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Thermal depinning of the modulation wave in the presence of random impurities

F. Milia, G. Papavassiliou, and A. Anagnostopoulos
Institute of Materials Science, National Center for Scientific Research, Demokritos
GR-153 10 Aghia Paraskevi Attiki, Attiki, Greece

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High-temperature-resolution nuclear-quadrupole-resonance (NQR) measurements in mixed $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$ that has a controlled amount of impurities show the existence of a temperature region where the incommensurate inhomogeneous broadening of the NQR spectra is averaged out. As a result, the characteristic line splitting starts at a temperature T_S which is lower than the phase-transition temperature T_I, an effect enhanced by the presence of impurities. This work presents experimental evidence that impurities might prevent the onset of the incommensurate long-range order in incommensurate insulators.

I. INTRODUCTION

In ideal incommensurate systems, there should be a sliding modulation wave which moves through the system without friction. In real crystals however the modulation wave is pinned by the unavoidable presence of an effective number of impurities and discrete-lattice effects.[1-3] As a consequence we take the "static" picture of the modulation wave and the onset of the incommensurate long-range order, resulting in the characteristic inhomogeneous broadening of the nuclear quadrupole resonance (NQR) or NMR spectrum (splitting of the lines). In the case of $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$ and for the Cl(1) nuclear site very close to T_I, the frequency depends quadratically on the incommensurate displacement $\bar{u}=\bar{u}_0\cos\phi$ of the nucleus from its position in the paraelectric phase.[4]

$$\nu=\nu_0+a|\bar{u}_0|^2\cos^2\phi+\cdots . \tag{1a}$$

The frequency distribution is then given by

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

and is limited by two edge singularities at

$$\nu-\nu_0=0,\ \nu-\nu_0=\nu_2 . \tag{1c}$$

Recent NMR,[1,5,6] NQR,[7] and electron-paramagnetic resonance[8] (EPR) experiments reported the existence of a floating of the modulation wave close to the incommensurate-to-paraelectric (I-P) transition at T_I, where thermal fluctuations become large enough and thermally depin the modulation wave from the underlying lattice. However, the nature of this sliding modulation wave in the presence of a finite number of random impurities has not been systematically investigated. Also their influence is not very well understood.

Random quenched impurities generally tend to prevent long-range order by creating a random phase-pinning field. The range of the created short-range order seems to be too large to be directly observed by conventional neutron scattering and x-ray spectroscopy. At the same time the impurities induce random changes in the interaction constants, which alter T_I. It is not yet very clear which effect, the random field or the random interactions, is dominant. Recent studies in pure and mixed $[Rb_{1-x}K_x]_2ZnCl_4$ (Ref. 9) and $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$ (Ref. 10) show that even the smallest amount of doping increases the I-P transition temperature T_I and considerably decreases the incommensurate-to-commensurate (I-C) transition temperature T_C. Discrete-lattice-pinning effects should be ignored very close to T_I, as the strength of the discrete-lattice pinning[11] is $\propto\exp(-\xi/a_0)$ where ξ is the width of the soliton and a_0 the lattice constant. In the high-temperature part of the incommensurate phase where the plane-wave modulation limit is valid, the phase of the modulation wave consists of very thick overlapping solitons.[2,12]

According to the existing theoretical models, the main effect of impurity-induced phase distortions is the "melting" of the incommensurate lattice.[13] We may then assume that two completely different mechanisms result in melting effects: (i) Thermal depinning due to large thermal fluctuations of the modulation wave. (ii) Impurity-induced phase distortions. It is not yet quite clear which of the two mechanisms is dominant. It may be that in pure systems floating effects dominate, but by increasing the impurity concentration random impurities should play a more significant role in the melting mechanism. In order to clarify this question we decided to investigate nominally pure and mixed $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$ with a controlled amount of $NH_4{}^+$ ions acting as random impurities. The measurements have been done very close to the I-P transition and with a very high-temperature resolution.

II. EXPERIMENT

The method for this investigation is ^{35}Cl NQR spectroscopy. The measurements were done using Fourier-transformed spectra on single crystals of $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$ with different impurity doping, $x=0.00$ (nominally pure crystal), $x=0.01$, and $x=0.04$. Spin-echo absorption spectra were used, and at higher impurity concentrations 10 000 accumulations were necessary in order to improve the signal-to-noise ratio. The temperature stability was better than 0.02 K over the measured period.

