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^{35}Cl spin-lattice relaxation and temperature-dependent phason gaps in substitutionally disordered incommensurate systems

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The spin-lattice relaxation time T_1 of the Goldstone mode has been studied as a function of temperature and impurity concentration in pure and mixed $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$. The results clearly show that close to the "lock-in" transition T_1 becomes temperature dependent, reflecting the temperature dependence of the acousticlike branch in the multisoliton lattice. For higher concentration of impurities, steps in the T_1 as a function of temperature show that the wave vector **q** locks for certain temperature intervals. The phason gap $(\Delta_\phi)_{op}$ of the opticlike branch was calculated.

I. INTRODUCTION

In the last few years several attempts have been made by us and other groups[1–4] to verify experimentally the existence of a devil's staircase (DSC) in incommensurate (I) systems. Many of these systems provide a good illustration of the DSC. In our earlier work[3] it was shown that very close to the "lock-in" transition temperature T_c, where a metastable chaotic phase appears, a DSC might exist.[4] Steps were also recently observed in the soliton density of Rb_2ZnCl_4 as a function of temperature.[5] In order to provide some additional information for solving the problem, we measured the spin-lattice relaxation time T_1 for the Goldstone mode (from now on, the term "phason" will be used in the text) as a function of temperature and impurity concentration in $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$. Our aim was to examine the region very close to T_c, where the multisoliton lattice (MSL) appears. In this region, the chaotic phase which forms due to the pinning of the discommensurations—solitons—to the discrete lattice and the impurities, will be more pronounced for higher impurity concentration, and as a consequence the steps of a DSC might be observable.[3,5]

II. THEORY

The plane-wave modulation (PWM) limit is appropriate for the high-temperature part of the I phase. Inside the I phase the soft mode splits in two modes: (i) the opticlike amplitude mode (amplitudon) and (ii) the acousticlike phason which has a linear dispersion and is gapless in the absence of any pinning of the modulation wave:

$$\omega_\phi^2=\kappa^2k^2\,, \tag{1}$$

where ω_ϕ is the phason frequency, $\mathbf{k}=\mathbf{q}-\mathbf{q}_s$, and κ is a constant. The presence of impurities produces a gap Δ_ϕ in the phason spectrum, which locks the modulation wave to the underlying lattice.[6] In this case relation (1) transforms to

$$\omega_\phi^2=\Delta_\phi^2+\kappa^2k^2\,. \tag{2}$$

Within the PWM model and for the case where the phason gap Δ_ϕ exceeds the resonance frequency ω_0, one finds that the nuclear spin-lattice relaxation time of the phase fluctuations $T_{1\phi}$ is equal to[6]

$$T_{1\phi}=\Delta_\phi/C\Gamma_\phi\,. \tag{3}$$

C is a constant proportional to the square of the fluctuating electric-field-gradient tensor components and Γ_ϕ is the phason damping constant which remains finite in the long-wavelength limit. A nominally pure crystal has a temperature-independent phason gap Δ_ϕ, which means that $T_{1\phi}$ is also temperature independent.[7,8] In the weak-pinning limit and for the case of a mixed crystal, the phason gap becomes temperature and impurity-concentration dependent.[9]

On approaching the lock-in transition temperature T_c, in the MSL, this model starts to break down and the $T_{1\phi}$ increases becoming thus, even in the case of a pure crystal, temperature dependent.[10] The explanation is that in this region the phason branch splits into "acousticlike" and "opticlike" parts. The dispersion relation for the acousticlike part is, for $\mathbf{k}\rightarrow 0$, given by

$$(\omega_\phi)_{ac}^2=(\Delta_\phi)_{ac}^2+\mathcal{K}k_\perp^2+\mathcal{K}_zk_z^2\,, \tag{4}$$

where $\mathcal{K}_z=\mathcal{K}'(T-T_c)$ and for the opticlike part is

$$(\omega_\phi)_{op}^2=(\Delta_\phi)_{op}^2+\mathcal{K}[k_\perp^2+(k_z-\pi/b)^2]\,, \tag{5}$$

where $(\Delta_\phi)_{ac}$ and $(\Delta_\phi)_{op}$ are the corresponding phason gaps and $\mathcal{K}$ is a constant. The acousticlike part corresponds to $|k_z|\leq\pi/b$ and the opticlike part to $|k_z|\geq\pi/b$. Here b is the intersoliton distance and for $T\rightarrow T_c^\dagger$, $b\rightarrow\infty$.

