1,7]

The temperature depenednce and actual magnitude of σ^2 can be estimated from the equipartition theorem and expression (3a). Expressing the phase fluctuations as a set of standing waves

$$\phi_k(\vec{r}_j,t)=\phi_{0k}\sin(\omega_{\phi k}t)\sin(k_x x)\sin(k_y y)\sin(k_z z) \tag{9}$$

in the coherence volume $\bar{l}^3$, one finds from the equipartition theorem for the contribution of the kth mode:

$$\sum_j\langle m_j\dot{u}_j^2/2\rangle_t=k_BT/2 \; . \tag{10}$$

Here we are summing over all nuclei inside the coherence volume and the dot stands for the time derivative. From expression (10) we find the positionally averaged mean-square phase fluctuation as

$$\sigma^2\approx\frac{1}{16}\sum_k\phi_{0k}^2 \; , \tag{11a}$$

where

$$\phi_{0k}\approx[32k_BTV_0/(N_0m\bar{l}^3)]^{1/2}/(A\,\omega_{\varphi k}) \; . \tag{11b}$$

Here N_0 is the number of nulcei of average mass m in the unit cell V_0.

In Ref. 1 we treated the case of weak pinning where $\bar{l}$ is strongly temperature dependent. Here we shall discuss the case of strong pinning where $\omega_{\varphi k}$ is k independent and equals the phason gap frequency, $\omega_{\varphi k}\simeq\omega_{\varphi 0}$, whereas $\bar{l}\approx$ const.

In such a case σ^2 is inversely proportional to the amplitude of the modulation wave

$$\sigma^2\propto\frac{1}{A^2}\propto(T_I-T)^{-2\beta} \; . \tag{12}$$

The above result cannot be valid very close to T_I where $A\rightarrow 0$ and the coherence volume $\bar{l}$ becomes temperature dependent so that we are in the weak pinning regime.[1] In many crystals, e.g., in those where no sharp lines are seen in addition to the edge singularities, this region will never be reached within the available temperature resolution. It

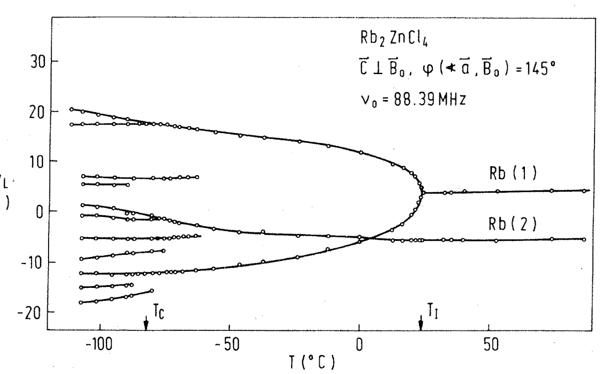

FIG. 1. Temperature dependence of the ^{87}Rb $\frac{1}{2}\rightarrow-\frac{1}{2}$ NMR transition frequencies in a Rb_2ZnCl_4 crystal grown in the I phase.

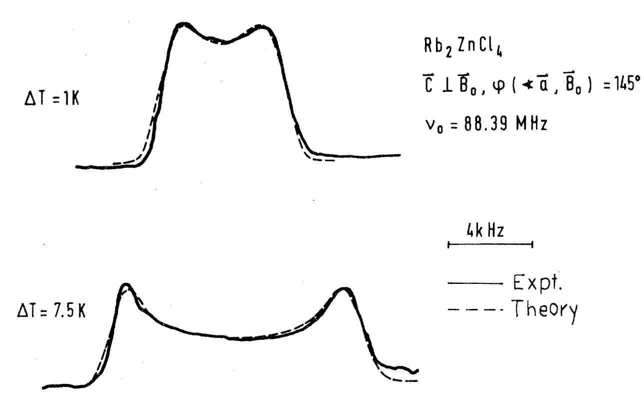

FIG. 2. Theoretical and experimental ^{87}Rb NMR $\frac{1}{2}\rightarrow-\frac{1}{2}$ line shapes close to T_I. The theoretical line shape has been obtained by convoluting expression (7) with a Gaussian reflecting the width of the paraelectric line.

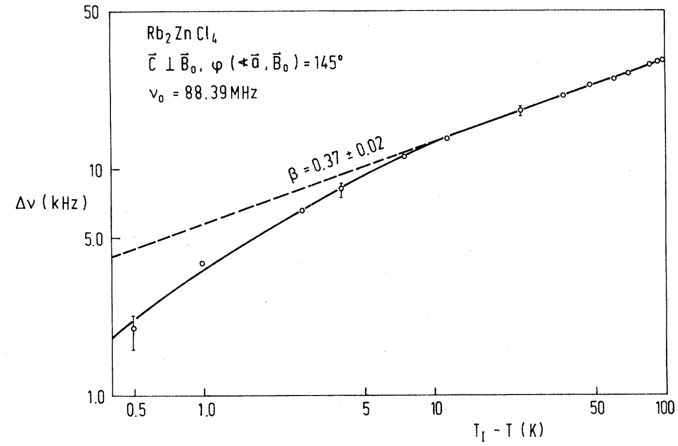

FIG. 3. Log-log plot of the splitting between the two edge singularities $\Delta\nu$ vs $T_I - T$.

