^{35}Cl NQR in incommensurate bis(4-chlorophenyl) sulfone

U. Mikac, T. Apih, M. Koren, J. Dolinšek, J. Seliger, J. Slak, and R. Blinc
J. Stefan Institute, University of Ljubljana, Ljubljana, Slovenia
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The temperature dependence of the ^{35}Cl NQR spectra has been measured for $1q$ modulated incommensurate bis(4-chlorophenyl) sulfone between 300 and 6 K. Large thermal fluctuations of the modulation wave are found to smear out the typical incommensurate edge singularities over a range of 10 K below the paraelectric-incommensurate transition T_{I}. The gradual evolution of the modulation wave from the plane wave to the broad multisoliton lattice regime has been observed. The soliton density n_s stays however high over the whole incommensurate phase. [S0163-1829(96)00638-8]

I. INTRODUCTION

Bis(4-chlorophenyl) sulfone (BCPS) is together with $ThBr_4$, $ThCl_4$, and biphenyl one of the few examples of structurally incommensurate (I) crystals[1] where the I phase is reported to persist[2,3] from $T_{\mathrm{I}}=150$ K down to the lowest temperatures investigated. This is rather unusual since in most cases the I phase is intermediate between a high-temperature paraelectric (N) phase and a low-temperature commensurate (C) phase. The modulation wave which is sinusoidal and plane-wave like in the high-temperature part of the I phase normally becomes multisoliton latticelike[4,5] in the low-temperature part of the I phase. In this regime the phase $\phi(x)$ of the modulation wave becomes a nonlinear function of the coordinate x. Commensuratelike regions where the phase is nearly constant are separated by soliton-like domain walls—discommensurations—where the phase changes rapidly. This should show up in the appearance of higher-order satellites in the x-ray diffraction as well as in the appearance of ''commensuratelike'' soliton lines in the NQR spectra.[6] The intersoliton distance increases with decreasing temperature and becomes infinite at the ''lock-in'' transition temperature T_c where the crystal becomes commensurate. The order parameter of the I-C transition is thus the soliton density n_s which vanishes below T_c.

The change from the plane wave to the multisoliton lattice-type modulation regime can be described by the nonlinear Sine-Gordon equation.[4–6] The nonlinear behavior is connected with the presence of a ''lock-in'' term in the Landau potential.[6,7] It is this term which is also responsible for the occurrence of the lock-in transition and the disappearance of the I phase at low temperatures. The absence of a lock-in transition should be thus accompanied by the persistence of a plane-wave-type modulation wave. The presence of soliton effects is always the precursor of the occurrence of a lock-in transition as $T\rightarrow 0$.

The absence of a lock-in transition would thus mean that the modulation wave is plane-wave like over an unusually wide T range and that the phason gap induced by the discreteness of the crystal lattice, i.e., by the lock-in term, is rather small. Incommensurate phases which persist to very low temperatures are thus prime candidates for the appearance of truly gapless phason modes in the solid. The occurrence of such gapless phason modes has been recently demonstrated by light scattering[8] in ferroelectric and antiferroelectric liquid crystals where the period of the helicoidal order-parameter modulation is incommensurate to the distance between the smectic layers. The only examples where such a behavior, e.g., a phason gap smaller than 500 kHz, has been reported to occur in solids are claimed to be biphenyl[9] and BCPS.[10] The evidence in these two cases comes from the Larmor frequency dependence of the proton spin-lattice-relaxation time T_1.[5,6]

The reported absence of a phason gap and a lock-in transition in BCPS,[10] which would both require a plane-wave-like modulation wave, is also hard to reconcile with the presence of higher-order satellites in the neutron diffraction[11] in BCPS which seem to signal the presence of a nonsinusoidal solitonlike modulation. In contrast no higher-order satellites were seen in $ThCl_4$ and $ThBr_4$.

The ^{35}Cl NQR data[2,3,12] in BCPS published so far are to some extent conflicting. The line shapes[2,3] have been measured between room temperature and 77 K and no evidence[3] for a lock-in transition at 115 K has been found. A sudden increase in the ^{35}Cl spin-lattice-relaxation time below 110 K has been, on the other hand, interpreted[2] by some authors as demonstrating the occurrence of a lock-in transition. This increase in T_1 is also found in a recent NQR reinvestigation[3] of BCPS where it was tentatively assigned to soliton effects resulting in the opening of a gap in the dispersion relation of the phason branch.[3] A similar increase in the deuteron T_1 in biphenyl at the II-III transition has been, on the other hand, interpreted as indicating a ''partial-lock-in'' transition[13] so that phase III is not really an incommensurate phase. Here we present a study of the local nature of the modulation wave in BCPS via ^{35}Cl NQR line-shape measurements between $T=300$ and 6 K. Thus we extend the measurements of the Guibé group[3] to low temperatures.