The acoustic phason-induced relaxation time $(T_{1\phi})_{ac}$, for the case where the phason gap $(\Delta_\phi)_{ac}$ exceeds the resonance frequency ω_0, increases on approaching T_c in a similar way as the intersoliton distance b

$$(T_{1\phi})_{ac}=[8(\Delta_\phi)_{ac}^4b]/(\Lambda^2\Gamma_\phi)\,. \tag{6}$$

Λ is an effective maximal value of the wave vector **q**. The opticlike phason contribution is given by the relation[11]

$$(T_{1\phi})_{op}=(\Delta_\phi)_{op}/C\Gamma_\phi\,. \tag{7}$$

In the MSL, close to the transition temperature T_c

(strong pinning case), $(\Delta_\phi)_{ac}$ is temperature independent and is related to the concentration of the impurities by the relation[12]

$$(\Delta_\phi)_{ac} \propto n_i^{1/3} . \tag{8}$$

This means that the phason-induced spin-lattice relaxation contribution $(T_{1\phi})_{ac}$ is according to relation (6) temperature dependent mainly via the intersoliton distance b.

The deviation of the average wave vector q from q_c, the wave vector of the commensurate (C) phase, is inversely proportional to the intersoliton distance b (Ref. 4), and the order parameter of the I to C transition is the phase soliton density n_s which vanishes on approaching T_c from above.[6,13] From the relation between the soliton density n_s and the wave vector[4,14]

$$n_s \propto q - q_c \propto 1/b , \tag{9}$$

we deduce that if the wave vector "locks" at different values for certain temperature intervals, this should show up directly in the soliton density n_s and the phason-induced $(T_{1\phi})_{ac}$ will exhibit "steps."

III. EXPERIMENTAL RESULTS AND DISCUSSION

The method used for this investigation is the ^{35}Cl nuclear quadrupole resonance spectroscopy. The measurements were done on single crystals of $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$ for impurity concentrations $x=0.00$, 0.01, 0.04. The small admixture of $(NH_4)^+$ acts here as an impurity.

Figure 1 shows the temperature dependence of the I splitting for the ^{35}Cl NQR lines for $x=0.00$, 0.01, 0.04 for only one Cl site: namely, the one with the highest NQR frequency. This choice was made because the quasicontinuous I spectrum covers only a range of 100 kHz and not 500 kHz as the other lines.[8,15] For this Cl site we have three edge singularities. The $\nu_\pm$ depend critically on the order parameter as $\Delta\nu \propto (T_I - T)^\beta$ and their relaxation process is governed mainly by amplitude fluctuations. The singularity ν_3 continues the paraelectric behavior ν_0 and corresponds to $\cos(\phi)=0$ in the development of the frequency (local case),

$$\nu = \nu_0 + \nu_1 \cos(\phi) + \nu_2 \cos^2(\phi) + \cdots , \tag{10}$$

relaxing thus via phasons.[8,11] Its frequency and width do not depend on temperature and it does not continue in the C phase.[8] In the MSL, ν_3 relaxes by phase fluctuations of the acousticlike part of the phasons. A new C line appears a few degrees above T_c, indicating that the soliton lattice becomes observable. This new line relaxes above T_c by phase fluctuations of the opticlike part of the phason.

