NQR Study of the Pinning and Depinning of the Incommensurate Modulation Wave in the Presence of Impurities *

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High temperature-resolution NQR measurements in an ultra pure Rb_2ZnCl_4 crystal and a mixed $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$ crystal with a controlled amount of impurities ($x=0.01$) verify the existence of a temperature region where the characteristic incommensurate line splitting is averaged out. The results show that for the system with high purity the averaging of the incommensurate splitting is due to large thermal fluctuations. In contrast, for the mixed crystal the added impurities seem to play the predominant role.

I. Introduction

In ideal incommensurate (I) systems, in the continuum limit, there should be a sliding modulation wave which moves through the system without friction. The excitation of this mode represents a gapless excitation or phason in which no position is favored over any other. This is the Goldstone mode recovering the broken translational symmetry: It is acoustic-like and has a linear dispersion [1]. In real crystals, however, the modulation wave is considered as pinned and static, giving the well known picture of the NQR/NMR spectrum as far as large sliding motions are concerned. In these systems there exist imperfections and random impurities which probably "pin" the modulation wave. An other reason of pinning, namely the discrete lattice pinning, seems to be very small in the high temperature region close to the paraelectric to incommensurate transition at T_I [2], so we can neglect it.

Recently it has been reported [3, 4] that in charge density waves (CDW) compounds, the incommensurate modulation wave can be depinned by an external electric field. The value of the depinning field E_T strongly depends on temperature, thus indicating close to T_I large thermal fluctuations. It was also observed by us and other groups [5–8] that very close to T_I, in the high temperature region of the incommensurate phase, large thermal fluctuations are able to depin the modulation wave in structurally incommensurate system, resulting in a characteristic change of the NQR/NMR spectrum. This change has been explained as a motionally averaged out line [8] or motionally narrowing of the line [6, 9]. Thermally activated flux creep effects have also been obseved in flux line lattices of conventional type II superconductors as well as in high T_c superconductors [10]. We may thus conclude that these effects are common in a variety of systems [11]. On the other hand, the impurities are also affecting the pinning and depinning of the modulation wave and this effect should be observable in a NMR or NQR experiment. However the microscopic nature of the pinning and its effect on the long range order is not well understood; similarly the influence of impurities is not yet quite clear.

In an NQR/NMR experiment, the characteristic static picture of the modulation wave starts at T_I to show an inhomogeneous broadening of the spectrum limited by two edge singularities with a splitting proportional to the amplitude of the modulation wave [12, 13]. This is so if the fast amplitudon and phason fluctuation modes [13] have a too small amplitude to be effective in producing motional averaging or even narrowing of the NQR line [6, 8].

In order to add to our understanding of these effects and check our previous measurements [8] on a nominally pure system, we decided to repeat our high temperature-resolution NQR line shape and T_1 measurements in an ultra crystal of Rb_2ZnCl_4 and in a $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$ mixed crystal with $(NH)_4$ acting as a small controlled amount of impurities ($x=0.01$).

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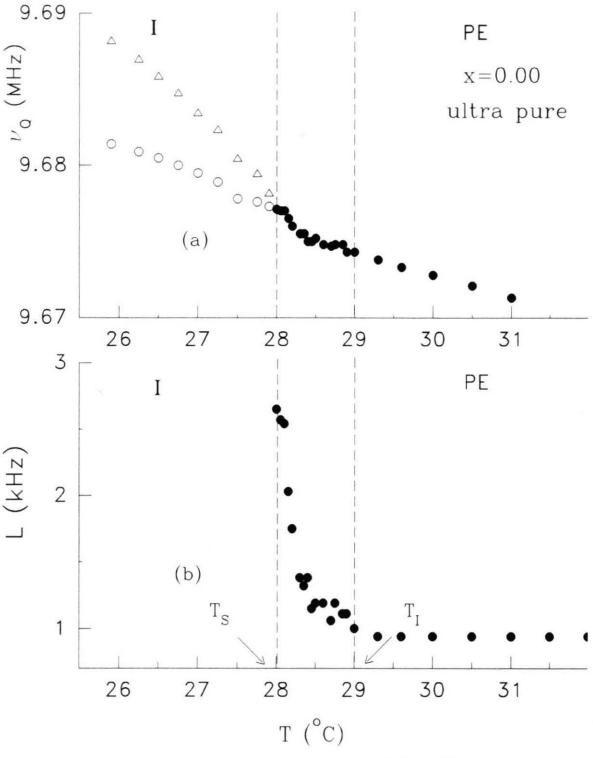

Fig. 1. (a) Temperature dependence of the Cl(1) NQR frequencies close to T_I for an ultra pure Rb_2ZnCl_4 single crystal. (b) Temperature dependence of the inhomogeneous broadening of the Cl(1) NQR line of the same crystal close to T_I.

