

Evidence for nonclassical critical behavior of a one-dimensional incommensurately modulated crystal: A ^{35}Cl NQR study of bis(4-chlorophenyl)sulfone

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The temperature dependence of ^{35}Cl nuclear quadrupole resonance (NQR) spectra and the respective spin-lattice relaxation times have been measured between room temperature and 120 K on high quality single crystals of bis(4-chlorophenyl)sulfone $[(\text{C}_6\text{H}_4\text{Cl})_2\text{SO}_2]$. Spectra with the typical incommensurate edge singularities were found at temperatures below the transition temperature T_i into the incommensurate (IC) phase. This holds in particular for temperatures very close to T_i . The exponent describing the temperature dependence of the distance between the edge singularities of the incommensurate spectrum is near T_i about 0.35 ± 0.03 which is identified with the critical exponent β of the order parameter. Above T_i a considerable critical contribution to the spin-lattice relaxation rate $1/T_1$ is detected which can be described by some critical exponent ζ of about 0.69 ± 0.02 . The data are interpreted in terms of the three-dimensional (3D) XY model. In the IC phase T_1 stays low indicating a considerable influence of the phason excitations on every part of the IC spectrum. Contrary to the behavior of other systems the minimum of T_1 does not occur at T_i . Rather, it is shifted some degrees from T_i to lower temperatures. 2D ^{35}Cl NQR exchange spectra show no indication for large scale fluctuations of the modulation wave above about 500 Hz.

I. INTRODUCTION

Some insulating crystals pass over from a high-temperature normal (N) phase to a one-dimensionally structurally incommensurately (IC) modulated phase at a certain temperature T_i . In the IC phase at least one physical property is modulated in such a way that the characteristic wave number q_i is not a rational multiple of the reciprocal-lattice vectors of the N phase.¹ The incommensurate modulation wave is in most cases, at least close to T_i , a single harmonic function of space ('plane-wave limit'). It can be represented by an order parameter (OP) with two thermodynamic degrees of freedom, e.g., amplitude and initial phase. In most cases, the IC phase transforms into a commensurate phase at some temperature below T_i .

Quadrupolar perturbed nuclear magnetic resonance (NMR) (Refs. 2–4) and nuclear quadrupole resonance (NQR) (Ref. 5) have been proved to be accurate and sensitive tools for investigating IC phases. These methods take advantage of the coupling between the order parameter and the electric-field gradient (EFG) at the site of the nucleus under investigation. While the inhomogeneously broadened spectrum of NMR/NQR frequencies is determined by the static part of the EFG, its fluctuating part is related to the probabilities of transitions between the nuclear-spin levels. The spin-lattice relaxation rate $1/T_1$ of the nuclear magnetization is given as a linear combination of these probabilities which are a measure of the spectral density of the EFG fluctuations at the Larmor frequency ($\nu_L = \omega_L/2\pi \approx 100$ MHz) and the NQR frequency ($\nu_Q \approx 34$ MHz in the present case), respectively. Extremely slow motions of the modulation wave can be detected by two-dimensional (2D) NMR/NQR exchange spectroscopy. In these experiments $1/T_1$ defines the lower bound for the detectable frequencies of the motions.

Bis(4-chlorophenyl)sulfone (BCPS) which is the topic of the present work has recently attracted considerable interest. It undergoes a transition from a normal N phase with a monoclinic $I2/a$ structure into an one-dimensionally modulated IC phase at a temperature T_i of about 150 K.^{6–16} Recently, the lattice dynamics of this substance has been investigated by inelastic neutron scattering.¹⁷ The phase transition involves a twist of the two phenyl rings around the respective $C1-C-S$ axis and small rotations and translations of the molecule as a whole.^{7,16} The IC wave vector $\mathbf{q}_i = (1/5 + \delta)\mathbf{b}^*$, with \mathbf{b}^* being a reciprocal-lattice vector, varies between $\delta = 0.021$ at 150 K and $\delta = 0.014$ at 20 K.⁸ Contrary to the behavior of most IC systems the IC phase in BCPS persists to the lowest temperatures investigated so far, i.e., to temperatures below about 1 K.^{11,15} The absence of a low-temperature C phase is one reason explaining the attention which is presently paid to BCPS.

Because of the big quadrupole interaction of ^{35}Cl in BCPS and because sufficiently high magnetic fields are not attainable so far quadrupolar perturbed NMR could not be performed. Therefore only ^{35}Cl nuclear quadrupole resonance (NQR) measurements have been reported for this substance.^{9,10,12–15} They indicate rather unresolved spectra in a temperature interval up to about 10 K below T_i . This effect presumably has to be ascribed to a considerable influence of sample imperfections. Moreover, in the temperature region where the spectra could be resolved, i.e., more than 10 K below T_i , a classical mean-field-type behavior seems to be the adequate description of the critical behavior. This is contradictory to the fact that many substances different in composition and structure but equally characterized by the occurrence of an one-dimensional incommensurate modulation can be described by the same critical exponents of the 3D XY model as required by the universality hypothesis.² This model is characterized by a two-dimensional order pa-

rameter with three-dimensional interactions and consequently applies to a one-dimensionally incommensurately modulated lattice. Note, moreover, that the critical behavior of a substance is generally assumed to be strongly influenced by imperfections and that its accurate detection at so big distances from T_i may be subject to some doubts. Thus the previous experiments failed in deriving precise results for the most interesting temperature region near T_i . In order to remove these shortcomings, in the present work special emphasis is laid upon the growth and preparation of high quality BCPS single-crystal samples. By that means it will be shown that the ^{35}Cl NQR spectra can be considerably improved. In particular, in Sec. II we will report ^{35}Cl NQR spectra which allow for an accurate determination of the static critical behavior of the OP in the vicinity of T_i .