We specifically wished to determine

(i) is the incommensurate modulation wave plane-wave like or solitonlike, and if it is solitonlike, what is the temperature dependence of the soliton density;

(ii) what is the effect of thermal fluctuations[14] close to T_1;

(iii) is the value of the critical exponent β for the amplitude of the modulation wave indeed mean-field[3] like or not. We also wished to check for possible lock-in effects at low temperatures where chlorine NQR measurements have not yet been performed so far.

II. STRUCTURE AND EXPERIMENTAL DETAILS

BCPS crystallizes at room temperature in the monoclinic space group $I2/a$ with four molecules per unit cell.[15] The molecule $(C_6H_4Cl)_2SO_2$ consists of two chlorophenyl groups connected by an SO_2 group. The sulfur atom is located on the twofold symmetry axis of the molecule. All four molecules in the unit cell are equivalent so that there is only one chemically nonequivalent Cl site and therefore only one Cl NQR line is expected. The incommensurate distortion below T_1 consists[11] of a modulation of the dihedral angle between the benzene rings and the Cl-S-Cl plane. It can be described[11] by $\mathbf{q}=\mathbf{a}^*\pm(1/5+\delta)\mathbf{b}^*$ and alternatively by $\mathbf{q}=\pm\delta'\mathbf{b}^*$ where the misfit parameter δ' varies between 0.2238 in the high T part of the I phase and 0.2135 at 20 K.

The Fourier transform ^{35}Cl NQR spectra were measured on a polycrystalline sample using the 90°-τ-180°-τ-echo sequence. The purity of the sample was checked by chemical analysis and gas chromatography. It was determined that the sample is 98.5% pure. The paraelectric-incommensurate transition temperature T_1 was determined from the temperature variation of the chlorine NQR linewidth. The temperature of the sample in the cryostat was controlled to ±0.1 K. The temperature gradient over the sample was estimated to be less than 0.5 K. In the incommensurate phase where the ^{35}Cl NQR spectrum is broad the spectra were determined point by point from the echo signals recorded at different frequencies. A computer controlled automatic adjustment of the Q factor of the coil circuit was used so that the echo signal at any given frequency was indeed proportional to the number of nuclei resonating in this frequency interval.

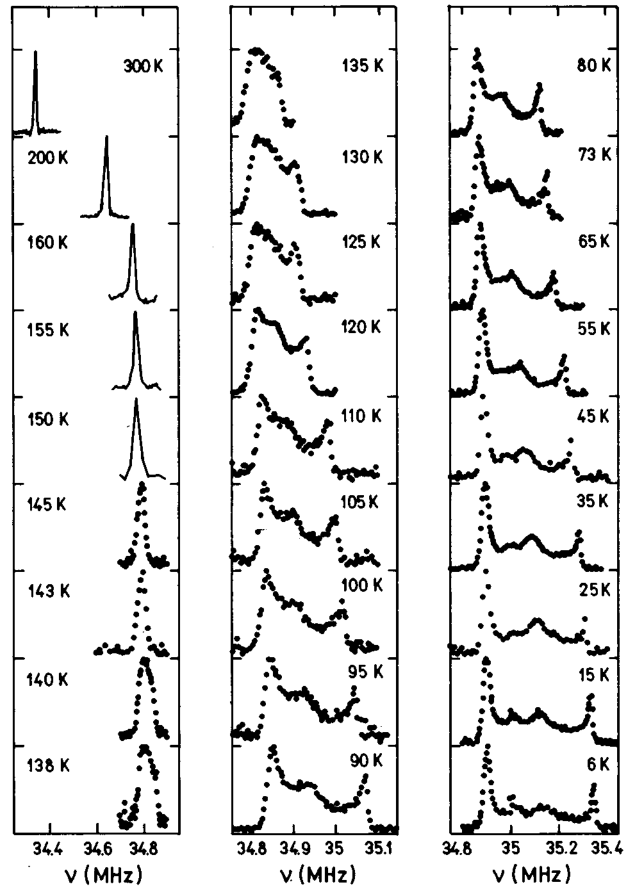

FIG. 1. Experimentally observed ^{35}Cl NQR spectra of BCPS between room temperature and 6 K.

