

## <sup>35</sup>Cl nuclear magnetic resonance study of critical fluctuations in bis(4-chlorophenyl)sulphone [(ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SO<sub>2</sub>]

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The temperature dependence of the resonance frequency of the <sup>35</sup>Cl NMR central transitions lines  $-1/2 \leftrightarrow +1/2$  has been measured using a high-quality organic single crystal of bis(4-chlorophenyl)sulphone. The recorded spectra show an increasing characteristic broadening of the NMR line indicating the phase transition in a structurally incommensurate phase at the temperature  $T_i = 149.7$  K. Moreover, the dynamics of the incommensurate modulation is investigated in the normal high-temperature phase close to the temperature  $T_i$  by means of nuclear spin-lattice relaxation measurements. The temperature dependence of the critical contribution to the spin-lattice relaxation rate above  $T_i$  can be described by the critical exponent  $\zeta \approx 0.67$  which is fully consistent with the predictions of the universality class of the three-dimensional XY model. The results from a conventional treatment of the critical contribution are compared with the predictions of a comprehensive field-theoretical model.

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### I. INTRODUCTION

We investigate bis(4-chlorophenyl)sulphone [(ClC<sub>6</sub>H<sub>4</sub>)<sub>2</sub>SO<sub>2</sub>], henceforth abbreviated as BCPS, because it is a very interesting substance for studies of the phase transitions in structurally incommensurately (IC) modulated systems and for proof of universal properties. BCPS forms monoclinic crystals at room temperature with a space group of  $I_2/a$ , containing four molecules ( $Z=4$ ) per unit cell. The molecules are located on the twofold axis and are all equivalent in the crystalline lattice. The structure of BCPS single crystals was first studied by means of x-ray diffraction at room temperature.<sup>1,2</sup> The cell dimensions of the single crystal of BCPS are  $a=2.0216$  nm,  $b=0.5004$  nm,  $c=1.2248$  nm, and  $\beta=90.34^\circ$ . The dihedral angle between the planes of the aromatic rings is  $79.27^\circ$  and the angle between the plane of each ring and the common Cl-S-Cl plane is  $84.6^\circ$ . The structural phase transition was investigated by means of x-ray diffraction (XRD).<sup>3</sup> It has been found that the crystal shows a phase transition from a normal high-temperature phase into a structurally incommensurately modulated phase at ca. 150 K with a modulation wave vector  $q=0.78b^*$ . The IC phase exists apparently down to 0 K. The structure of the incommensurate phase of a BCPS single crystal was determined at 90 K.<sup>4</sup> A significant intramolecular twist of the phenyl groups and a slight bending of the molecule have been found.

NMR techniques have also been extensively used in order to obtain information about the dynamics in the normal and incommensurate phases of BCPS. Moreover, NMR on nuclei with quadrupole moments is very sensitive to study subtle changes of local electric fields. The spatial variation of the IC modulation leads to the known frequency distribution and thus to an anomalous NMR line shape with edge singularities.<sup>5</sup> Most of these studies were performed by means of <sup>1</sup>H and <sup>2</sup>H NMR measurements. Single-crystal proton<sup>6,7</sup> and deuteron<sup>8</sup> NMR measurements both in the nor-

