Commensurability and Defect-Induced Phason Gaps in Incommensurate Systems

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The phason energy gap has been observed to increase on going from the incommensurate to higher-order commensurate phases in the "devil's staircase" compound $[N(CH_3)_4]_2ZnCl_4$. The gap was determined via the phason-induced ^{14}N spin-lattice relaxation contribution, which was obtained from the variation of the effective spin-lattice relaxation rate over the inhomogeneous incommensurate frequency distribution. Here, as well as in Rb_2ZnCl_4 and Rb_2ZnBr_4, the phason gap in the incommensurate phase is defect induced.

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The theory of incommensurate (I) systems[1] predicts the existence of a gapless, acousticlike phason branch in the I phase in addition to an opticlike amplitudon branch. The phason represents the sliding of the incommensurate modulation wave and corresponds to the Goldstone mode recovering the broken translational periodicity of the I phase. Discrete lattice effects[2] in the complete devil's staircase model[3] and impurities[4] may produce a locking of the modulation wave to the underlying lattice and introduce a gap into the phason spectrum.

Whereas amplitudons[5] have been observed in many I systems, the available data[6] on phasons are rather scarce and inconclusive as to the existence of a gap Δ_ϕ in the phason spectrum:

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

where $\mathbf{k} = \mathbf{q} - \mathbf{q}_I$. In particular, the phason dynamics of systems exhibiting more than one stair in the devil's staircase has not been investigated up to now, to the best of our knowledge.

Here we wish to report the observation of a phason gap in $[N(CH_3)_4]ZnCl_4$ in the incommensurate phase. The gap increases on going from the incommensurate to higher-order commensurate (C) phases in this crystal where an incomplete devil's staircase, implying a gapless phason, has been suggested[7,8] to exist. The gap has been determined via the phason-induced ^{14}N NMR spin-lattice relaxation contribution ($T_{1\phi}^{-1}$) which was obtained from a measurement of the variation of the effective spin-lattice relaxation rate T_1^{-1} over the inhomogeneous incommensurate frequency distribution. This method is quite generally applicable and represents a highly sensitive technique for the determination of the existence of a gap Δ_ϕ in the phason spectrum even as small as the nuclear Larmor frequency $\omega_L = 10^7$–10^8 Hz.

For direct one-phonon processes (which dominate the relaxation rate if the order-parameter modes are overdamped) one finds in the plane-wave modulation regime[9] a rather large, frequency-independent phason-induced spin-lattice relaxation rate,

$$T_{1\phi}^{-1} = C\frac{\pi}{2\sqrt{2}}\kappa^{-3/2}(\Gamma_\phi/\omega_L)^{1/2}, \qquad \Gamma_\phi \gg \omega_L \geqslant \Delta_\phi, \tag{2}$$

if the phason gap is smaller than the Larmor frequency ω_L. Here C is a constant[9] 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[10] (in contrast to the acoustic modes) and is comparable with that of the soft mode at T_C (i.e., $\Gamma_\phi = 10^{11}$–10^{12} s^{-1}).

In the opposite case where the phason gap exceeds the Larmor frequency, the phason-induced $T_{1\phi}$ is much longer, frequency independent, and directly proportional to the phason gap Δ_ϕ:

$$T_{1\phi}^{-1} = C(\pi/4)\kappa^{-3/2}\Gamma_\phi/\Delta_\phi, \qquad \Delta_\phi \gg \omega_L, (\Gamma_\phi\Delta_\phi)^{1/2}. \tag{3}$$

An expression analogous to (3) with Δ_ϕ replaced by the commensurability-induced phason gap Δ_C determines the spin-lattice relaxation rate $(T_1^{-1})_C$ in the higher-order C phases. A measurement of $T_{1\phi}^{-1}$ and $(T_1^{-1})_C$ thus enables one to express with the help of Eq. (3) the phason gap in the I phase in terms of the commensurability gap Δ_C:

$$\frac{(T_{1\phi})_I}{(T_1)_C} = \frac{(\Delta_\phi)_I}{(\Delta_\phi)_C}, \quad (\Delta_\phi)_I \gg \omega_L. \tag{4}$$

For a higher-order C phase with a unit cell $p = \frac{1}{2}n$ larger than that of the high-temperature phase the commensurability gap is predicted[10] to be of the form

$$\Delta_C^2 = K^2(\tfrac{1}{2}n)^2 A^{n-2}, \tag{5}$$

where $K(\frac{1}{2}n)$ turns out to be of order of a phonon frequency and $|A| \leq 1$ is the normalized amplitude of the modulation wave. Δ_C goes to zero as $n \rightarrow \infty$ (i.e., as the truly I phase is approached).