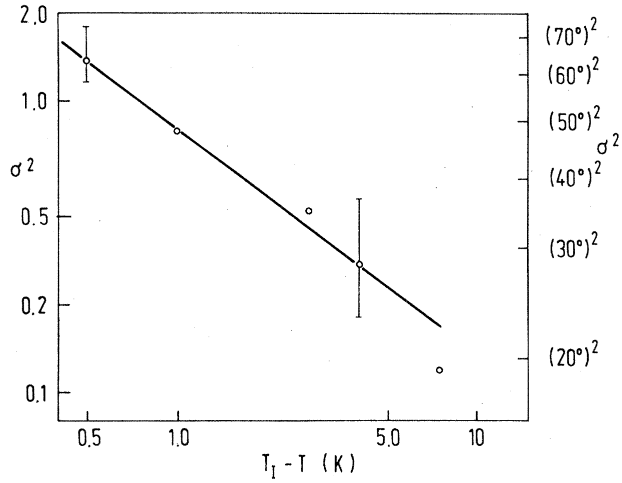

FIG. 4. Log-log plot of the mean-square phase fluctuations $\sigma^2 = \langle \phi^2 \rangle$ in Rb_2ZnCl_4 vs $T_I - T$.

should also be noticed that expression (12) is as well predicted by the continuum Landau theory in the absence of any pinning.

III. EXPERIMENT

The temperature dependence of the ^{87}Rb $\frac{1}{2} \rightarrow -\frac{1}{2}$ quadrupole perturbed NMR transitions are presented in Fig. 1 for $\vec{c} \perp \vec{B}_0$ and $\measuredangle\ \vec{a}, \vec{B}_0 = 145°$ at Larmor frequency $\nu_L = 88.34$ MHz and rf frequency $\nu_0 = 88.39$ MHz. The sharp paraelectric line of Rb(1) undergoes a characteristic incommensurate broadening[6] limited by two edge singularities (Fig. 2) on going into the incommensurate phase at $T_I = 24 \pm 0.5\,°C$. This value of the transition temperature is significantly lower than found in other crystals grown in the paraelectric phase ($T_I = 30\,°C$). No sharp lines—as observed[1] in Rb_2ZnBr_4—are found for $T_I - T > 0.5$ K in agreement with previous studies.[6,8,9] The incommensurate-commensurate transition takes place around $T_c = -81\,°C$. Sharp "commensurate" lines demonstrating the transition from the "plane wave" to the "multisoliton lattice" modulation regime[8] are found well above T_c in the incommensurate phase. This result is as well analogous to the ones reported[6,8,9] previously for Rb_2ZnCl_4 crystals grown in the paraelectric phase.

The temperature dependence of the splitting between the two edge singularities[6,8,9] $\Delta\nu = \nu_+ - \nu_-$ is plotted against $T_I - T$ in a log-log scale in Fig. 3. The plot is not a straight line and can be characterized by two exponents rather than a single one. In the absence of effective amplitude averaging by phase fluctuations one expects that

$$\Delta\nu_0 \propto A \propto (T_I - T)^\beta \ , \tag{13}$$

so that the above plot should yield a straight line with a critical exponent $\beta = 0.35$ as expected for the $d = 3$ XY Heisenberg model. Such an exponent has been indeed observed by x-ray measurements[10] as well as by NMR.[6] The experimental data (Fig. 3) yield such an exponent $\beta = 0.37 \pm 0.02$ for $T_I - T \geqslant 9$ K, whereas for $T_I - T \leqslant 9$ K the $\Delta\nu$ vs $T_I - T$ plot yields an effective exponent $\beta_{\rm eff} \approx 0.6 \pm 0.1$. This behavior can be understood if we remember that in the presence of phase fluctuations the effective modulation amplitude and the splitting between the two edge singularities is reduced:

$$\Delta\nu = \Delta\nu_0 e^{-\sigma^2/2} \propto A e^{-\sigma^2/2} \propto (T_I - T)^\beta e^{-\sigma^2/2} \ . \tag{14}$$

By subtracting in the log-log plot (Fig. 3) the observed splitting from the one extrapolated from the data "far" from T_I where $\beta = 0.37$ one thus finds the temperature dependence of the mean-square phase fluctuations in Rb_2ZnCl_4 as well as the magnitude of these fluctuations. The results are shown in Fig. 4. $\sigma^2 = \langle \phi^2 \rangle$ is found to vary between 20° at $T_I - T = 7$ K and 65° at $T_I - T = 0.5$ K. The corresponding translations of the modulation wave σ / k_I vary between 1.6 and 5 paraelectric unit cells. Whereas these phase fluctuations are too small to average out the incommensurate broadening and to produce a sharp central line as in Rb_2ZnBr_4 (Ref. 1) they are large enough to produce a partial motional averaging which significantly affects the temperature dependence of the line splitting $\Delta\nu$ close to T_I. The log-log plot of σ^2 vs $T_I - T$ does not yield a good single straight line. If, however, we make a power law fit we find an exponent 0.80 ± 0.15 which is rather close to the value 2β predicted by expression (12).

We believe that the above phenomena should be quite general and should be found also in other incommensurate crystals close to T_I.

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