It is well known that NQR relaxation measurements are often very well suited for investigating the extremely soft OP fluctuations in the N and IC phase of IC systems. In the case of BCPS ^{35}Cl NQR T_1 measurements exist only in the IC phase at temperatures below about 10 K below T_i .¹⁴ Thus no data are available on the influence of the critical behavior of this substance on T_1 . These unsatisfactory circumstances are very likely due to a considerable influence of sample imperfections on T_1 which in view of the problems with the spectra just discussed can be assumed to be present in the previous investigations of BCPS, too. In Sec. III it will be demonstrated that indeed a considerable improvement of T_1 can be achieved from corresponding experiments on high quality single crystals. As in the case of the NQR line investigations mentioned special emphasis will be laid upon the temperature interval around T_i .

^{35}Cl 2DNQR exchange spectra will be reported in Sec. IV aiming at some possible extremely low-frequency dynamics. Finally, in Sec. V a general discussion of our results will be given.

II. ^{35}Cl NQR SPECTRA

BCPS single crystals were grown from commercial powder (Aldrich) using a home-built zone melting oven. The material was purified by zone melting for about ten times and large single crystals ($>10\text{ cm}^3$) were grown by a modified Bridgman method. The crystals were cut to fit into standard 7-mm tubes. ^{35}Cl NQR measurements were done on a Bruker CXP spectrometer with a home-built probehead in combination with an Oxford CF1200 cryostat and an ITC502 temperature controller. The high quality of our samples is demonstrated by the very small ^{35}Cl NQR linewidth full width at half maximum (FWHM) in the N phase which is smaller than 800 Hz at room temperature. This must especially be compared to the linewidth of about 11 kHz at room temperature of our unpurified material. The latter order of magnitude is also known from previous works.¹³

An echo sequence with phase cycling and a pulse width of 3 μs for a 90° pulse was used for the NQR measurements of the line shape. The pulses were irradiated at a frequency near the line in the N phase or the center of the line distribution in the IC phase. Because of the small linewidth in our experiments there exists a significant influence of small magnetic fields on the NQR line shape. Special care was taken to exclude this effect.

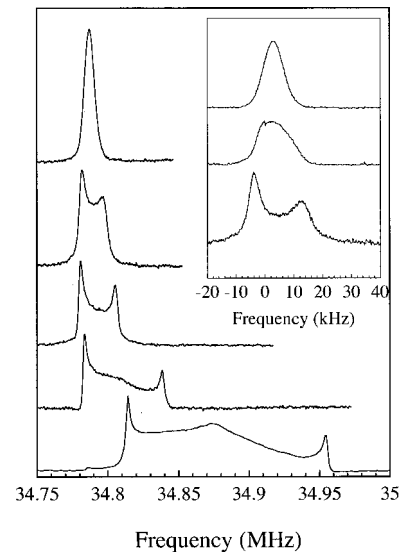


FIG. 1. ^{35}Cl NQR line shape in BCPS single crystals at temperatures (from bottom to top) $T_i - T = 32, 7, 1.4, 0.2, -0.2$ K and (inset) 0.25, 0.1, -0.12 K. In the inset the frequency distance from the irradiation frequency (34.787 MHz) is given. The spectra are not normalized.

The temperature was measured with a calibrated diode sensor with an absolute accuracy of better than ± 0.05 K. It was located about 1 cm apart from the sample. The temperature stability over the measuring time determined this way was better than ± 0.05 K. Figure 1 shows some spectra of the ^{35}Cl NQR line above and below T_i . As it is demonstrated by the inset of Fig. 1, the phase-transition temperature can be fixed with an accuracy of better than ± 0.1 K by directly inspecting the NQR spectra. The same result with the same accuracy is obtained by taking the temperature wherein the temperature dependence of T_1 in Fig. 4 a sharp bending occurs. Therefore $|T - T_i|$ is given with an accuracy of about ± 0.1 K. The temperature gradient over the sample volume is estimated to be better than ± 0.1 K by directly inspecting the width of the edge singularities of the IC spectra. The absolute value of the phase-transition temperature as measured by the diode was $T_i = 148.2\text{ K} \pm 0.1\text{ K}$. This value is about 1.8 K below that usually reported. This difference is very likely due to the fact that we use single crystals of high purity.