The amplitudon-induced spin-lattice relaxation rate T_{1A}^{-1} is obtained as

$$T_{1A}^{-1} = C(\pi/4)\kappa^{-3/2}\Gamma_A/\Delta_A, \tag{6}$$

where $\Delta_A = [2a(T_I - T)]^{1/2}$ in the mean-field approximation and represents the temperature-dependent energy gap in the amplitudon spectrum. Δ_A is of order of a phonon frequency at temperatures different from the paraelectric-incommensurate transition temperature T_I. Since $\Gamma_\phi \simeq \Gamma_A = \Gamma$ and $\omega_L << \Gamma \leq \Delta_A$, one finds

$$\frac{T_{1\phi}}{T_{1A}} = \frac{\Delta_\phi}{\Delta_A}, \quad \Delta_\phi >> \omega_L \tag{7}$$

and

$$\frac{T_{1\phi}}{T_{1A}} = \frac{(\omega_L \Gamma)^{1/2}}{\Delta_A} << 1, \quad \Delta_\phi \leq \omega_L \tag{8}$$

so that a measurement of $T_{1\phi}$ and T_{1A} in the I phase allows for a determination of the phason gap Δ_ϕ in terms of the amplitudon frequency Δ_A which can be easily determined.[5]

The temperature dependence of the quadrupole-perturbed ^{14}N nuclear magnetic resonance frequency for one of the two chemically nonequivalent nitrogen sites in $[N(CH_3)_4]_2ZnCl_4$ is shown in Fig. 1. The sharp paraelectric line is replaced by an incommensurate frequency distribution limited by two edge singularities immediately below $T_I = 23\,°C$, as predicted for a static plane-wave type modulation along one axis.[9] The fact that T_1^{-1} varies over the inhomogeneous incommensurate frequency distribution as strongly as shown in Fig. 2 indicates[9] the presence of phason and amplitudon contributions. Five "commensurate" lines are found in the first C phase[8] between $T_{C1} = 7\,°C$ and $T_{C2} = 3.5\,°C$ where the unit cell is five times larger ($c = 5c_0$) than in the paraelectric phase. In the second C phase[8] below T_{C2} where $c = 3c_0$ there are as expected only three C lines.

The temperature dependence of the positions of the two edge singularities in the I phase (Fig. 1) and the variation of the effective T_1 over the incommensurate frequency distribution (Fig. 2) cannot be described quantitatively within the usually used "local" model.[9] In this model the incommensurate shift of the resonance frequency of a given nucleus is assumed to depend only on the incommensurate displacement of that nucleus so that the effect of other nuclei is neglected. Similarly, the local model[9] neglects the fact that the real incommensurate displacement is a superposition of two components[11] out of phase by $\pi/2$. In the general case, we find[12] the spatial modulation of the resonance frequency in the I phase to be

$$\nu(x) = \nu_0 + \nu_1 \cos[\psi(x) + \tilde{\phi}] + \nu_2' + \nu_2 \cos^2\psi(x) + \cdots, \tag{9}$$

whereas $\tilde{\phi} = 0$ and $\nu_2' = 0$ in the "local" model.[9] Here $\psi(x)$ is a renormalized phase of the modulation wave, $\nu_0 = \text{const}$, $\nu_1 \propto A$, whereas ν_2 as well as ν_2' are proportional to A^2.

For the case shown in Figs. 1 and 2, $\nu_1 = 0$ by symmetry and, in the plane-wave and constant-amplitude approximations,[9] the frequency distribution $f(\nu)$

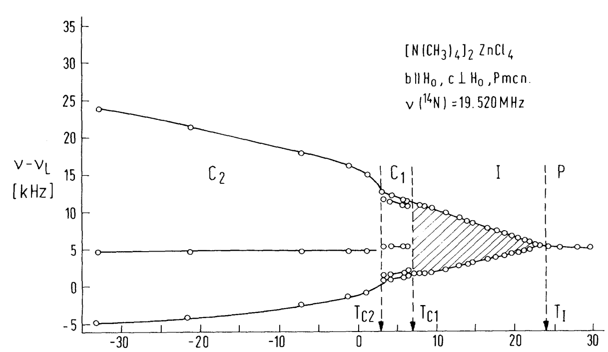

FIG. 1. Temperature dependence of one of the ^{14}N NMR frequencies in $[N(CH_3)_4]_2ZnCl_4$. The splitting between the two edge singularities in the I phase varies approximately as $\Delta\nu \propto A^2 \propto (T_I - T)^{2\beta}$ where $2\beta = 0.88 \pm 0.1$. The commensurate lines in the "soliton" region $T \geq T_{C1}$ are not shown.

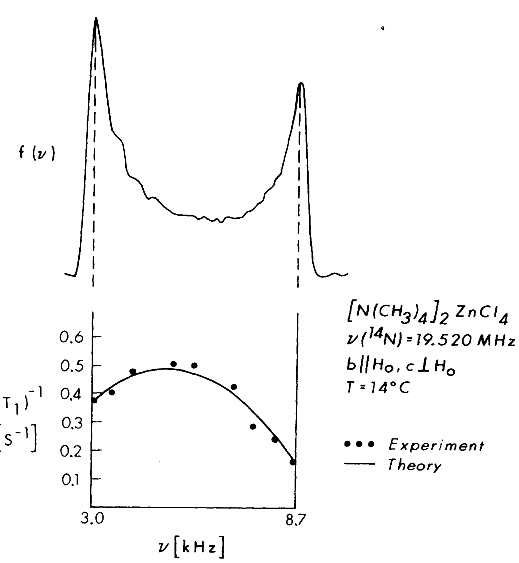

FIG. 2. Variation of the effective ^{14}N spin-lattice relaxation rate over the inhomogeneous incommensurate frequency distribution $f(\nu)$. The upper curve represents the line shape and the lower curve the relaxation rate.

