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

F. Milia, G. Papavassiliou, and A. Anagnostopoulos
National Center for Scientific Research "Demokritos", Ag. Paraskevi, Attiki, 153 10 Attiki, Greece
Z. Naturforsch. 47a, 237–240 (1992); received December 2, 1991

High temperature-resolution NQR measurements in an ultra pure Rb$_2$ZnCl$_4$ crystal and a mixed [Rb$_{1-x}$(NH$_4$)$_x$]ZnCl$_4$ 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 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 observed 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 $T_T$ 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 $T_T$ measurements in an ultra crystal of Rb$_2$ZnCl$_4$ and in a [Rb$_{1-x}$(NH$_4$)$_x$]ZnCl$_4$ mixed crystal with (NH$_4$)$_4$ acting as a small controlled amount of impurities (x = 0.01).

0932-0784 / 92 / 0100-0237 $ 01.30/0. – Please order a reprint rather than making your own copy.
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 \(\text{Rb}_2\text{ZnCl}_4\) 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. \(T_\text{f}\) was obtained by the inversion recovery spin echo pulse sequence. The thermocouples used were 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 \(T_\text{f}\) was investigated. In agreement with our earlier measurements [8], the NQR frequency of an ultra pure \(\text{Rb}_2\text{ZnCl}_4\) 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 \(v_Q\) vs \(T\) plot, indicates the transition temperature \(T_\text{f}\). 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.

\[ v = v_0 + v_2 \cos^2 \varphi , \]
\[ v_2 \propto |\vec{u}_0|^2 \propto (T_1 - T)^2 \theta . \]

The incommensurate frequency distribution is given by [14]

\[ F(v) = \frac{\text{const}}{[(v_2 + v_0 - v)^2]^{1/2}} , \]
where \( \Gamma \) is a factor representing the floating effects [14],

\[ \Gamma \propto \exp(-ct/|\vec{u}_0|^2) . \]

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

\[ F(v) = \frac{\text{const}}{[(v-v_0)(v_2 + v_0 - v)]^{1/2}} \]

which exhibits two edge singularities at

\[ v - v_0 = 0 \quad \text{and} \quad v - v_0 = v_2 . \]

The HHFW of the incommensurate frequency distribution \( L \) is equal to

\[ L \approx \Delta v + L_0 , \]

where \( L_0 \) is the HHFW of the paraelectric line and \( \Delta v \) is the distance between the two edge singularities,

\[ \Delta v = v_2 L . \]

The experimental data given in Fig. 1b fit very well to (5) only if we take the existence of large thermal fluctuations (\( \Gamma \approx 1 \)) into consideration. At temperatures below \( T_s \), \( v_2 \) 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 \( T_1 \) 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 \( T_1 \), 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 3a). On approaching \( T_1 \) from above, \( T_1 \) decreases as predicted from the theory [1]. At exactly \( T_1 \) 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 $T_i$ seems to reach its minimum at $T_i$ (Figure 3b). The observed temperature dependence of $T_i$ 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]

\[
(T_i^{-1})_o \propto (J_i)_o \propto (T_i - T)^{3\beta} \exp \left\{-\frac{T - T_i}{T_i - T}^{2\beta} \right\}.
\]

Equation (7) predicts also the change of the slope in the $T_i$ 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 1D and 2D NQR and NMR experiments in order to clarify the behaviour of impurities (for $x=0.01$ and $x>0.01$).

Acknowledgement

Useful discussions and suggestions by R. Blinc are gratefully acknowledged. The authors would like also to thank K. Hamano for providing the samples.