Dynamics of the Pinned Modulation Wave in Incommensurate bis (4-chlorophenyl) sulfone (BCPS)

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We show that both the anomalously huge resonance-frequency dependence of the ^{35}Cl nuclear quadrupole resonance (NQR) spin-lattice relaxation time in BCPS, reported here for the first time, and its anomalous temperature dependence can be explained by large-scale fluctuations of the pinned modulation wave instead of small-scale fluctuations (phasons and amplitudons). The results were obtained by measuring the laboratory (T_{1Q}) and rotating frame ($T_{1Q,\rho}$) ^{35}Cl relaxation times. This is the first time that an effective resonance frequency dependence of the spin-lattice relaxation rate was measured in pure NQR.

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The dynamics of incommensurate (IC) crystals, such as bis (4-chlorophenyl) sulfone [1], $(C_6H_4Cl)_2SO_2$ (abbreviated as BCPS), is characterized by a doubly degenerate soft mode which condenses to the incommensurate modulation wave on approaching the normal (N) to IC transition temperature T_I from above [2]. Since the periodicity of the frozen out eigenvector of the soft mode (i.e., the modulation wave) is incommensurate to the periodicity of the basic lattice, translational periodicity is lost in the direction of the modulation wave below T_I in spite of perfect long range order. The soft mode splits at T_I into an opticlike amplitudon mode the frequency of which increases with decreasing temperature, and a temperature-independent gapless acousticlike phason mode which is the symmetry-recovering Goldstone mode of the N-IC transition. One of the signatures [2] of IC phases is an anomalously strong phason-induced spin-lattice relaxation rate T_{1Q}^{-1} of quadrupolar nuclei, resulting in a T_{1Q} minimum at T_I. This is due to the fact that phason excitations are of low frequency at high q vectors (in contrast to normal acoustic modes) and thus produce a rather strong modulation of the electric field gradient (EFG) tensor at the quadrupolar sites. However, recent very precise measurements of the ^{35}Cl nuclear quadrupole resonance (NQR) spin-lattice relaxation rate in BCPS have clearly demonstrated [3,4] that the ^{35}Cl T_{1Q} in BCPS does not show a minimum at $T_I = 150$ K but shows a shallow minimum at 10–20 K below T_I [i.e., at around 140 K (Fig. 1)]. Such a behavior has not been observed in any other IC systems studied so far. The fact that the T_{1Q} minimum occurs not at $T_I = 150$ K but rather 10–20 K lower, i.e., deeply in the IC phase, is further supported by the fact that the typical incommensurate ^{35}Cl NQR line shapes [2–4] as well as neutron scattering data [5] show the onset of the IC phase at 150 K and not at the T_{1Q} minimum around 140 K.

The above anomalous behavior cannot be understood within the standard description of relaxation in IC systems [2]. In this Letter we show that this anomaly is due to the breakdown of the linearized description of the elementary excitations in real IC systems induced by the presence of standing wave-type large phase fluctuations of the impurity-pinned IC modulation wave. Furthermore, the theory, which is summarized later in this Letter, predicts an exponential dependence on the resonance frequency of the spin-lattice relaxation rate as well as a minimum in a temperature plot occurring at temperatures significantly below that of the IC transition temperature T_I. These results differ from corresponding results appropriate to smaller fluctuations.

A difficulty exists in attempting to measure the resonance frequency dependence in pure NQR, since the energy level spacing (and thus the resonance frequency) is fixed by internal interactions and cannot be varied by the experimenter. We were able to circumvent this problem by measuring the spin-lattice relaxation time in the rotating frame rather than only in the lab frame. Since the energy level spacing in the rotating frame (even in pure