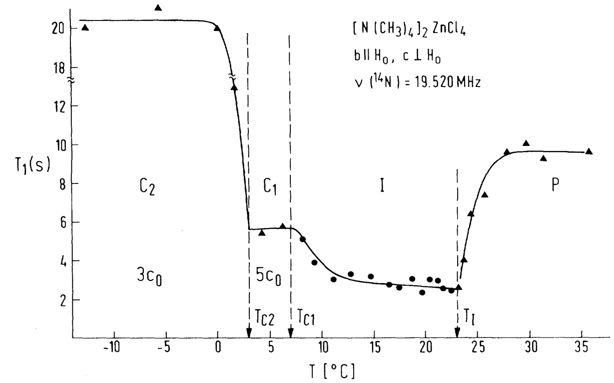

FIG. 3. Temperature dependence of the ^{14}N spin-lattice relaxation time. In the I phase, only the phason contribution $T_{1\phi}$ is shown. The increase in $T_{1\phi}$ in the low-temperature part of the I phase close to T_{C1} indicates the transition from the plane wave to the multisoliton lattice modulation regime.

$=\text{const}/(d\nu/dx)$ becomes

$$f(\nu)=\text{const}/(1-Z^2)^{1/2}, \tag{10}$$

where $Z=(\nu-\nu_0-\nu_2'-\frac{1}{2}\nu_2)/(\frac{1}{2}\nu_2)$. The variation of the effective T_1 over $f(\nu)$ is

$$T_1^{-1}=(K+Z)^2T_{1A}^{-1}+(1-Z^2)T_{1\phi}^{-1}, \tag{11}$$

where K is a constant equaling 1 in the local model. In deriving Eq. (11) we assumed that the electric-field-gradient fluctuations are spatially modulated in phase with the resonance frequencies. Expressions (10) and (11) well describe the data from Figs. 1 and 2. Expression (11), in particular, allows for a determination of T_{1A}^{-1} and $T_{1\phi}^{-1}$ from the measured frequency variation of T_1. The fit between the experimental and theoretical curves at $T=14\,°C$ shown in Fig. 2 yields $K=-0.18$, $T_{1A}^{-1}=0.26\ s^{-1}$ and $T_{1\phi}^{-1}=0.47\ s^{-1}$. An order-of-magnitude estimate[6] with $\kappa^2=0.4\times10^6\ m^2\ s^{-2}$ yields $T_{1\phi}=2.6(\Delta_\phi/\Gamma)$ s according to Eq. (3) and $T_{1\phi}\approx2.6(\omega_L/\Gamma)^{1/2}\approx10^{-2}$ s according to Eq. (2). The above data thus show that the observed phason-induced $T_{1\phi}$ is much longer than expected for a gapless phason so that we are forced to conclude that a gap exists and Eq. (3) is applicable.

The temperature dependence (Fig. 3) of the ^{14}N T_1 in $[N(CH_3)_4]_2ZnCl_4$ and of $T_{1\phi}$ in the I phase thus reflect for $T<T_I$ the temperature variation of the phason gap and demonstrate that the phason gap increases by a factor of 2 on going from the I to the $5c_0$ C phase and again by an additional factor of 4 on going into the $3c_0$ C phase, $(\Delta_\phi)_I:\Delta_{5c_0}:\Delta_{3c_0}=1:2:8$. As $\frac{1}{3}<|A|<\frac{1}{2}$ at the $5c_0\to3c_0$ transition the observed ratio $\Delta_{5c_0}/\Delta_{3c_0}=\frac{1}{4}$ is compatible with the predictions of Eq. (5). In Rb_2ZnCl_4 one similarly finds from the T_1 data[9] $(\Delta_\phi)_I:\Delta_{3c_0}\approx1:7$, whereas in Rb_2ZnBr_4 the T_1 data[9] suggest $(\Delta_\phi)_I:\Delta_{3c_0}=1:8$.

The presence of a gap in the I phase is as well demonstrated by the Larmor-frequency independence of $T_{1\phi}$. From Eqs. (1) and (7) or Eq. (3) and the values of κ, Γ, and C one can also estimate the actual magnitude of the gap in the I phase. The values one finds for the above systems are of the order of $(\Delta_\phi)_I\approx10^{11}$–$10^{12}\ s^{-1}$.

Since a gap of this magnitude exists already in the plane-wave modulation regime where discrete lattice effects are unimportant, we believe that $(\Delta_\phi)_I$ is induced by random frozen defects.[13,14] This conclusion is also supported by the near temperature independence of Δ in the incommensurate phase.

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