III. THEORY

A. Static NQR line shape

The ^{35}Cl nuclear quadrupole resonance (NQR) frequency is given by

$$\nu_Q=\frac{eQV_{ZZ}}{2h}\sqrt{1+\eta^2/3}, \tag{1}$$

where V_{ZZ} is the largest eigenvalue of the electric-field-gradient (EFG) tensor and η is the asymmetry parameter. Since the dependence of ν_Q on η is small it is fair to say that the chlorine NQR frequency is mainly determined by V_{ZZ}. The incommensurate modulation wave induces changes in the EFG tensor at the chlorine sites.[1–3,5,6] The relation between the NQR frequency and the nuclear displacement

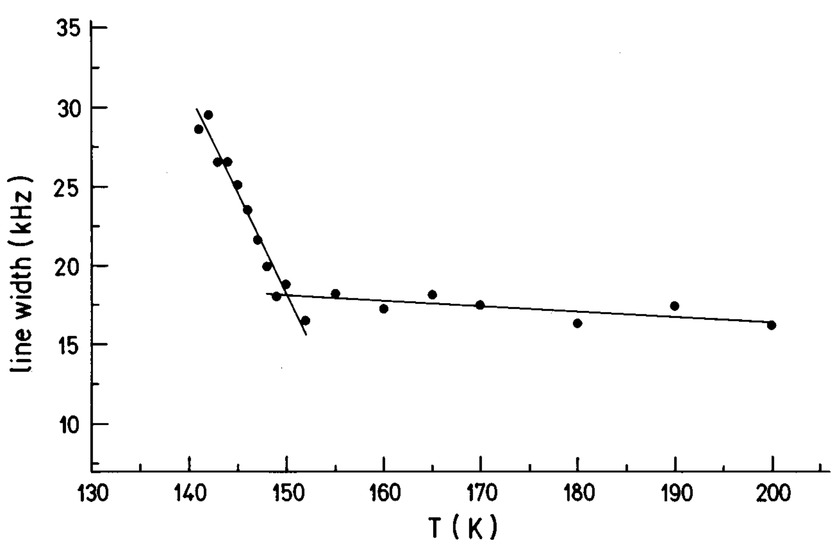

FIG. 2. Temperature dependence of the ^{35}Cl NQR linewidth in BCPS.

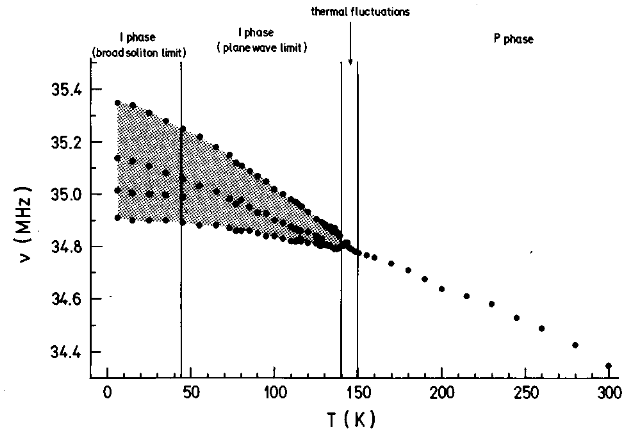

FIG. 3. Temperature dependence of the ^{35}Cl NQR lines in BCPS showing the transition from the plane wave to the broad multisoliton lattice regime.

$u(Q_{\pm})$ can be expanded in a power series. In the general case the dependence of the resonance frequency on the nuclear displacements is nonlocal: $\nu_i=\nu[u_i(x_i),u_j(x_j)\ldots]$. In such a case one finds[6] up to second-order terms

$$\nu(x)=\nu_0+\nu_1\cos[\phi(x)-\phi_1] + \frac{1}{2}\{\nu_{2'}+\nu_{2''}\cos 2[\phi(x)-\phi_2]\}, \qquad (2a)$$

where ϕ_1 and ϕ_2 are constant phase shifts and $\nu_{2'}$ and $\nu_{2''}$ are proportional to the square of the amplitude of the modulation wave. An alternative form of Eq. (2a) is