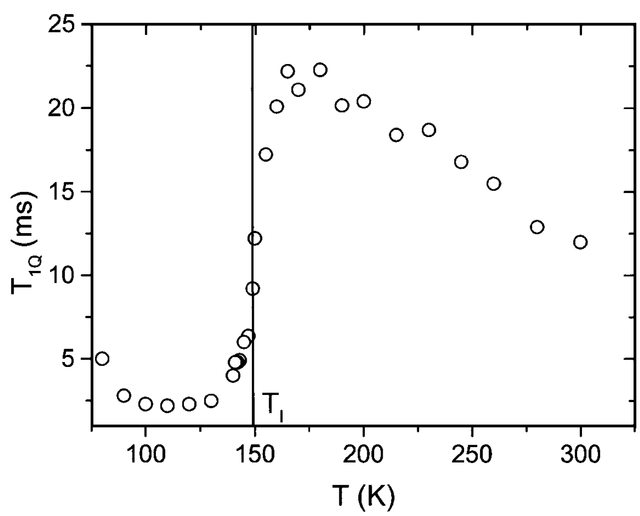

FIG. 1. Temperature dependence of ^{35}Cl NQR laboratory frame spin-lattice relaxation time T_{1Q} measured in a BCPS single crystal.

NQR) is determined by the rf magnetic field B_1, measurements of the NQR rotating frame spin-lattice relaxation ($T_{1Q,\rho}$) vs B_1 can in principle be used to determine the resonance-frequency dependence of the spin-lattice relaxation time and so discriminate between different possible relaxation mechanisms.

We performed in a BCPS single crystal ^{35}Cl pure NQR rotating frame spin-lattice relaxation ($T_{1Q,\rho}$) measurements, which show the predicted exponential dependence on resonance frequency of the relaxation rate for large phase fluctuations and, similar to the T_{1Q} data, exhibit no anomaly at $T_{\rm I}$. The observed temperature dependences of both the T_{1Q} and $T_{1Q,\rho}$ in BCPS can be quantitatively described within the above model thus allowing for a detailed insight into the low frequency dynamics of the pinned modulation wave.

Inelastic neutron scattering [5] measurements recently resulted in a direct determination of the phason frequency in BCPS at the satellite position $\vec{k}_I = \vec{a}^* \pm (1/5 + \delta)\vec{b}^*$ in the IC phase. Here $\vec{a}^*$ and $\vec{b}^*$ are reciprocal lattice vectors and δ varies [6] between $\delta = 0.021$ at 150 K and $\delta = 0.014$ at 20 K. The splitting of the condensing soft mode into phason and amplitudon modes below $T_{\rm I} =$ 150 K was clearly observed. The phason frequency gap Δ_φ was found to be huge. It is equal to 90 ± 10 GHz from $T_{\rm I}$ down to 19 K, whereas the amplitudon frequency gap $\Delta_{\rm A}$ increases from 90 to 450 GHz in this temperature interval. The phason damping constant is $\Gamma_\varphi(T_{\rm I}) =$ 160 ± 20 GHz. In addition to phason and amplitudon excitations a critical central peak was observed as well [5]. The resolution of the neutron scattering measurements [5] did not allow a detailed study of the central peak. The width of the central peak was estimated [7] from ^{35}Cl NQR and ^{2}H NMR spin-lattice relaxation data to be of the order of several GHz in the temperature range from 200 K to $T_{\rm I}$. The fact that the phason frequency is not zero at the critical wave vector $\vec{k}_I$ but exhibits a rather large frequency gap $\Delta\varphi \approx 90$ GHz demonstrates that the modulation wave $u(\vec{r},t) = A(\vec{r},t)\cos\varphi(\vec{r},t) = u(\vec{r}) + \delta u(\vec{r},t)$ in BCPS is strongly pinned.