For the above mixed systems the NQR line shape is not affected by the small amount of doping. The transition temperature T_I is shifted to higher values and the lock-in transition temperature T_c to lower values. These results are in agreement with the NMR measurements on the ^{87}Rb nuclear sites.[9]

The doping has a larger effect on the phason-induced spin-lattice relaxation time $T_{1\phi}$ (Fig. 2). As the measurements of the spin-lattice relaxation time were done at the

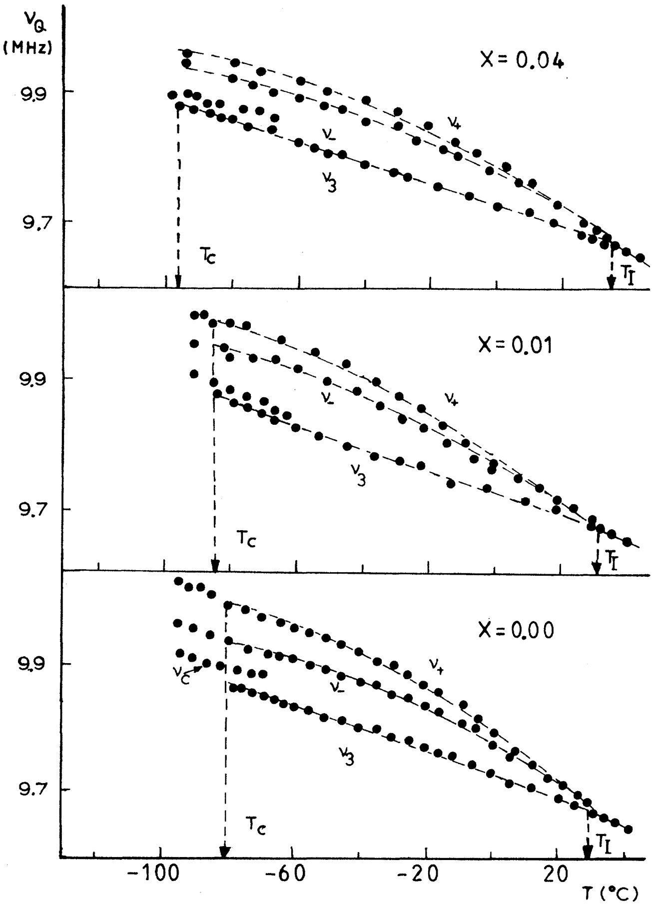

FIG. 1. Temperature dependence of the experimental values of the NQR lines in $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$ for different x values.

phason relaxing edge singularity ν_3, the term $T_{1\phi}$ in the MSL, actually means $(T_{1\phi})_{ac}$. In the pure crystal ($x=0.00$) the $T_{1\phi}$ is temperature independent and very low, 0.6 msec as predicted from the PWM model. Only very close to the transition temperature $T_c (T-T_c \cong 6\,°C)$ does the $T_{1\phi}$ becomes temperature dependent and show the formation of the acousticlike and opticlike branch in the MSL. For $x=0.01$, $T_{1\phi}$ increases nearly linearly from T_I down to $\cong -62\,°C$, where it starts increasing very fast until the lock-in transition temperature T_c. The formation of steps cannot be excluded between $T \cong -65\,°C$ and $T \cong -78\,°C$. For $x=0.04$, $T_{1\phi}$ increases again nearly linearly from T_I down to $T \cong 60\,°C$ where the MSL starts to appear. With further decreasing the temperature, $T_{1\phi}$ remains constant for an interval of $\cong 10\,°C$ (until $T \cong -70\,°C$), then it increases steeply until $T \cong -72\,°C$, then again remains constant for $\cong 8\,°C$ ($T \cong -80\,°C$), and finally increases until T_c where it vanishes, as predicted by the theory.[10] As far as we know, this is the first time that $T_{1\phi}$ steps are observed.

