Elementary Excitations in Order-Disorder Systems Studied by NQR *

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The ^{35}Cl spin-lattice and spin-spin relaxation times T_1 and T_2 as functions of temperature and impurity concentration were analytically calculated and experimentally verified for the incommensurate phase of $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$. The results agree with the theoretical predictions for both the amplitude and Goldstone modes of fluctuations.

I. Introduction

NQR and NMR methods allow for the investigation of incommensurately modulated structure because the resonance frequencies change in space in such a way that they reflect the variation of the incommensurate (I) modulation. Much work has been carried out on the steady state of these systems, but dynamical studies are limited [1, 2]. The NQR spin-lattice relaxation time T_1 has been studied by us and other groups [3–5] in Rb_2ZnCl_4 at the Cl anion position. For the homogeneous linewidth (spin-spin relaxation time T_2), the only information available concerns pure crystals of the A_2BX_4 family [6–8]. In continuation of our previous investigation on the elementary excitations of these systems we decided to study $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$, where $(NH_4)^+$ acts as an impurity ($x=0.00$, $x=0.01$, $x=0.04$), as a function of temperature.

II. NQR Spectra of Incommensurate Systems

Extensive line shape calculations of (I) systems have been done for several compounds of the A_2BX_4 family [1, 2]. In phase (I), where the nuclei are displaced and the translational periodicity is lost, the usually sharp NQR lines result in a quasi-continuous frequency distribution., In the local approximation, the NQR frequencies change as a function of the nuclear displacement $u(z)$ as:

$$\nu = \nu\,[u(z)]\,, \tag{1}$$

where

$$u(z) = A\cos\varphi(z)\,. \tag{2}$$

Here A is the amplitude of the frozen-in modulation wave, and the phase $\varphi(z)$ is, in the plane wave modulation (PWM) approximation, a linear function of the z coordinate in the direction of the modulation. The NQR line shape and EFG tensor were already described elsewhere [9]. Here we want to mention that, in order to calculate the line shape for Rb_2ZnCl_4 (Cl(1) nuclear site [3]), the following expression of the expansion of the quadrupolar frequencies in terms of the order parameter was used:

$$\nu = \nu_0 + \nu_1\cos\varphi + \nu_2\cos^2\varphi\,. \tag{3}$$

Here, the first order (linear) term was taken equal to zero ($\nu_1=0$). This condition, otherwise right for an NMR experiment, only partially fits our NQR experimental data for Rb_2ZnCl_4. In order to clarify this problem, we calculated theoretically the line shape for an NQR measurement and for the A_2BX_4 family at the X(4) nuclear site [10]. According to these calculations for Rb_2ZnCl_4 and for this special nuclear ^{35}Cl ($I=3/2$) site, the expansion of the quadrupolar frequencies, namely the ν_Q, is given as

$$\nu_Q = (\nu_0 + \nu_2\cos^2\varphi + \nu_4\cos^4\varphi)^{1/2}, \tag{4}$$

where ν_0 is equal to the frequency of the unperturbed paraelectric line and

$$\nu_2 = a_1(T_I - T)^{2\beta}, \quad \nu_4 = a_2(T_I - T)^{2\beta}. \tag{5}$$

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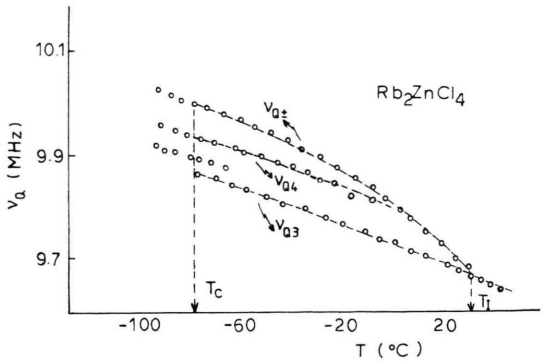

Fig. 1. Temperature dependence of the experimental (points) and calculated (dashed) values of the ^{35}Cl NQR frequencies in a nominally pure compound.