The standard theory of spin-lattice relaxation in IC systems [2] considers only small thermal fluctuations of the modulation wave $\delta u(\vec{r},t) = \delta A(t)\cos(\varphi) - A\sin(\varphi)\delta\varphi(t)$ (i.e., amplitudons and phasons) where $\overline{\delta A^2}$ and $\overline{\delta\varphi^2} \ll 1$. The amplitudon-induced NQR spin-lattice relaxation rate is given by [2]

$$(T_{1Q}^{-1})_A = C\int_{-\infty}^{\infty}\overline{\delta A(0)\delta A(t)}e^{i\omega t}\,dt = K\sqrt{\frac{\Gamma_A}{\Delta_A}} = K\sqrt{\frac{\Gamma_A}{\Delta_{A0} + 2a(T_{\rm I} - T)}}, \quad T \le T_{\rm I} \tag{1a}$$

and the phason-induced rate is [2]

$$(T_{1Q}^{-1})_\varphi = C\int_{-\infty}^{\infty}\overline{\delta\varphi(0)\delta\varphi(t)}e^{i\omega t}\,dt = K\sqrt{\frac{\Gamma_\varphi}{\Delta_\varphi}}, \tag{1b}$$

where $\Gamma_\varphi \approx \Gamma_{\rm A}$, a is a positive constant, and C is proportional to fluctuations in the EFG tensor components produced by the motion of the modulation wave. The effective spin-lattice relaxation rate T_{1Q}^{-1} varies [2] over the IC line shape in the simplest linear case $\nu = \nu_0 + \nu_1 u(\vec{r})$ as

$$T_{1Q}^{-1} = [(\nu - \nu_0)/\nu_1](T_{1Q}^{-1})_A + (1 - [(\nu - \nu_0)/\nu_1]^2)(T_{1Q}^{-1})_\varphi .$$

The above expressions are derived [2,8] for the large gap limit $\Delta_\varphi \gg \omega_Q, \sqrt{\Gamma_\varphi\omega_Q}$ and $\Delta_A \gg \omega_Q, \sqrt{\Gamma_A\omega_Q}$. Since the ^{35}Cl resonance frequency in BCPS is $\omega_{\rm Q}/2\pi \cong$ 35 MHz, these conditions are obviously fulfilled in BCPS where the gaps are in the 10^2 GHz regime (as shown by the inelastic neutron scattering data [5]). The above theory thus predicts that the T_{1Q} versus temperature plot should have a minimum at $T_{\rm I}$, which obviously disagrees with the experimental data [3,4]. It also predicts that T_{1Q} should be independent of the resonance frequency.

Let us now drop the assumption of small phase $\delta\varphi(t)$ and amplitude $\delta A(t)$ fluctuations of the modulation wave. Instead we assume that the phase fluctuations between the pinning centers may become so large ($\overline{\delta\varphi^2} \ge 1$) that the linearized description of the excitations in the IC system is no longer valid [9]. We now have to consider the spectral density of the autocorrelation function of the fluctuations of the pinned modulation wave $G(\vec{r}_j,t) = \overline{u(\vec{r}_j,0)u(\vec{r}_j,t)}$, where $\vec{r}_j$ is the position of the jth nucleus. For large standing wave phase fluctuations, which we believe [9] determine the central peak dynamics in BCPS, we have to consider

$$G_{j\varphi} = A^2\overline{\cos[\varphi(\vec{r}_j,0)]\cos[\varphi(\vec{r}_j,t)]}, \tag{2}$$

instead of $G_{j\varphi} = \overline{\delta\varphi(\vec{r}_j,0)\delta\varphi(\vec{r}_j,t)}$.

To make the problem tractable we write $\varphi(\vec{r}_j,t)$ as a sum of the large quasistatic part φ_{0j} and a time-dependent part $\varphi_k(\vec{r}_j,t)$,

$$\varphi(\vec{r}_j,t) = \varphi_{0j} + \sum_{k=k_{\min}}^{k_{\max}}\varphi_k(\vec{r}_j,t), \tag{3}$$