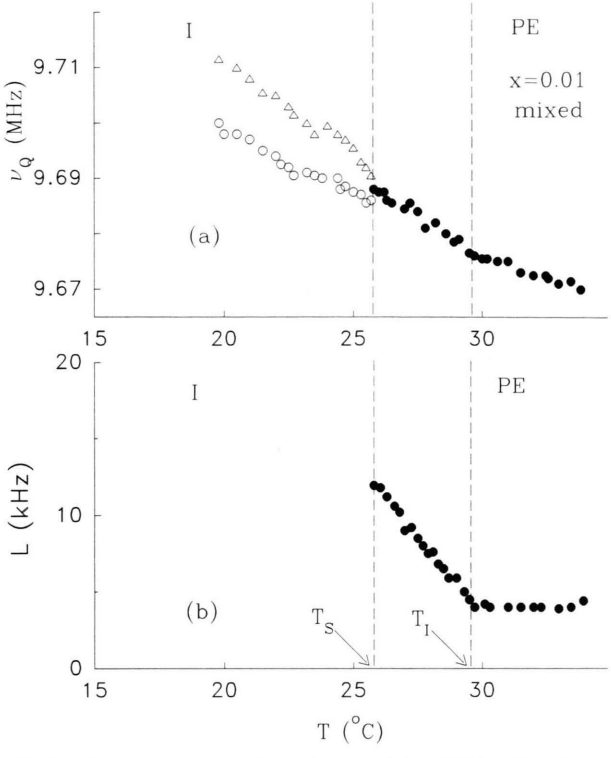

Fig. 2. (a) Temperature dependence of the Cl(1) NQR frequencies close to T_I for a $[Rb_{1-x}(NH_4)_x]ZnCl_4$ single crystal with $x=0.01$. (b) Temperature dependence of the inhomogeneous broadening of the Cl(1) NQR line of the same crystal close to T_I.

II. Experimental

Fourier transformed ^{35}Cl NQR spin echo spectra of pure and mixed single crystals were recorded of the Cl(1) nucleus which lies on a mirror plane. The ultra pure crystal of Rb_2ZnCl_4 was prepared as usually from an aqueous solution of RbCl and $ZnCl_2$ in a 2:1 molar ratio. In contrast to the case of the nominally pure crystal mentioned above, the method of repeated crystallization was used. T_1 was obtained by the inversion recovery spin echo pulse sequence. The thermocouples used are specially calibrated chromel-constantan. The temperature regulation provided a stability better than 0.02 K over the measuring period. During the measurements, the samples were kept in a specially designed oven immersed in a bath in order to minimize the temperature gradient. The sample was kept long enough at each temperature so as to reach thermal equilibrium.

III. Results and Discussion

The temperature dependence of the Cl(1) NQR frequencies for the different crystals is shown in Figs. 1 a and 2 a. Figures 1 b and 2 b show the temperature dependence of the inhomogeneous broadening of the Cl(1) NQR line, measured by the half height full width (HHFW), for the pure and mixed crystals. Only the region very close to T_I was investigated. In agreement with our earlier measurements [8], the NQR frequency of an ultra pure Rb_2ZnCl_4 single crystal (Fig. 1 a) slowly increases with decreasing temperature from 35 °C down to 29.00 °C, where an inhomogeneous broadening of the NQR line vs. T, accompanied by a change of the slope of the ν_Q vs T plot, indicates the transition temperature T_I. The changing of the inhomogeneous broadening of the NQR line and of the slope continues till a temperature $T_s=28.00$ °C, where the characteristic incommensurate spectrum

appears limited by two edge singularities, as expected. For the case of Cl(1) the NQR frequency depends quadratically on the incommensurate displacement of the nucleus from its position in the high temperature paraelectric phase.

$$\nu = \nu_0 + \nu_2 \cos^2 \varphi\,, \tag{1}$$

$$\nu_2 \propto |\bar{u}_0|^2 \propto (T_I - T)^{2\beta}.$$

The incommensurate frequency distribution is given by [14]

$$F(\nu) = \frac{\text{const}}{[(\nu_2 \Gamma/2)^2 - (\nu - \nu_0 - \nu_2/2)^2]^{1/2}}\,, \tag{2}$$

where Γ is a factor representing the floating effects [14],

$$\Gamma \propto \exp(-ct/|\bar{u}_0|^2)\,. \tag{3}$$

In case of zero floating, $\Gamma = 1$ and we get the usual static frequency distribution given by the formula

$$F(\nu) = \frac{\text{const}}{[(\nu - \nu_0)(\nu_2 + \nu_0 - \nu)]^{1/2}} \tag{4}$$

which exhibits two edge singularities at

$$\nu - \nu_0 = 0 \quad \text{and} \quad \nu - \nu_0 = \nu_2\,.$$

The HHFW of the incommensurate frequency distribution L is equal to

$$L \cong \Delta\nu + L_0\,, \tag{5}$$

where L_0 is the HHFW of the paraelectric line and $\Delta\nu$ is the distance between the two edge singularities,

$$\Delta\nu = \nu_2 L. \tag{6}$$

The experimental data given in Fig. 1 b fit very well to (5) only if we take the existence of large thermal fluctuations ($\Gamma \neq 1$) into consideration. At temperatures below T_s, ν_2 is large enough and the amplitude of the fast fluctuations becomes too small to average out the incommensurate splitting of the NQR line, although they still affect the width of the lines.