The frequency of the NQR line follows above T_i essentially a linear temperature dependence with no indication for a substantial precursor effect of the phase transition at T_i . Far above T_i the linewidth is about 1 kHz and approaching T_i from above starts to increase significantly at about $T_i + 10$ K reaching a value of about 10 kHz at T_i . Both effects are presented in Fig. 2. The behavior of the linewidth demonstrates that in the spectrum of the fluctuations of the order parameter considerable intensity is present at small frequencies below about 10 kHz. Subtracting a constant background value of 1 kHz the temperature dependence of the remaining linewidth can be well represented in terms of some critical exponent 0.7 ± 0.03 . In addition, we note that the steepness of the outer flanks of the edge singularities observed in the IC phase which is a measure for the underlying linewidth increases on approaching T_i from below. Both effects are a clear indication for a critical behavior of the ^{35}Cl NQR linewidth near T_i .

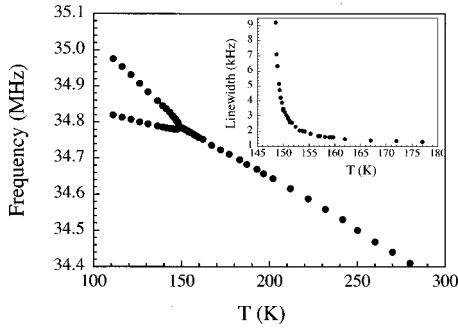


FIG. 2. Temperature dependencies of the frequency of the ^{35}Cl NQR line above T_i and of the frequencies of the edge singularities of the ^{35}Cl NQR line spectra below T_i . Inset: Temperature dependence of the ^{35}Cl NQR linewidth above T_i .

Clearly, according to Fig. 1 distinct IC spectra with typical edge singularities can be resolved as close as about 0.2 K below T_i . The shape of the spectra, however, deviates even close to T_i considerably from a symmetric form which is well known from NMR experiments on other substances: The intensity of the low-frequency edge singularity exceeds noticeably that of the high-frequency edge singularity. Note, moreover, that in the middle part of the spectra some intensity additional to the IC background becomes obvious at a temperature as close as about 4 K below T_i . This additional intensity apparently does not originate from a splitting of one of the two edge singularities on lowering the temperature. The fact that it can be detected even close to T_i excludes the possibility to ascribe it to the formation of nearly commensurate regions in the crystal.

The distance of the edge singularities of the ideal IC spectrum generally follows some critical temperature dependence which is related to that of the order parameter. A corresponding evaluation of the measured spectra must take into consideration the effect of a convolution of the homogeneous line with the ideal spectrum. As a consequence, the apparent distance of the edge singularities of the measured spectrum is diminished with respect to that of the ideal spectrum. This effect is more pronounced the smaller the ratio is between the width of the spectrum and the homogeneous linewidth, i.e., close to T_i . In particular, for the case of BCPS where the widths of the IC NQR spectra are comparatively small and only weakly temperature dependent a careful deconvolution of the spectra must be required. We carried out corresponding simulations of IC spectra on the basis of realistic data. As a result it can be stated that the distance $\delta\nu_{\text{IC}}$ of the edge singularities of the ideal spectrum can be very well approximated by taking for the measured spectrum the distance of the outermost points at about 85% of the maximum height of the respective singularity. This holds for both Lorentzian and Gaussian lines.

The results for the frequencies of the edge singularities and their distance as a function of temperature are presented in Figs. 2 and 3, respectively. Figure 3 demonstrates that the ^{35}Cl NQR edge singularity distance in BCPS does not follow a simple power law with a single critical exponent 0.5. Rather a bending occurs which can be described by some apparent critical exponent of about 0.35 ± 0.03 near T_i (i.e., $T_i - T < 1.5$ K) and 0.75 ± 0.05 far above T_i ($T_i - T \approx 25$ K). This result which corrects previous ones is a con-

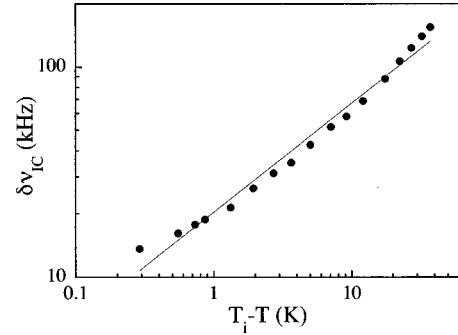


FIG. 3. Temperature dependence of the distance of the edge singularities of an ideal ^{35}Cl NQR IC spectrum determined as described in the text. The line corresponds to a power law with an exponent 0.5.

sequence of the high quality of our crystals which render it possible to derive reliable data in a temperature interval of about 10 K below T_i . On the basis of the results presented in Fig. 3 it is imaginable that for the case of poor crystal quality resulting in rather unresolved considerably broadened NQR spectra an apparent “mean” critical exponent of about 0.5 can be easily derived.