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

where

$$\psi(x)=\phi(x)-\phi_2,$$

$$\tilde{\phi}=\phi_2-\phi_1,$$

$$\nu_2=\nu_{2''},$$

$$\nu_2'=\frac{1}{2}[\nu_{2'}-\nu_2].$$

As shown before[2,3,5,6] we find instead of a single sharp NQR line for each physically nonequivalent site in the high-temperature unit cell in the I phase a characteristic frequency distribution $f(\nu)$

$$f(\nu)=\int d\phi\,\delta[\nu-\nu(\phi)]. \qquad (3)$$

In the plane-wave limit, the spatial variation of the phase is linear ($d\phi/dx$=const). In the NQR spectrum we get here singularities[5,6] when $d\nu/d\phi=0$. In the nonlocal case up to second-order terms [Eqs. (2a), (2b)] we have two edge singularities for $|\nu_2/\nu_1|<1/2$. For $|\nu_2/\nu_1|=1/2$ $\tilde{\phi}=0°$, $\pm 90°$, we have three edge singularities. For $1/2\leqslant|\nu_2/\nu_1|\leqslant 1$ and $\tilde{\phi}\neq 0°$, 90° we may have here—in contrast to the local case—four edge singularities as the additional singularity splits into two at lower temperatures. The position of the fourth singularity

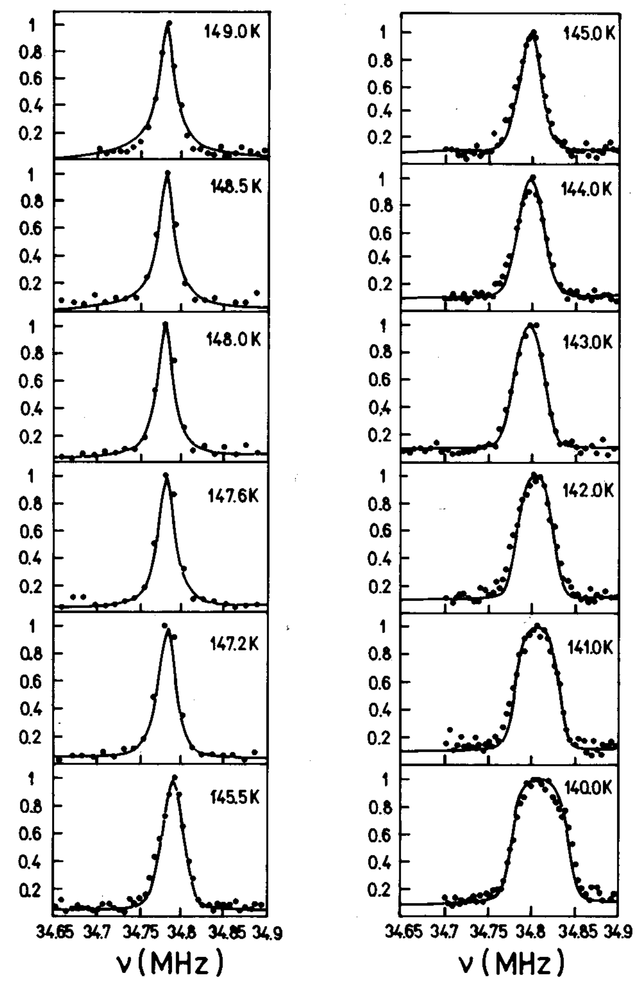

FIG. 4. Comparison between experimental and theoretical ^{35}Cl NQR line shapes between 149 and 140 K for the case when the large thermal fluctuations are present. The static inhomogeneous line shape is here convoluted by the fluctuation correlation. The experimental points are designated by ·, whereas the theoretical curve is represented by a solid line.

and the value of $|\nu_2/\nu_1|$, where this singularity shows up, depend on the relative phase shift between the linear and the quadratic term $\tilde{\phi}$.