Finally, after appropriate calculations [10], singularities will appear at the following NQR frequencies:

(i) for $X=\cos\varphi=0$,
$\nu_{Q3}=\nu_0^{1/2}$,

(ii) for $X=\cos\varphi=\pm 1$,
$\nu_{Q\pm}=(\nu_0+\nu_2+\nu_4)^{1/2}$, (6)

(iii) for $X=\cos\varphi=(|\nu_2|/2\nu_4)^{1/2}$,
$\nu_{Q4}=(\nu_0-|\nu_2|^2/4\nu_4)^{1/2}$ if $\nu_2<0$ and $|\nu_2|/2\nu_4<1$.

We therefore conclude that for this particular case of quadrupolar nuclei, the expansion of NQR frequencies in powers of the order parameter has only even terms in the square root. This is in agreement with the experimental results [3], and as a consequence, at the extreme nuclear displacements $X=\pm 1$ we have only one singularity $(\nu_{Q+})=(\nu_{Q-})$. For the case where $X=0$, a second singularity exists, which is denoted as (ν_{Q3}), and finally, under certain conditions, a third one will appear, (ν_{Q4}) (see Figure 1).

III. Elementary Excitations

1. Spin-Lattice Relaxation Time T_1

It is well known [4, 5, 11, 12] that the PWM approximation is appropriate only for the high temperature part of phase (I). Inside this phase, the soft mode splits in two modes (i) the optic-like amplitude mode (from now on the term amplitudon will be used in the text) which relaxes via amplitude fluctuations of the modulation wave, and (ii) the acoustic-like Goldstone mode (from now on phason) which relaxes via phase fluctuations of the modulation wave, has a linear dispersion and is gapless in the absence of any pinning of the modulation wave [1].

$$\omega_\Phi^2=\varkappa^2 k^2. \tag{7}$$

ω_Φ is the phason frequency, $k=q-q_s$, and $\varkappa$ is a constant. In the presence of impurities, a gap Δ_Φ is introduced in the phason spectrum. The modulation wave then is locked to the underlying lattice and (7) transforms to [1]

$$\omega_\Phi^2=\Delta_\Phi^2+\varkappa^2 k^2. \tag{8}$$

Similarly, for the amplitudon spectrum we have

$$\omega_A^2=\Delta_A^2+\varkappa^2 k^2. \tag{9}$$

Assuming that the order parameter fluctuation modes are overdamped, then the relaxation rate will be dominated by the direct one-phonon process. In this case T_1^{-1} is calculated as [10]

$$\begin{aligned}T_1^{-1}=24E^2[&1/4(V_{xx}^{(2)}A\cos\varphi)^2+1/4(V_{yy}^{(2)}A\cos\varphi)^2\\&+(V_{xz}^{(2)}A\cos\varphi)^2+(V_{xy}^{(1)})^2+(V_{yz}^{(1)})^2]\\&\times[\cos^2\varphi J_A+\sin^2\varphi J_\Phi].\end{aligned} \tag{10}$$

V_{ij}^k are the EFG tensor elements ($k=1, 2$ and $i, j=x, y, z$) and J_A, J_Φ are the spectral densities of the autocorrelation function of the EFG tensor fluctuations for the amplitudon and phason modes, respectively. For the sake of simplicity we neglect here a small dipolar contribution, which becomes important only in the case of the phason induced spin-spin relaxation time $T_{2\Phi}$ [8]. Taking now into consideration (4) and (5), we see that for the line (ν_{Q3}), where $X=0$, T_1^{-1} will be determined by phasons, whereas for the $(\nu_{Q\pm})$ line, where $X=\pm 1$, mainly by amplitudons. For the (ν_{Q4}) singularity which appears at $T\cong 0\,^\circ C$, X becomes temperature dependent, takes values between 1 and 0.6, and therefore we can say that this singularity relaxes via a mixture of phasons and amplitudons. However, since the lower values of X are valid close to the transition temperature T_c, where the PWM approximation starts to break down and commensurate (solitons) lines appear which coincide with the singularities $(\nu_{Q\pm})$ and (ν_{Q4}), we may assume that the (ν_{Q4}) singularity is also relaxing mainly by amplitudons.