III. ^{35}Cl NQR SPIN-LATTICE RELAXATION

The softening of the OP fluctuations on approaching T_i from above causes a considerable increase of the spectral density of the thermal OP fluctuations at the NMR/NQR resonance frequency and thus results in a corresponding increase of the quadrupolar induced spin-lattice relaxation rate T_1^{-1} . Therefore the fluctuations of the order parameter around its static value cause an additional relaxation effect of the nuclear-spin system. As long as the fast motion condition is fulfilled, i.e., as long as the soft-mode frequency of the OP exceeds the NQR frequency, this additional relaxation process can be related to the static critical behavior above T_i . Below T_i , the OP has two degrees of freedom, the amplitude and the initial phase of the modulation. Conveniently, one can introduce corresponding excitations, termed amplitudon and phason, which are decoupled for small values of the OP (near T_i). The most interesting feature of IC crystals is the energetic degeneracy of the structure with respect to a shift of the initial phase of the modulation wave. As a result, the phason stays soft throughout the IC phase.^{1,18} On the other hand, the amplitudon hardens below T_i as a usual soft mode. In the IC phase the nuclear frequencies as well as the spin-lattice relaxation rate are spatially modulated and thus one obtains a characteristic frequency distribution for each line of the high-temperature phase and a characteristic variation of the spin-lattice relaxation rate over that frequency distribution.

For the NQR relaxation measurements a special echo sequence was employed which directly gives the difference between the equilibrium magnetization and the magnetization detected after a given recovery time following a 180° pulse. Thus one parameter is eliminated from the relaxation-time fit.

We measured the ^{35}Cl NQR spin-lattice relaxation time T_1 from room temperature down to 110 K. The results are

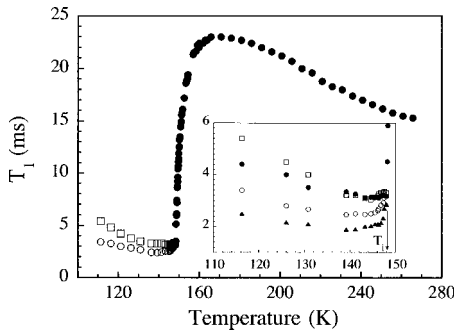


FIG. 4. Temperature dependence of the ^{35}Cl NQR spin-lattice relaxation time T_1 . Inset: local extreme values of T_1 (Fig. 6) as measured in the inner part of the spectrum (\bullet and \blacktriangle) and T_1 values measured at the edge singularities (\square and \circ).

shown in Fig. 4. As in the present case we are dealing with NQR on nuclei with spin $I = \frac{3}{2}$ only one transition exists and thus the magnetization recovery is always single exponential in the N phase. On the contrary, in the IC phase at each frequency of the inhomogeneous broadened spectrum the magnetization recovery is generally not a single exponential. The reason for this behavior is the fact that nuclei with the same NQR frequency can be located at different sites in the modulation wave and thus generally will have different relaxation times which are superimposed in the magnetization recovery. Since the relaxation times occurring in the magnetization recovery differ only little, in the IC phase a mean relaxation time can reasonably be given.

Between ambient temperature and about 180 K the relaxation is governed by a noncritical background mechanism. Then on approaching T_i over a temperature region of about 20 K a very efficient critical contribution takes over. At T_i the background value of T_1 extrapolated from the behavior at higher temperatures is about ten times the values actually measured. An analysis of the temperature dependence of this effective additional relaxation mechanism therefore can be reasonably achieved: Assuming as usual two independent processes the measured relaxation rate T_1^{-1} is represented as the sum of a critical relaxation rate T_{1c}^{-1} and a noncritical one. The latter can be obtained by fitting the values measured at higher temperatures where the background mechanism is dominating to the smoothly varying function $aT^2 - b$ where a and b are positive constants. This relation was derived previously for quadrupolar relaxation by two phonon Raman processes.¹⁹ The critical temperature dependence of T_{1c} can be represented by a critical exponent ζ according to

$$T_{1c} \propto (T - T_i)^\zeta. \quad (1)$$

According to Fig. 5 this relation is verified in a critical temperature region of more than 10 K above T_i with the exponent $\zeta = 0.69 \pm 0.006$ where the margin of error is given by the scatter of the points. It should be noted, however, that the critical exponents determined this way depend strongly on the determination of T_i . A slight variation of T_i of only ± 0.1 or ± 0.1 K leads to critical exponents $\zeta = 0.622 \pm 0.011$ or $\zeta = 0.73 \pm 0.01$, respectively. Given the fact that T_i is determined through our experiments with an accuracy of better than ± 0.1 K these values can be regarded as the extreme exponents which are consistent with our measure-

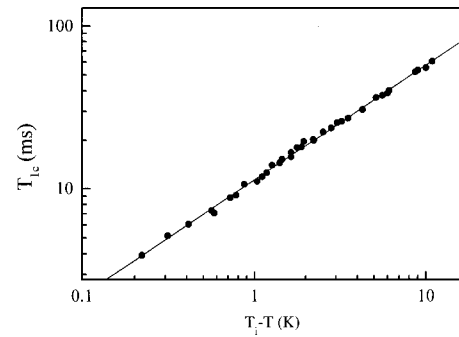


FIG. 5. Double logarithmic plot of the temperature dependence of the ^{35}Cl NQR critical spin-lattice relaxation time T_{1c} above T_i .

ments. Using the most probable temperature T_i results in the best fit of T_1 to a power law, i.e., that with the smallest margin of error. Moreover, no deviation from this power law even close to T_i is shown in Fig. 5. Consequently, in BCPS there is no transition to the slow motion limit which for instance is well known to occur in another system^{20,21} and thus the soft-mode frequency stays well above the NQR frequency of about 35 MHz. Following the previous argumentation,^{20,21} this means that the phason gap frequency in the IC phase is also well above this value. This result is contradictory to a previous one¹¹ stating that in the IC phase the ^1H NMR T_1 is frequency dependent down to 500 kHz indicating a phason gap frequency below this value.