where $\varphi_{0j} = \vec{k}_I \cdot \vec{r}_j + \varphi_0$, $(k_i)_{\min} = \pi/\bar{l}$, and $(k_i)_{\max} = \pi/a$, $i = x, y, z$. Here a is an average normal-phase unit cell size and $\bar{l}$ is the mean distance between those impurity centers that are effective in pinning the modulation wave at a given temperature. $\bar{l}$ is independent of temperature in the strong coupling limit, but in the weak coupling limit effectively increases with increasing temperature as the modulation wave becomes more depinned. In this limit, it can be shown that [10] $\bar{l} \propto (T_I - T)^{-\beta[(\gamma-1)/3]}$, where $\gamma \approx 2$ and $\beta = 0.35$ near $T_{\rm I}$ ($T_{\rm I} - T < 1.5$ K) and 0.75 far below $T_{\rm I}$ ($T_{\rm I} - T \approx 25$ K) [3]. This temperature dependence of $\bar{l}$ is small compared to that arising from large phase fluctuations and will be neglected in our subsequent treatment. The time-dependent part of $\varphi(\vec{r}_j, t)$ is given by standing waves $\varphi_k(\vec{r}_j, t)$ in a coherence volume $\overline{l}^3$ which can be approximated by a square box:

$$\varphi_k(\vec{r}_j, t) = \varphi_{0k} \sin(\omega_k t + \alpha_k) \sin(k_x x_j) \times \sin(k_y y_j) \sin(k_z z_j) . \quad (4)$$

Here $\omega_k = \sqrt{\kappa}\, k$ are standing-wave phase fluctuation mode frequencies and κ is a constant determining the slope of the dispersion branch. The phases α_k are assumed to be randomly distributed in the interval $\alpha_k \in [0, 2\pi]$ and the distribution of the amplitudes φ_{0k} is assumed to be Gaussian. We now find

$$G_{j\varphi}(t) = \frac{A^2}{2} \left[\prod_k e^{-z_1} I_0(z_1) + \cos(2\varphi_{0j}) \prod_k e^{-z_2} I_0(z_2) \right]_j , \quad (5)$$

where $I_0(z) = \sum_{m=0}^{\infty} (z/2)^{2m}/(m!)^2$ is the zeroth order modified Bessel function, $z_1 = \frac{1}{2}\overline{\varphi_{0k}^2} \sin^2(\omega_k t/2)$, and $z_2 = \frac{1}{2}\overline{\varphi_{0k}^2} \cos^2(\omega_k t/2)$.

In general the resulting spectral densities have to be evaluated numerically. If, however, $G_{j\varphi}(t)$ decays to zero in a time $t \ll \omega_k^{-1}$ for all ω_k, the problem can be solved analytically. The relaxation rate for large phase fluctuations of the pinned modulation wave is now given by

$$(T_{1Q}^{-1})_\varphi(\omega) \propto \left(\frac{T_{\mathrm{I}} - T}{T_{\mathrm{I}}} \right)^{3\beta} \exp\!\left(-\frac{\omega^2}{4p_0^2} \left[\frac{T_{\mathrm{I}} - T}{T_{\mathrm{I}}} \right]^{2\beta} \right), \quad (6)$$

instead of by Eq. (1b).

If the small-scale amplitude fluctuations are much faster than the large phase fluctuations, the two modes are essentially uncoupled and the amplitudon relaxation rate is still given by Eq. (1a). The parameter p_0 varies slowly with temperature and is given [9] by $p_0 \approx \sqrt{k_B T V_0 N_\varphi / N_0 m \overline{l}^3}\, 1/A_0$. Here V_0 is the volume of the unit cell in the normal phase, N_0 is the number of nuclei in this cell, m is an average nuclear mass, $N_\varphi = \pi/6[(k_{\max}/k_{\min})^3 - 1]$ is approximately given by the number of nuclei in the coherence volume, and $A = A_0[(T_{\mathrm{I}} - T)/T_{\mathrm{I}}]^\beta$.