III. RESULTS AND DISCUSSION

The temperature dependence of the Cl(1) NQR frequencies as a function of temperature for the different crystals is shown in Figs. 1(a), 2(a), and 3(a). As was reported in our earlier work,[14] for pure crystals of Rb_2ZnCl_4, ν_Q vs T of Cl(1) slowly increases with decreasing temperature, and at $T_I = 29.40\,^{\circ}C$ changes its slope down to temperature $T_S = 28.20\,^{\circ}C$, where the typical onset of the incommensurate spectrum is shown with the characteristic edge singularities. Here we notice that the change of the slope is accompanied by an inhomogeneous broadening which starts immediately below T_I, although the splitting is at a lower temperature T_S. The transition temperature T_I is then demonstrated by the broadening of the sharp paraelectric line [Fig. 1(b)]. We may say that the region between T_I and T_S represents a thermally depinned incommensurate phase due to the floating of the modulation wave. The large thermal fluctuations average out, by motion, the line splitting and we have thus only one line. The change of the slope can be explained by a shift of the center of gravity of the motionally averaged spectrum.[1,6,14] By increasing the amount of impurities we observe that the region between T_I and T_S, the averaged-out incommensurate line, is increased. From Fig. 2(a) we see that for even a very modest doping ($x = 0.01$) the onset of long-range order (characterized by the NQR splitting) is prevented for about 3 °C more than in the nominally pure crystal. Here $T_I = 29.90\,^{\circ}C$ and $T_S = 25.70\,^{\circ}C$. For even larger doping ($x = 0.04$) the effect is more pro-

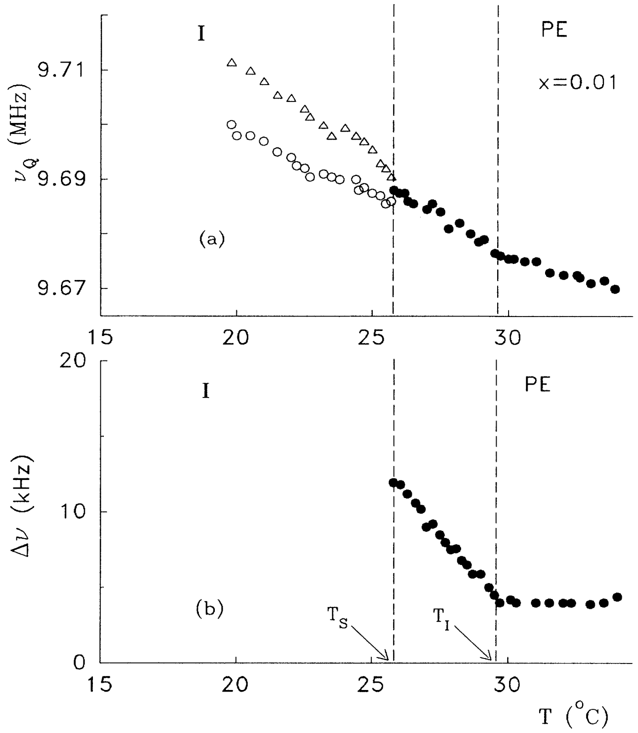

FIG. 2. (a) Temperature dependence of the Cl(1) NQR frequencies of $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$ for $x = 0.01$ close to T_I. (b) Inhomogeneous broadening of the Cl(1) NQR line close to T_I.

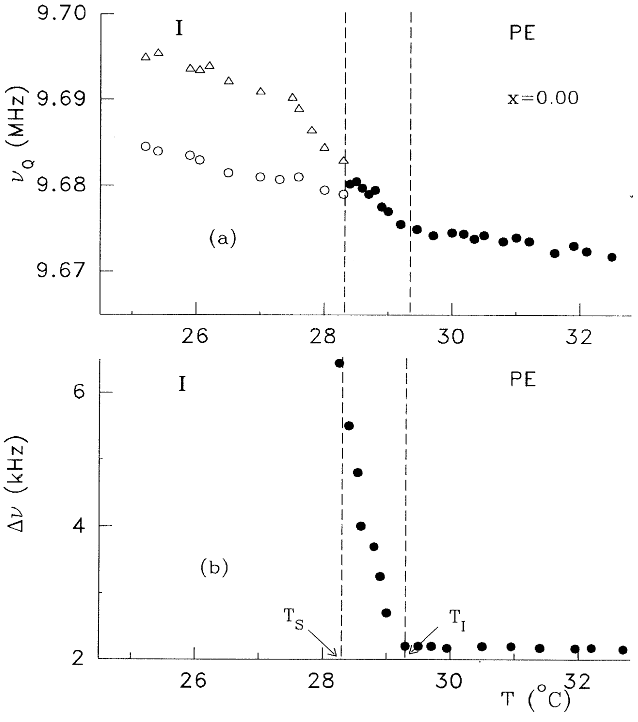

FIG. 1. (a) Temperature dependence of the Cl(1) NQR frequencies of $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$ for $x = 0.00$ close to T_I. (b) Inhomogeneous broadening of the Cl(1) NQR line close to T_I.