According to Fig. 6 the ^{35}Cl NQR spin-lattice relaxation rate T_1^{-1} varies noticeably over the incommensurate spectrum even at temperatures near T_i . The general character of this variation is essentially the same for all temperatures although the spectra change considerably. The main result is that in the IC phase all T_1 values are small compared to those measured about 20 K above T_i (see also Fig. 4). This result demonstrates that the soft phason excitations contribute dominantly to the relaxation of the whole IC NQR spectrum. In particular, the weak temperature dependence observed for the smallest T_1 value below the temperature where it takes its minimum indicates that the corresponding part (approximately in the middle) of the spectrum is predominantly relaxed by the phason excitation.

Below T_i the relaxation time shows a very unusual behavior. According to Fig. 4, the values of T_1 continue to decrease even below T_i . The minimum of T_1 is found about 7–9 K below the transition temperature. There is no doubt

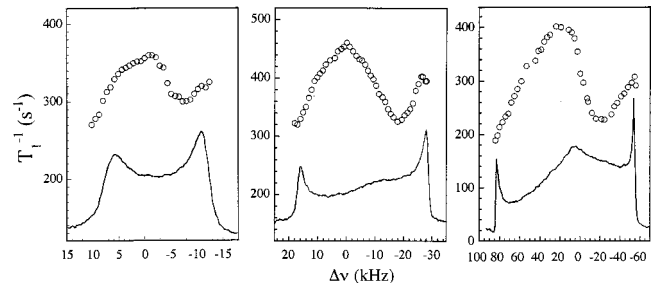


FIG. 6. Variation of the ^{35}Cl NQR spin-lattice relaxation rate T_1^{-1} over the IC spectrum ($\Delta\nu$ is the distance from the irradiation frequency) at temperatures $T_1 - T = 0.7, 7, 32$ K (from left to right). Note that for convenience different scales have been used.

that the measured relaxation rates belong to the IC phase because the corresponding spectra clearly show the typical IC line shape (see Fig. 1). The usual argumentation is the following: With the susceptibility of the OP taking its maximum at T_i , the relaxation time T_1 is expected to have a minimum at T_i . Below the phase transition the phason conserves the fluctuation spectrum of the soft mode at T_i , whereas the amplitudon will get harder with decreasing temperature.^{1,18} This is reflected by the fact that the relaxation time due to phason excitations remains constant below T_i , whereas the relaxation time due to amplitudon excitations increases on lowering the temperature.²² Therefore on the basis of this usual argument the observed decrease of T_1 below T_i cannot be understood.

IV. ³⁵Cl NQR 2D EXCHANGE SPECTRA

The continuum theory of IC phases predicts the existence of a gapless phason mode.¹⁸ It is generally assumed, however, that in a real IC crystal several effects lead to a pinning of the modulation wave and therefore to a nonzero gap in the phason spectrum. This implies that the modulation wave is actually static and cannot move freely through the crystal. It is sometimes assumed, however, that at least close to T_i the modulation wave can overcome the pinning effect by thermal excitation and undergoes a kind of Brownian or diffusionlike motion termed “floating.”

On certain conditions this should give rise to a motional averaging of the static IC spectra near T_i . As it has been argued recently,^{4,23} a deviation from the static distribution of NMR lines in the IC phase is obtained if the following two conditions are simultaneously fulfilled: The amplitude of the phase fluctuations must be sufficiently large. Additionally, the characteristic frequencies of these fluctuations must be comparable to or exceed the interval of NQR frequencies which results from the amplitude of the phase fluctuations via the coupling of the EFG to the modulation wave. If one or both of these conditions are not fulfilled the measured spectrum is the static one.

According to Fig. 1 static IC spectra with a width of about 10 kHz and distinct edge singularities can be resolved about 0.2 K below T_i . There is no indication for motional averaging. Thus the frequency of the phase fluctuations of the IC modulation wave must be smaller than 10 kHz and/or the amplitude of the phase fluctuations of the modulation wave must be small compared to 2π .

To extend the studied frequency range down to even smaller frequencies we recorded ³⁵Cl 2D NQR exchange spectra in the incommensurate phase of BCPS for two different temperatures close to T_i with different mixing times defining the time scale of the experiment.