The predicted temperature and resonance frequency dependence of T_{1Q} is illustrated in Fig. 2. On cooling from above through the normal to IC transition temperature T_{I}, the spin-lattice relaxation time T_{1Q} first decreases with increasing $T_{\mathrm{I}} - T$, then goes through a broad asymmetric minimum well below T_{I}, and finally increases with decreasing temperature at still larger $T_{\mathrm{I}} - T$ values. The minimum disappears if $\omega/p_0 < 5$ (Fig. 2). This behavior is completely different from that observed for small phase fluctuations [Eq. (1b)], where the minimum value of T_{1Q} is always found at T_{I}. Another important point is that the resonance frequency dependence of T_{1Q}^{-1} predicted by Eq. (6) can be rather strong if $\omega/p_0 > 5$ and will vary

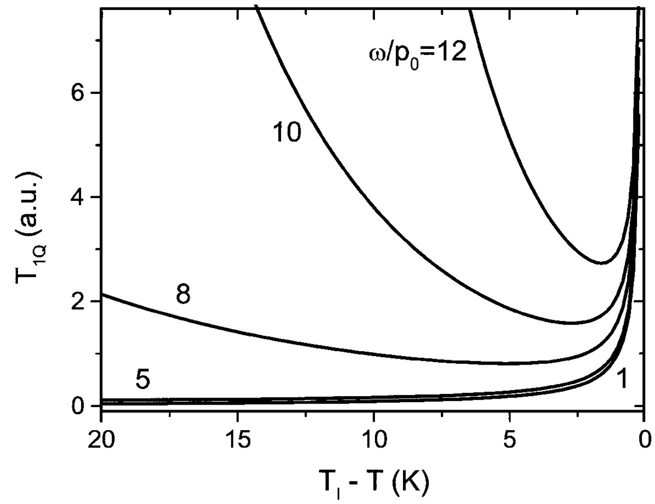

FIG. 2. Theoretical temperature dependence of the spin-lattice relaxation time T_{1Q} in the presence of large phase fluctuations of the pinned modulation wave for different values of ω/p_0.

with temperature. It is nonexistent in the small phase fluctuation case given by Eq. (1b). The resonance frequency dependence of T_{1Q}^{-1} can thus prove or disprove the above model given by Eq. (6). To check this feature we decided to measure the ^{35}Cl rotating frame spin-lattice relaxation rate $T_{1Q,\rho}^{-1}$.

For the large phase fluctuation case the temperature and resonance frequency dependence of the rotating frame spin-lattice relaxation rate $T_{1Q,\rho}^{-1}(\Omega)$ is also essentially given by Eq. (6) provided the NQR resonance frequency $\omega = \omega_Q$ is replaced by the effective ^{35}Cl resonance frequency Ω in the rotating frame [11], where Ω is

$$\Omega = \gamma B_1 \sqrt{\alpha^2 + \beta\beta^*} . \quad (7)$$

Here γ is the ^{35}Cl gyromagnetic ratio, B_1 is the amplitude of the rf field, $\alpha = \sin(2\psi)\cos\theta$, and $\beta = (\sqrt{3}/2)\cos(2\psi)\sin\theta e^{-i\phi} + \frac{1}{2}\sin(2\psi)\sin\theta e^{i\phi}$. Furthermore, θ and ϕ are the polar and azimuthal angles of the direction of the rf field with respect to the principal axis frame of the EFG tensor, and the angle ψ is related to the asymmetry parameter $\eta = (V_{XX} - V_{YY})/V_{ZZ}$ of the EFG tensor via $\eta = \sqrt{3}\tan(2\psi)$. Since $\eta \approx 0.2$ in the paraelectric phase of BCPS [12], ψ is here about 3°. Ω in our case amounts to $\approx 0.8\gamma B_1$.

The ^{35}Cl NQR relaxation times [11] were measured in the rotating and the laboratory frames on a BCPS single crystal by the pulse sequences, as discussed in Ref. [11]: $T_{1Q,\rho}$ by a $90°_x$-locking pulse$_y$-τ-$180°_x$-τ-echo pulse sequence and T_{1Q} by a $180°_x$-t-$90°_x$-τ-$180°_x$-τ-echo sequence. A computer controlled automatic adjustment of the Q factor of the coil circuit was used.