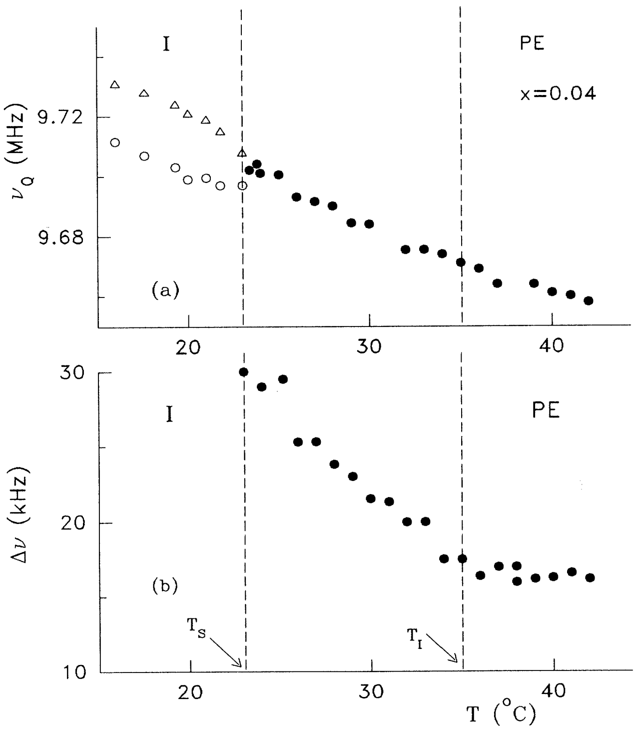

FIG. 3. (a) Temperature dependence of the Cl(1) NQR frequencies of $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$ for $x = 0.04$ close to T_I. (b) Inhomogeneous broadening of the Cl(1) NQR line close to T_I.

nounced and the region from T_I to T_S extends for about 12 °C ($T_I = 35.40\,^\circ\mathrm{C}$ and $T_S = 23.15\,^\circ\mathrm{C}$). In addition, we observe that by increasing the doping (i) the shift of the paraelectric line away from ν_0 and towards $\nu_0 + \nu_2$ is reduced, and (ii) the transition at T_I is not as sharply defined as in the pure case. We also must note that the phase-fluctuation singularity in all the measured samples is a continuation of the high-temperature paraelectric line (ν_0). From Figs. 1(b) to 3(b) we see that the inhomogeneous broadening of the NQR lines begins immediately below T_I: in addition, we observe that impurities introduce a broadening also in the sharp paraelectric NQR line above T_I where the lines are mostly homogeneously broadened ($\Delta\nu \cong 1/\pi T_2$).

IV. CONCLUSION

The above experimental data show that impurities prevent the onset of incommensurate long-range order. The higher the doping, the lower the temperature at which this long-range order is established. In earlier NMR experimental work[1,15] a coexistence of a narrow line with the broadened inhomogeneous frequency distribution was observed. This was explained as a result of the coexistence of floating regions and regions where the modulation wave was static. In the present experiment on Rb_2ZnCl_4 this "central paraelectriclike" line was not observed. This might be explained as follows: (i) The above-mentioned NMR measurements were done on ultrapure crystals, after zone refinement, while in the present NQR experiment the crystal is as mentioned a nominally pure one. This additionally supports the assumption that impurities even in the slightest concentration influence the behavior of incommensurate systems. (ii) The coexistence of the two regions was observed, as far as we know, only in certain systems and in optically clear and relatively fresh crystals. After use the quality of the crystals was, as reported, decreased and the sharp lines became unobservable.[1] (iii) in Rb_2ZnCl_4 at T_S —the temperature where the splitting of the lines start —the central line is not sharp but broad, small, and thus hidden in the noise. Further experiments on both doped and ultrapure crystals with one- and two-dimensional NMR and NQR are needed to find a definite answer to the problem.

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