Employing two-dimensional exchange NQR spectroscopy allows one to study the exchange of nuclear magnetization between different positions in the spectrum during the so-called mixing time t_m by inspecting the off-diagonal intensities in a two-dimensional NQR spectrum. The time constants t_m must be of the same order of magnitude or smaller than the spin-lattice relaxation time T_1 . Thus within this limitation 2D experiments provide the possibility to choose freely the time scale probing the motion of the modulation wave. A change of the resonance frequency of a given nucleus during

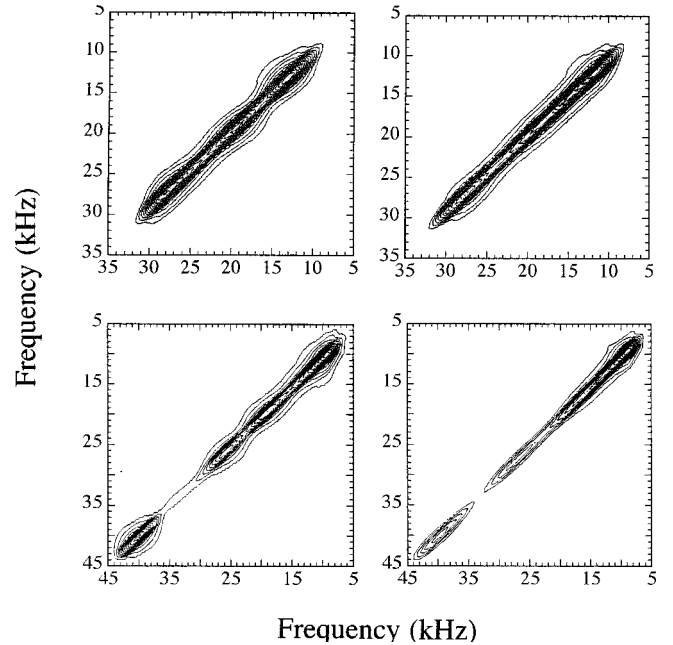


FIG. 7. ³⁵Cl 2D NQR exchange spectra for two different temperatures (top: $T_i - T = 1.2$ K, bottom: $T_i - T = 4$ K) and mixing times (left: 0.1 ms, right: 1.2 ms). The contour plots are drawn down to very low intensities where the influence of noise becomes already visible.

the mixing time due to a sliding or an oscillating modulation wave leads to an off-diagonal intensity where the distance from the diagonal in the 2D spectrum is given by the change of the frequency of the nucleus. For a continuous spectrum like an IC spectrum one expects a broadening of the diagonal intensity surpassing the homogeneous linewidth. If the modulation slides during the mixing time t_m over 180° for a linear coupling to the EFG or 90° for a quadratic coupling the intensity will be distributed over the whole area of possible cross peaks, resulting in a filled rectangle around the diagonal. On the other hand, if the modulation wave is static with relatively small phase fluctuations around the average value, the spectrum should consist of the diagonal part only which is identical to the one-dimensional NQR spectrum. The same holds if the modulation wave is floating but its mean free path during the mixing time is small compared to its wavelength. Therefore principally a motion of the modulation wave cannot be excluded by two-dimensional exchange experiments. Rather, only an upper limit for the amplitude of this motion during the mixing time can be given.

A standard three-pulse 2D exchange NMR sequence including an appropriate pulse cycling was slightly modified by using a spin-echo sequence instead of the last 90° pulse to detect the magnetization, thus leading to a four-pulse sequence. The high-frequency pulses were irradiated outside and near the IC NQR spectrum. The width of the pulses was such that the whole IC spectrum was uniformly excited. The spectra we obtained are presented in Fig. 7. The change in the relative intensity for different parts of the spectrum for different t_m is caused by the variation of the spin-lattice relaxation rate and the spin-spin relaxation rate over the spectrum. The shortest $T_1 \approx 2$ ms (Fig. 4) defines the maximum value of t_m . In all cases, even for the longer mixing time, a noticeable off-diagonal intensity cannot be resolved. More-

over, a loss of diagonal intensity exceeding that due to T_1 effects is not detectable. This result restricts the frequency of possible large scale phase fluctuations to the range below about 500 Hz. Similar results were obtained in previous two-dimensional exchange experiments in the IC phases of Rb_2ZnBr_4 and Rb_2ZnCl_4 (^{87}Rb NMR satellite spectra)^{4,23} and biphenyl (^2H NMR spectra).²⁴

V. DISCUSSION

Discussing first the shape and width of the inhomogeneous line distribution in the IC phase we have to start out with the well-known relation for the NQR frequency ν_Q of an $I = \frac{3}{2}$ nucleus:²⁵

$$\nu_Q = \frac{eQV_{zz}}{2h} \left(1 + \frac{\eta^2}{3} \right)^{1/2}, \quad (2)$$

where the symbols have the usual meaning. In particular, $\eta = (V_{xx} - V_{yy})/V_{zz}$ is the asymmetry parameter and V_{xx} , V_{yy} , and V_{zz} are the diagonal (principal) elements of the EFG in the principal axes reference frame which obey $|V_{zz}| \geq |V_{yy}| \geq |V_{xx}|$. Moreover, the Laplace condition $V_{xx} + V_{yy} + V_{zz} = 0$ holds in every reference frame. In the IC phase the five independent EFG components are generally spatially modulated. As a consequence, the orientation of the principal axes reference frame is modulated, too. This modulation has no influence on the distribution of NQR frequencies. Rather, according to Eq. (2), the distributions of V_{zz} and η determine completely the distribution of the NQR line. This implies that, in general, from the measured NQR line distribution no unambiguous conclusion can be drawn on the distribution of the EFG elements.