In the multisoliton regime, the spatial variation of the phase is nonlinear and additional lines appear in the spectrum where $d\phi/dx\to 0$. The phase ϕ is here given by a solution of the Sine-Gordon equation

$$\frac{d^2\phi}{dx^2}=-\frac{n\gamma}{2\kappa}\rho^{n-2}\sin(n\phi), \qquad (4)$$

where ρ is the amplitude of the modulation wave, n is the ''Umklapp'' or commensurability exponent, γ is the coefficient of the ''Umklapp'' term in the Landau expansion[1] and κ is an elastic constant. The physical meaning of n is that the ''anisotropy'' term in the Landau expansion driving the lock-in transition is of the ''nth'' order in the amplitude of

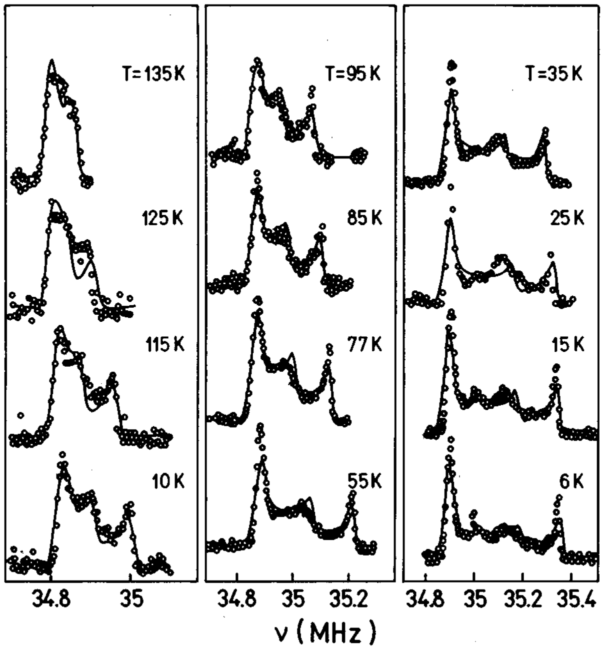

FIG. 5. Comparison between experimental and theoretical ^{35}Cl NQR line shapes between 135 and 6 K. The frequency shift depends here on both linear and quadratic terms in the incommensurate nuclear displacements. Experimental points: ∘, theory −.

the modulation wave. For Na_2CO_3 $n=12$, for $[N(CH_3)_4]_2ZnCl_4$ $n=10$, for Rb_2ZnCl_4 $n=6$, for $(NH_4)_2BeF_4$ $n=4$, for ferroelectric liquid crystals in a magnetic field $n=2$, whereas $n=0$ for ferroelectric liquid crystals in the absence of a magnetic field where there is no lock-in transition. For BCPS n is not known. If there would be a lock-in transition with $b'=5b$, n would be equal to 10. In contrast to the incommensurate edge singularities, the positions of these new ''commensurate'' lines will depend on the initial phase ϕ_0.

B. Thermal fluctuation effects

In the case of a small phason gap, thermal phase fluctuations of the modulation wave are expected[14] to influence the NQR line shape. We get for the case of a gapless phason the NQR line shape[14] as

$$
\begin{aligned}
I(\omega) &= \int_0^\infty G(t)e^{i\omega t}dt \\
&= \int_{-1}^{1}\frac{dX}{(1-X^2)^{1/2}}\int_0^\infty dt\, e^{i(\omega-\Omega_0-\Omega_1 X)t} \\
&\quad\times e^{-[\omega_{\mathrm{loc}\,1}tX^2+(\omega_{\mathrm{loc}\,2}t)^{3/2}(1-X^2)]}.
\end{aligned}
\tag{5a}
$$

Here $\Omega_0=2\pi\nu_0$, $\Omega_1=2\pi\nu_1$, $X=\cos(qx)$ whereas[14]

$$
\xi_1=\frac{\omega_{\mathrm{loc}\,1}}{\Omega_1}\propto\frac{T}{T-T_1},\quad \xi_2=\frac{\omega_{\mathrm{loc}\,2}}{\Omega_1}\propto\frac{T^{2/3}}{(T_1-T)^{1/2}}
\tag{5b}
$$