Refering now to the T_1's of the phason $T_{1\Phi}$ and amplitudon T_{1A}, J_Φ and J_A are known to be given by the relations [1, 2, 4]

$$J_\Phi=C\Gamma_\Phi/\Delta_\Phi,\quad J_A=C\Gamma_A/\Delta_A. \tag{11}$$

C is a constant and Γ_Φ, Γ_A are the phason and amplitudon damping constants, respectively. Taking into

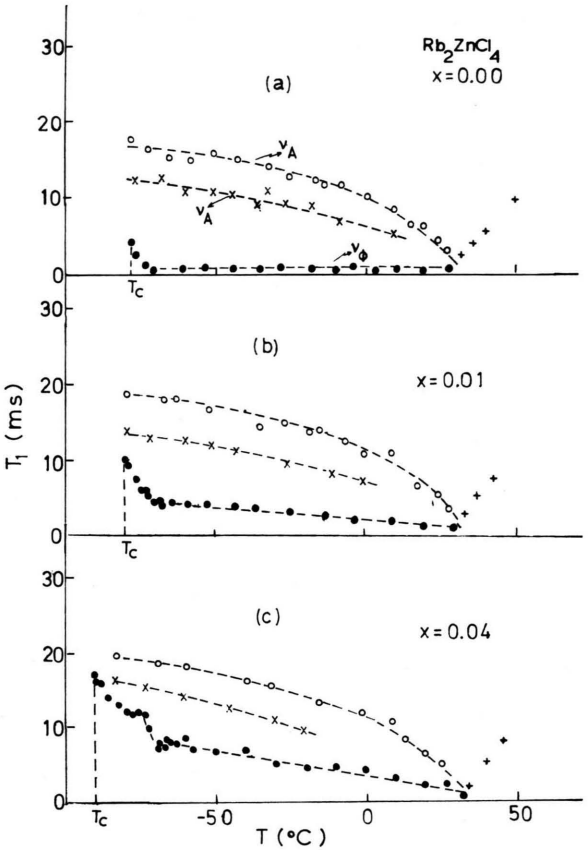

Fig. 2. Temperature dependence of the ^{35}Cl spin-lattice relaxation time T_1 at the phason relaxed singularity (ν_{Q3}) and the amplitudon relaxed singularities ($\nu_{Q\pm}$), (ν_{Q4}) for the pure compound (a) and the mixed crystals for $x=0.01$ (b) and $x=0.04$ (c).

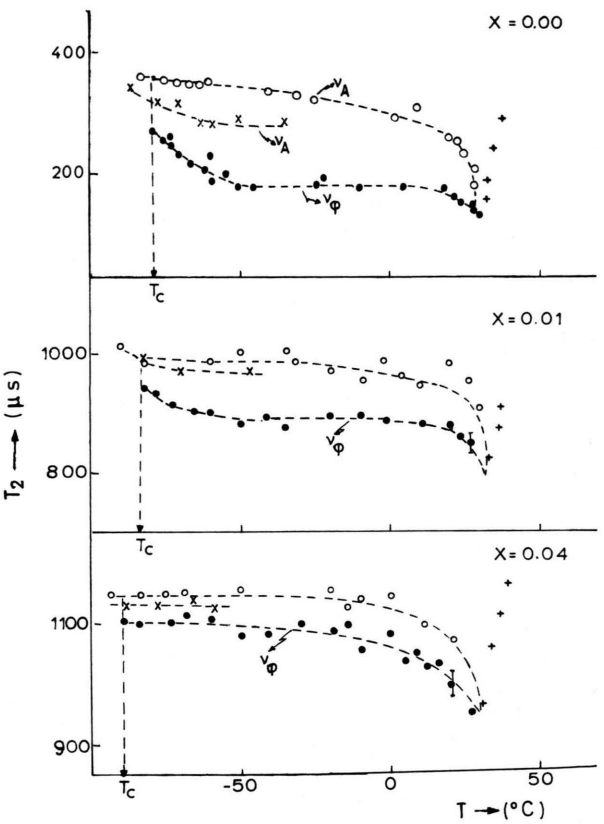

Fig. 3. Temperature dependence of the ^{35}Cl spin-spin relaxation time T_2 at the phason relaxed singularity (ν_{Q3}) and the amplitudon relaxed singularities ($\nu_{Q\pm}$), (ν_{Q4}) for the pure compound and the mixed crystals with $x=0.01$ and $x=0.04$.