In general, we can expand the EFG tensor as a local quantity in a Fourier series. Consequently, we can write the space dependence of the component V_{ij} as given in some fixed crystal reference frame taking into account only the leading terms as²⁶

$$V_{ij}(x) = V_{Nij} + V_{0ij} + V_{1ij} \cos[\Phi(x) + \Phi_{1ij}] + V_{2ij} \cos[2\Phi(x) + \Phi_{2ij}]. \quad (3)$$

By V_{Nij} we denote the tensor element in the N phase, V_{kij} are the corresponding Fourier amplitudes, $\Phi(x)$ is the space dependent phase and Φ_{kij} are the respective initial phases. In the plane-wave limit, $\Phi(x) = q_i x$.

If one takes into account the coupling between the Fourier amplitudes and the OP (Refs. 26 and 27) it can be shown that V_{1ij} is proportional to the amplitude of the modulation (critical exponent β), whereas, disregarding fluctuations, V_{2ij} is proportional to the square of it. Taking into account fluctuations of the order parameter leads to a different exponent for V_{2ij} which is called $\bar{\beta}$. Generally, $V_{ij}(x)$ is therefore dominated by the term linear in the OP at least in the vicinity of T_i in the case that no symmetry restrictions exclude the linear term.

Performing a principal axes transformation of the EFG given in Eq. (3), generally, all Fourier amplitudes V_{1ij} and V_{2ij} and corresponding initial phases enter into the orientation of the EFG principal axes system and its principal components. All these quantities are modulated and the modula-

tions of V_{zz} and η lead according to Eq. (2) to the inhomogeneous distribution of the IC NQR spectra. Thus the temperature dependence of the spectra and, in particular, of the distance between the edge singularities is determined by the temperature dependence of all EFG Fourier amplitudes and the phase relations between them.

For the case that the OP is small, i.e., close to T_i , an elementary calculation on the basis of Eqs. (2) and (3) shows that ν_Q is proportional to the OP. As a consequence, also the distance of the edge singularities of the IC spectrum is proportional to the OP. Thus the apparent critical exponent given in Sec. II for the temperature region near T_i is a strong indication for the applicability of the 3D XY model to BCPS, too. Accordingly, within the limits of experimental accuracy, BCPS fits to the universal critical behavior known from other one-dimensionally modulated IC systems.²⁻⁴ On the basis of the same arguments one can understand the increase of the apparent critical exponent becoming obvious in Fig. 3 at increasing distance from T_i . This is due to the fact that higher-order terms must be taken into account.

Moreover, we did some calculations of the IC line shape on the following basis: In a previous work,²⁸ for the N phase the asymmetry parameter $\eta \approx 0.2$ was estimated. Taking from Fig. 2 the frequency $\nu_Q \approx 34.8$ MHz close above T_i , Eq. (2) results in $|V_{zz}| = 34.8$ MHz, $|V_{xx}| = 20.8$ MHz, and $|V_{yy}| = 14$ MHz. This complete diagonal EFG was used as a basis for the simulations of the spectra in the IC phase. In doing this we disregard the weak temperature dependence of ν_Q above T_i . The modulation functions were introduced according to Eq. (3), where $V_{Nij} = 0$ for $i \neq j$. Whereas above T_i the Laplace condition is fulfilled by definition it was enforced below T_i . The temperature dependence of the Fourier amplitudes V_{1ij} and V_{2ij} were assumed to be given by the critical exponents $\beta = 0.345$ and $\bar{\beta} = 0.83$ of the 3D XY model.²⁷

According to this ansatz, each of the five independent EFG elements is determined by four independent fit parameters (two amplitudes and two initial phases) resulting in a total of 20 parameters. Therefore it is self-evident that it is not meaningful to try a real fit to the experimental spectra. Instead, we guessed at some of the parameters while disre-

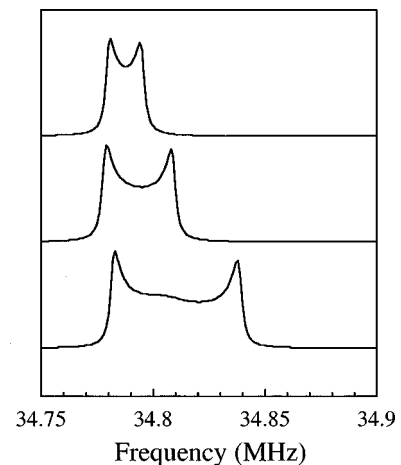


FIG. 8. ^{35}Cl NQR spectra calculated at temperatures $T_i - T = 7, 1.4, 0.2$ K (bottom to top) as explained in the text. The spectra are not normalized.