In an ideally pure compound the temperature interval between T_I and T_s is expected to disappear. We believe that this interval in the ultra pure crystal represents a thermally depinned incommensurate wave due to large scale thermal fluctuations where the incommensurate splitting, which happens at T_I, is motionally averaged out from the floating of the modulation wave [6, 8, 15]. In favor of the thermal depinning are the T_1 measurements (Figure 3 a). On approaching T_I from above, T_1 decreases as predicted

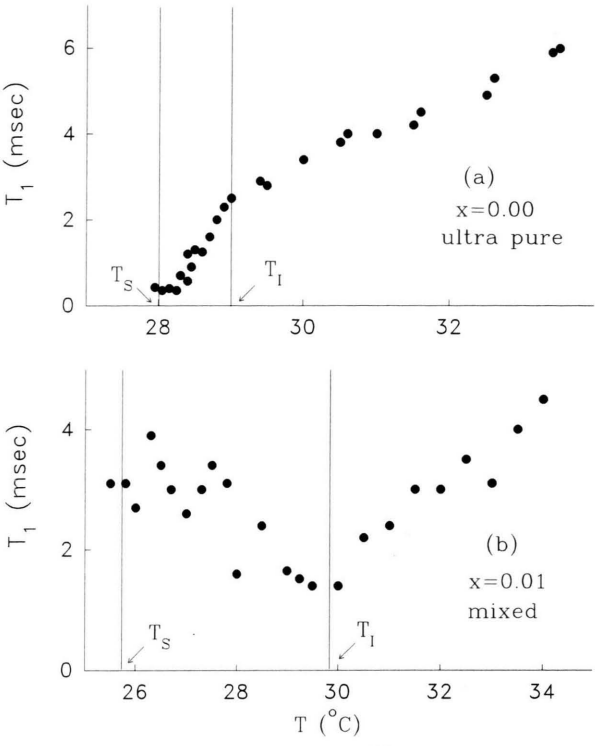

Fig. 3. Temperature dependence of the ^{35}Cl(1) T_1 close to T_I. (a) For an ultra pure Rb_2ZnCl_4 single crystal. (b) For a $[Rb_{1-x}(NH_4)_x]ZnCl_4$ single crystal with $x = 0.01$.

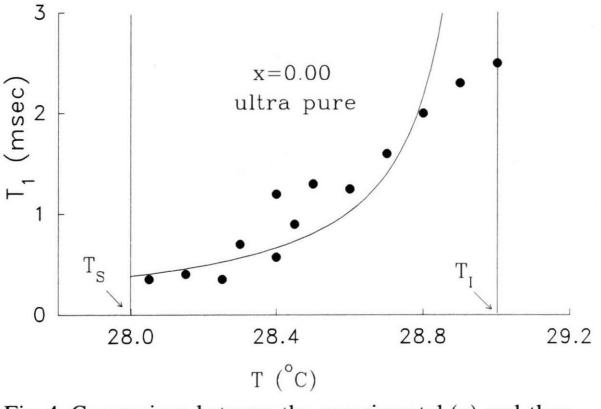

Fig. 4. Comparison between the experimental (•) and theoretical (——) temperature dependence of the Cl(1) T_1 in the floating phase for an ultra pure Rb_2ZnCl_4 single crystal.

from the theory [1]. At exactly T_I we observe a change of the slope of the T_1 values which is much more pronounced in the ultra pure sample than measured previously in a nominally pure crystal [7]. The interesting point here is that T_1 continues to decrease on

further cooling in the thermally depinned floating phase. This is not the case for the mixed compound, where T_1 seems to reach its minimum at T_I (Figure 3 b). The observed temperature dependence of T_1 can be explained in the pure system by the theory of spin-lattice relaxation via large scale phase fluctuations which has been recently developed [16]. Here the linearized description of the phase fluctuation is abandoned and the spin-lattice relaxation rate induced by floating of the modulation wave is given by [7]

$$(T_1^{-1})_\varphi \propto (J_l)_\varphi \propto (T_I - T)^{3\beta} \exp\left\{-\frac{\omega^2}{4p_0^2}\left[\frac{T_I - T}{T_I}\right]^{2\beta}\right\}. \tag{7}$$

Equation (7) predicts also the change of the slope in the T_1 measurements at exactly the temperature T_I (Figure 4). For the mixed compound the theoretical fit of (7) is very poor [14].

Work is still in progress by 1 D and 2 D NQR and NMR experiments in order to clarify the behaviour of impurities (for $x = 0.01$ and $x > 0.01$).

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