consideration (8), (9), (10), and (11) we may conclude that $T_{1\Phi}$ and T_{1A} can be written as

$$T_{1\Phi}^{-1} = 24E^2[(V_{xy}^{(1)})^2+(V_{yz}^{(1)})^2] \times [C\Gamma_\Phi/\Delta_\Phi], \tag{12}$$

$$T_{1A}^{-1} = 24E^2[1/4(V_{xx}^{(2)})^2+1/4(V_{yy}^{(2)})^2+(V_{xz}^{(2)}A)^2 + (V_{xy}^{(1)})^2+(V_{yz}^{(1)})^2] \times [C\Gamma_A/\Delta_A]. \tag{13}$$

For the pure compounds, according to (12), $T_{1\Phi}$ is temperature independent due to the fact that Δ_Φ is temperature independent in the part of phase (I) where the PWM approximation is valid. On approaching the locking transition temperature T_c, in the narrow-soliton region, the PWM model starts to break down, and in the resulting chaotic phase we are expecting the following:

Very close to T_c we observe steps in the values of $T_{1\Phi}$. These steps indicate the locking of the modulation wave for certain temperature intervals and the formation of steps in the soliton density n_s as a function of temperature.

For T_{1A}, according to (13) and the relation $\Delta_A = \sqrt{2a(T_I-T)}$ where a is defined in [2], we see that it is temperature dependent through the whole phase (I) [2].

For the mixed compounds the phason gap Δ_Φ becomes temperature and impurity concentration dependent according to the relation [3, 14]

$$\Delta_\Phi \propto |T_I-T|^{\beta(n-2)}\sqrt{n_i}. \tag{14}$$

Here n_i is the impurity concentration. The definition of β and n can be found in [3, 14]. The above relations show that for mixed crystals, $T_{1\Phi}$ becomes temperature dependent even in the PWM approximation.

2. Spin-Spin Relaxation Time T_2

As it was shown in our earlier work [6, 8] the spin-spin relaxation mechanism in the (I) region behaves exactly as T_1 (10). The analytically calculated T_2 was found to be

$$1/T_2 = \text{const}\,[\cos^2\varphi\, J_A + \sin^2\varphi\, J_\Phi]\,. \qquad (15)$$

The constant is a function of the EFG tensor elements, the dipolar tensor elements and the angle φ.

IV. Experimental Results and Discussion

All our experimental work was performed on a MATEC pulsed NQR spectrometer with a coherent pulse technique, based on the storage of the free-induction decay signals and Fourier transformation. T_1 and T_2 were measured using the $\pi/2-\tau-\pi/2$ and $\pi/2-\tau-\pi$ pulse sequence, respectively. The temperature accuracy was $\cong 0.1$ K.

Figures 2 and 3 show the experimental data at the different edge singularities (ν_{Q3}), ($\nu_{Q\pm}$) and (ν_{Q4}). According to the theoretical treatment, the relaxation process for the singularity, (ν_{Q3}) is governed mainly by phasons, while for the singularities ($\nu_{Q\pm}$) and (ν_{Q4}) by amplitudons. As we can see, T_2 shows the same behaviour as T_1 for the same compound and the whole temperature region. This is to be expected from the theory. Through the whole phase (I), for the nominally pure compound, both T_1 and T_2, measured on the singularity (ν_{Q3}) stay short, temperature independent and increase only in the region close to T_c, where the narrow solitons start to appear (Figures 2a and 3a). T_1 and T_2 of the amplitudon relaxing singularities on the other hand show a temperature dependence and the behaviour expected from the theory.

For the mixed compounds (Fig. 2b, 2c, 3b and 3c) we see that for (ν_{Q3}) both T_1 and T_2 become temperature dependent in the whole (I) region, in agreement with the theoretical predictions. Finally the fact that T_1 and T_2 of the singularity (ν_{Q4}) are slightly affected from the impurities and are the same as those of the singularity ($\nu_{Q\pm}$), is an extra support for our assumption that also the singularity (ν_{Q4}) is relaxed mainly by amplitudons. This work is still in progress.

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