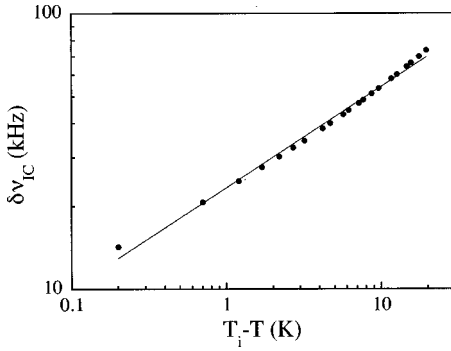


FIG. 9. Temperature dependence of the distance of the edge singularities of the calculated ^{35}Cl NQR IC spectra (Fig. 8). The line corresponds to a power law with an exponent 0.42.

garding others. A calculation of the resulting NQR frequencies on the basis of an equipartition of the phase $\Phi(x)$ between 0 and 2π leads to the theoretical IC spectra. In order to enable comparison between the measured (see Fig. 1) and the ideal IC spectra the latter were folded with the homogeneous line shape in the way explained above. In addition, the parameters of the model must result in reasonable widths and shapes of the spectra for different temperatures if the temperature dependence of the Fourier amplitudes mentioned before is used.

Many spectra calculations of this type were done. Figures 8 and 9 give the results for a set of parameters which lead to spectra most similar to the measured ones. As to be expected from the outset, the calculated spectra do not coincide exactly with the experimental ones. Nevertheless, they very much resemble the qualitative behavior. The spectra show the appearance of the broad additional intensity in the middle of the spectrum and hint at the asymmetry of the intensity of the edge singularities. The former can be related to the fact that higher-order terms become important. The occurrence of this additional intensity is obviously correlated to the successive deviation of the local slope in Fig. 3 from the initial one. Moreover, we note that the temperature dependence of the distance of the edge singularities of the calculated ideal spectrum cannot be represented by a power law with a single exponent.

These considerations demonstrate that the spectra found by experiment in BCPS are consistent with the critical behavior to be described by the 3D XY model. Due to the limitations given by the NQR method they are, however, not a rigorous proof for that model.

We now turn to a discussion of the critical behavior of T_{1c} in the N phase as given in the context of Eq. (1). Following the argumentation given in Ref. 2 we can write for a system with three-dimensional interactions

$$\frac{1}{T_{1c}} \propto T^2 e^{\Delta U/k_B T} \frac{\chi^2}{\xi^3} \int_0^{\xi k_c} \frac{x^2 dx}{(1+x^{2-\eta})^2}. \quad (4)$$

Here we have assumed order-disorder (relaxational) fluctuations of the OP with relaxation times fulfilling the condition $2\pi\nu_Q\tau(\mathbf{q}) \ll 1$ (fast motion limit) for all wave vectors \mathbf{q} , a direct process for the relaxation of the nuclear-spin system and the well-known van Hove theory for critical dynamics. The symbols in Eq. (4) have the usual meaning: by χ and ξ

we denote the static order-parameter susceptibility and the correlation length of the order-parameter fluctuations, respectively. Moreover, ΔU is the activation energy of the uncoupled system, k_c is a constant cutoff wave number whose magnitude is of the order of the radius of the Brillouin zone and η is the critical exponent which characterizes the long-range behavior of the correlation function. Rewriting Eq. (4) we get

$$\frac{1}{T_{1c}} \propto T^2 e^{\Delta U/k_B T} (T - T_i)^{-\zeta} \left(\int_0^\infty \frac{x^2 dx}{(1+x^{2-\eta})^2} - C(T) \right). \quad (5)$$

The critical temperature dependence of T_{1c} is given by the exponent $\zeta = 2\gamma - 3\nu$. The corresponding term in Eq. (5) dominates in the vicinity of T_i demonstrating the importance of having reliable data close to T_i . In a practical determination of the critical exponent, however, one must take into consideration the influence of the weak temperature dependence of the other quantities occurring in Eq. (5). In particular, the quantity $C(T)$ which, generally, is a small correction to the constant integral arises from the fact that the correlation length ξ depending critically on the temperature has some finite value above T_i : The smaller the correlation length the stronger the influence of $C(T)$. In this way the apparent exponent ζ in corresponding plots of experimental results is increased. In a similar manner also the first two terms in Eq. (5) limit the accuracy in the determination of the true exponent ζ . The critical exponent $\zeta = 0.69 \pm 0.02$ derived above from the experimental data differs noticeably from the value $\zeta = 0.624$ derived for the 3D XY model.²⁹ The latter is near the lower limit of the experimental error interval discussed in Sec. III. If one assumes that the discrepancy between the experimental and theoretical value is real on the basis of the argumentation just presented it can be ascribed to an influence of the temperature dependence of the correlation length.

VI. CONCLUSION

We have measured the temperature dependence of ^{35}Cl NQR spectra and the respective spin-lattice relaxation times between room temperature and 120 K on high quality BCPS single crystals. The interpretation of the data in terms of the 3D XY model is convincing. Nevertheless, it is desirable to have data which avoid the principle shortcomings of the NQR method. Principally, quadrupolar perturbed NMR may be looked upon as an adequate method. Given the ^{35}Cl NQR frequency of about 35 MHz and the fact that an NMR frequency of about 200 MHz is therefore desirable in such an experiment, an unreasonably high magnetic field of about 45 T is required. A more promising approach would be to apply extremely small magnetic fields, i.e., Zeeman perturbed NQR.

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