In Fig. 3 the temperature dependences of the ^{35}Cl T_{1Q} and $T_{1Q,\rho}$ are compared with theoretical predictions from Eqs. (6) and (7). Far above the transition temperature T_{I}, T_{1Q} is relaxed by slow molecular reorientations and

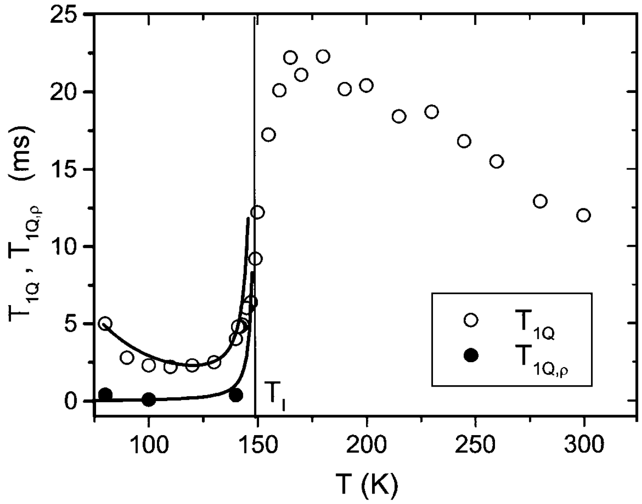

FIG. 3. Temperature dependence of the laboratory T_{1Q} (open circles) and rotating frame ^{35}Cl NQR spin-lattice relaxation times $T_{1Q,\rho}$ (solid circles) for $\Omega \approx 2\pi \times 9$ kHz; solid line: fit to Eq. (6) with the parameter $p_0 = 40.8$ MHz. Here $\omega_Q \approx 2\pi \times 34.79$ MHz.

increases with decreasing temperature. Some 20 K above T_I the condensing IC soft mode takes over and T_{1Q} then decreases with decreasing temperature. The decrease of T_{1Q} on approaching the phase transition from above in the N phase can be described in the same way as in Ref. [3], i.e., by $(T - T_I)^{\zeta}$, where $\zeta \approx 0.69$. T_{1Q} shows no anomaly at T_I (Fig. 1) but reaches a broad minimum at around 140 K, well below T_I [3,4]. T_{1Q} is nearly T independent between 140 and 120 K and then increases with decreasing T. The data were fitted by Eq. (6) and from the best fit the parameter p_0 was determined to be $p_0 \approx 40$ MHz. A similar temperature dependence was observed for $T_{1Q,\rho}$ at $\Omega \approx 2\pi \times 9$ kHz. $T_{1Q,\rho}$ is significantly shorter than T_{1Q} in a large T interval below T_I. The ratio $T_{1Q}/T_{1Q,\rho}$ varies with decreasing T between 16 at 140 K and 100 at 25 K in agreement with the frequency dependence predicted by Eq. (6). The T and resonance-frequency dependence of T_{1Q} and $T_{1Q,\rho}$ can be described by expression (6) using the same p_0 parameter (Fig. 3). $T_{1Q,\rho}$ as well increases with increasing B_1 as predicted by Eqs. (6) and (7).

The above results thus show that the ^{35}Cl spin-lattice relaxation rate in the molecular crystal BCPS, which occurs 10–20 K below T_I, is determined by large standing wave-type phase fluctuations, $\overline{\delta\varphi^2} \geq 1$, of the pinned modulation wave rather than by small-scale phason excitations as assumed so far. The results agree with the recent observation of a large phason gap and a distinct central peak in BCPS by neutron scattering [5]. This is the first time that a breakdown of the linearized description of excitations in the IC system has been observed over such a large T interval. Similar T_{1Q} and $T_{1Q,\rho}$ effects should also occur in other real IC systems with a large phason gap. A systematic measurement of the frequency and T dependence of the ^{35}Cl NQR spin-lattice relaxation time in the rotating frame should thus allow a detailed insight into the dynamics of the pinned IC modulation wave and the pinning process itself. It seems, however, that BCPS is unique in that such a large difference between the N-IC transition temperature T_I and the T_{1Q} minimum has not been reported in any other IC system so far.

In addition, our use of the rotating frame constitutes the first time that the resonance-frequency dependence of the spin-lattice relaxation time has been measured in a pure NQR experiment.

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