According to relations (6) and (9) the observed steps of $T_{1\phi}$ versus temperature, indicate the "locking" of the modulation wave at certain temperature intervals and the

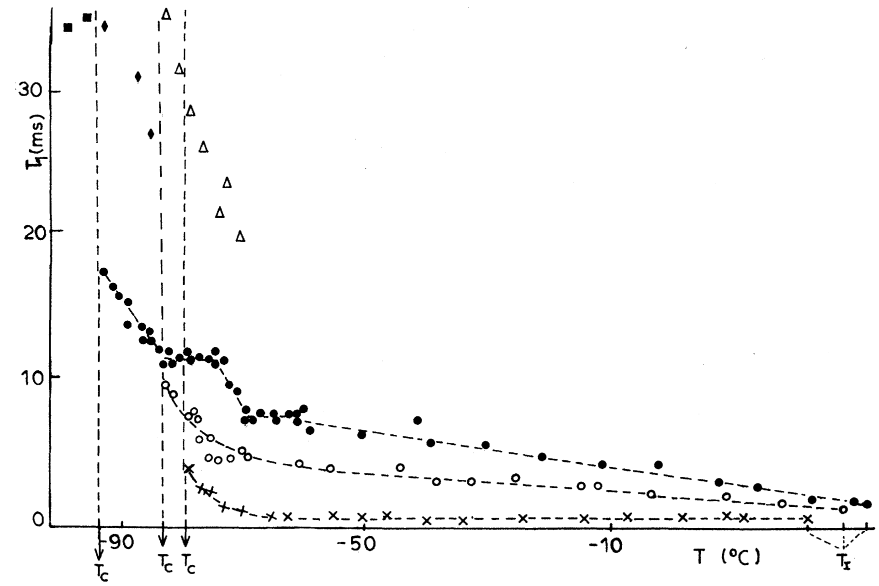

FIG. 2. Temperature dependence of the phason-induced ^{35}Cl spin-lattice relaxation time $T_{1\phi}$ at the ν_3 singularity in incommensurate $[Rb_{1-x}(NH_4)_x]_2ZnCl_4$ for $x=0.00$ (×), $x=0.01$ (○), and $x=0.04$ (●). T_1 measurements were also made on the commensurate (soliton) ν_c line for $x=0.00$ (△), $x=0.01$ (♦), and $x=0.04$ (■). Only for $x=0.00$ (△) do the measurements also cover the I phase due to the better signal-to-noise ratio.

formation of steps in the soliton density n_s as a function of temperature, thus forming in both cases a DSC.[3] As a matter of fact, the locking of the wave number q of the modulation wave has already been experimentally observed,[1,2] and the existence of steps in the soliton density n_s was recently reported.[3,5]

The following should be noted here.

(i) The transition temperature T_c is very sharp and well defined and the C "lines" are narrow and strong only in the nominally pure crystal with $x=0.00$. In crystals with higher x, even as modest as 0.01, the transition to the C phase starts to be difficult and is destroyed more as x increases. This shows that the low-temperature (I-C) transition at T_c is distorted with even the smallest amount of impurities. With a relatively higher amount of impurities the transition will be completely destroyed and the system will remain in the I state. This is in agreement with other measurements.[9,16]

(ii) Knowing that the $(T_{1\phi})_{op}$ of the C (soliton) line corresponds to the optic part of the phason branch, and that in the case of a pure crystal the phason gap Δ_ϕ is in the PWM approximation temperature independent and equal[8] to 0.90×10^{10} sec^{-1}, then from relations (3) and (7) we can determine $(\Delta_\phi)_{op}$ for different temperatures: $(\Delta_\phi)_{op}\cong3.00\times10^{11}$ sec^{-1} at $T=-70\,°$C; at $T=-75\,°$C, $(\Delta_\phi)_{op}\cong3.75\times10^{11}$ sec^{-1}; and finally at $T=79\,°$C, $(\Delta_\phi)_{op}\cong4.35\times10^{11}$ sec^{-1}. From the above measurements we observe that very close to T_c the optic-like phason gap $(\Delta_\phi)_{op}$ increases, reaching smoothly the value Δ_c of the gap in the C phase. The measurements were performed only for the $x=0.00$ case due to the better signal-to-noise ratio.

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