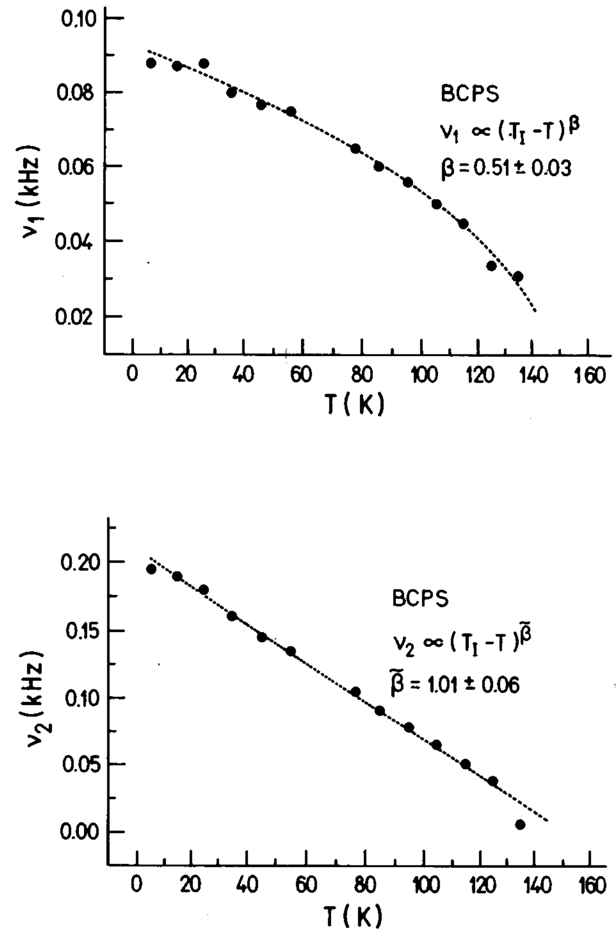

FIG. 6. Temperature dependences of the coefficients of the linear (ν_1) and quadratic (ν_2) terms in the expansion of the NQR frequency shift in powers of nuclear displacements.

measure the relative size of amplitudon and phason order-parameter fluctuations as compared to the static values of the order parameter. In the center of the inhomogeneous line where $X=0$, the dynamic line shape is determined[14] by the gapless phason fluctuation term, i.e., the $t^{3/2}$ term, whereas at the edge singularities, where $X=\pm 1$, the dynamic line shape is determined by the amplitudon fluctuations, i.e., the t term. If the phason is not gapless, both the amplitudon and the phason fluctuation contributions are proportional to t, resulting in a Lorentzian form of the dynamic line shape. The fluctuation corrections should be important close to T_{I}.

IV. RESULTS AND DISCUSSION

The ^{35}Cl NQR spectra of BCPS recorded at temperatures between room temperature and 6 K are shown in Fig. 1. The paraelectric-incommensurate transition temperature T_{I} determined from the inhomogeneous broadening of the ^{35}Cl NQR line was found to be 150 ± 0.5 K (Fig. 2). The sharp homogeneous paraelectric line broadens below T_{I} yielding an inhomogeneous incommensurate frequency distribution $f(\nu)$. In contrast to Rb_2ZnCl_4 and other $1q$ incommensurate systems investigated so far no typical edge singularities are seen between $T_{\mathrm{I}}=150$ and 140 K, i.e., in a range of nearly 10 K

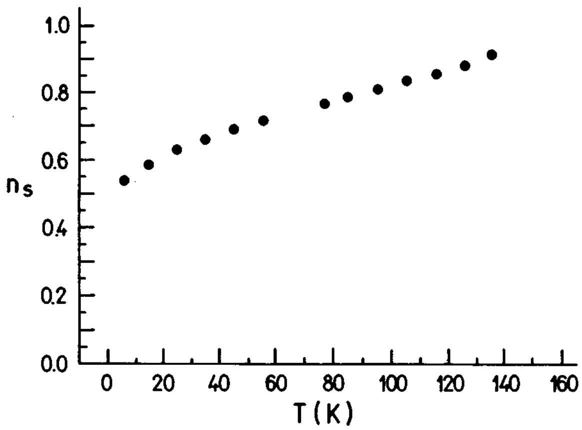

FIG. 7. Temperature dependence of the soliton density n_S.

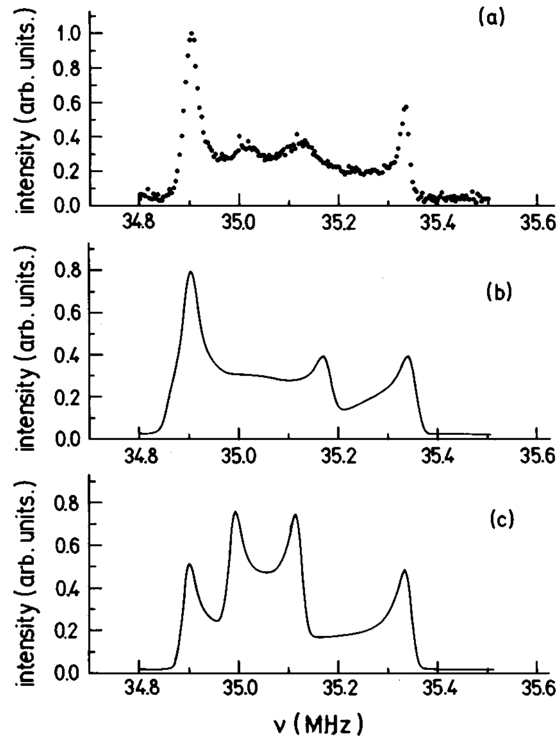

FIG. 8. (a) Experimental ^{35}Cl NQR line shape at 15 K. (b) Theoretical line shape in the broad multisoliton limit (n_s=0.58) for the nonlocal case where linear and quadratic terms are present. (c) Theoretical line shape in the plane-wave limit for the nonlocal case where linear and quadratic terms are present.

below T_{I}. Instead a ‘‘triangular’’ shaped spectrum slowly changes into a ‘‘bell’’-shaped spectrum with decreasing temperature. Such a bell-shape spectrum can be described by the effect of large thermal fluctuations[14] of the incommensurate modulation wave. The temperature dependence of the positions of the ^{35}Cl NQR lines, respectively, the singularities are shown in Fig. 3.

The comparison between experimental line shapes in the temperature range between 149 and 140 K and the theoretical spectra are shown in Fig. 4. Here thermal fluctuations have been taken into account assuming that the phason gap is much smaller than the NQR frequency ($\Delta_\phi \ll \omega_Q$). Thermal fluctuations are dominant in a range of 10 K below T_{I}. In this temperature interval the quadratic term is much smaller than the linear one so that only the linear term has to be taken into account. Below 138 K the spectrum becomes limited by two edge singularities but is still not the one expected for the static $1q$ case, e.g., as described by Eq. (2b). Thermal fluctuations are here important too. The two edge singularities become well pronounced only below 130 K where however a third intermediate peak starts to appear. At 77 K we have two sharp edge singularities and a third less sharp intermediate peak.

The line shape fits below 135 K (Fig. 5) can be quantitatively described with expression (2b), where we take into account linear and quadratic terms in the nonlocal case

$$\nu - \nu_0 - \nu_2' = \nu_1 \cos(\phi + \phi_0) + \nu_2 \cos[2(\phi + \phi_0) + \phi_1]. \tag{6}$$

Here we find ϕ_0=1.59 and ϕ_1=−0.37. The temperature dependences of ν_1 and ν_2 are shown in Fig. 6. The critical exponent of $\nu_1 \propto (T_{\mathrm{I}} - T)^\beta$ equals β=0.51±0.03 whereas the critical exponent derived from $\nu_2 \propto (T_{\mathrm{I}} - T)^{\tilde{\beta}}$ equals $\tilde{\beta}$=1.0 ±0.06. This demonstrates that the exponents are mean-field like and that the transition in BCPS can be described by the Landau theory where $\tilde{\beta}=2\beta=1$. Below 40 K four peaks are seen in the spectrum, i.e., the third peak is replaced by two peaks. The splitting takes place very probably already around 70 K but becomes clearly visible only below 40 K. It can be interpreted as showing the gradual evolution of the modulation wave from the sinusoidal plane wave to the multisoliton lattice-type regime.[6] Such an analysis is however difficult as the structure of the hypothetical lock-in phase and the exponent n are not known. We assumed that n=10. Line-shape fits do however show that the soliton density n_s stays high over the whole I phase and does not seem to vary significantly with decreasing temperature. n_s is higher than 0.5 even at 6 K (Fig. 7). These conclusions do not change if the value of the exponent n is varied. We are thus here in the ‘‘broad’’ soliton regime where the width of the solitons is comparable to the intersoliton distance. In such a case the plane-wave description of the modulation wave is a useful first approximation. Thus there is no sign of a lock-in transition to a low-temperature commensurate phase below T_c where n_S would vanish.

It should be mentioned that the splitting of the third peak into two components below 40 K could be also qualitatively described in the plane-wave limit as arising from the presence of the quadratic term in the nonlocal approximation. The intensities of the lines are however not well described by this model [Figs. 8(a)–8(c)]. The inclusion of a cubic term does not make the fit better. Therefore we prefer the broad multisoliton lattice description as described above.

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