mal (N) and IC phases of BCPS were performed. <sup>1</sup>H spin-lattice relaxation times have been measured with the aim to investigate the mechanism of the phase transition due to the molecular motion through the twisting of the two phenyl rings.<sup>6</sup> The proton spin-lattice relaxation times are found, however, to be constant over the whole temperature range. The principal conclusion of this study is that the molecules in BCPS crystals seem to be rigid on the NMR time scale, which suggests that there is a high activation barrier for the twisting of the phenyl rings about the Cl-S axis. One difficulty associated with studying the dynamics of the IC phase by measuring the spin-lattice relaxation times  $T_1$  of nuclei of  $I=1/2$  (like <sup>1</sup>H) with no quadrupole interactions arises from the very long values of the relaxation time.<sup>6,7</sup> To overcome this fact, <sup>1</sup>H NMR  $T_1$  measurements in BCPS have been performed<sup>7</sup> in which a faster proton nuclear polarization recovery has been achieved by level crossing between the proton Zeeman and <sup>35</sup>Cl quadrupole perturbed Zeeman levels. A sharp rise in the <sup>1</sup>H relaxation rate is observed which should be related to the short <sup>35</sup>Cl relaxation times close to  $T_i$  as discussed below. Deuteron NMR measurements<sup>8</sup> have shown that the quadrupole coupling tensors of the deuterons in the N phase are nearly axially symmetric and the symmetry axis was found coinciding with the C-D bond direction. The main problems in these measurements arise from the very long deuteron spin-lattice relaxation times ( $T_1$  values from 8 to 40 min).  $T_1$  measurements have been carried out to examine the reason for the broadening of the lines above  $T_i$ . The fact that the observed spin-lattice relaxation rates are almost the same far from  $T_i$  and different close to  $T_i$  for the considered deuterons means that when going from the N to the IC phase, the C-D bond directions experience rotations which are different in different unit cells. The formation of macroscopic domains with slightly different orientations of the aromatic groups was assumed to result in a broadening of the line shape. A difficulty arises here from an additional broadening of the line and a formation of shoulders due to an overlap of the

resonance frequencies of the ortho- and metadeuterons in opposite positions. These undesired effects complicate the interpretation of the  $^2\text{H}$  NMR frequency distribution in the IC phase of BCPS.

Because of the difficulties mentioned above, mainly  $^{35}\text{Cl}$  nuclear quadrupole resonance (NQR) was applied to characterize the phase transition in BCPS.<sup>6,9-15</sup> The inhomogeneous line shape of the  $^{35}\text{Cl}$  NQR spectra in the incommensurate phase of BCPS was analyzed<sup>14,15</sup> on the basis of a general treatment developed by Pérez-Mato, Walisch, and Petersson.<sup>16</sup> In other papers the line shape was analyzed on the basis of a nonlocal model.<sup>13</sup> NQR nuclear spin-lattice relaxation measurements were applied to study the critical dynamics in the N phase close to  $T_i$ .<sup>15,17,18</sup> The variation of the  $^{35}\text{Cl}$  spin-lattice relaxation rate over the incommensurate NQR frequency distribution in BCPS has been measured at various temperatures.<sup>10-12,15,18</sup> The characteristic features of the variation of the spin-lattice relaxation rate  $1/T_1$  over the incommensurate NQR frequency distribution were explained in terms of competing phason and amplitudon contributions. In a recent inelastic neutron scattering (INS) study<sup>19</sup> on deuterated BCPS the spectra were fitted by assuming a classical damped harmonic oscillator for the soft mode component. At the phase transition the splitting of the high-temperature soft mode into two new excitations, viz., the phason and amplitudon, has been observed, as found in other IC-modulated crystals too. Within the INS accuracy, the phason frequency is found to be constant with a mean value of ca. 90 GHz from  $T_i$  down to the lowest measured temperature of 19 K. The authors<sup>19</sup> argued that both the soft mode frequency saturation at the N-IC transition and the phason gap are of the same (intrinsic) microscopic nature, including a dynamical central peak in the spectral responses in both phases. In Ref. 17, however, the rapid decrease of the  $^{35}\text{Cl}$  NQR and  $^2\text{H}$  NMR spin-lattice relaxation times close to the transition phase is accounted for by the presence of the central peak instead of the contribution of the soft mode. The relaxation mechanism below the N-IC phase transition is expected to be driven by the same process and not by the phason mode. In a quite recent paper<sup>18</sup> laboratory ( $T_{1Q}$ ) and rotating frame ( $T_{1Q,\varrho}$ )  $^{35}\text{Cl}$  NQR spin-lattice relaxation times were measured. The resonance frequency and temperature dependences of the  $^{35}\text{Cl}$  NQR spin-lattice relaxation rates are interpreted here in terms of large-scale fluctuations of the pinned modulation wave instead of small-scale fluctuations (phasons and amplitudons).

A still open question in the previous papers is whether the temperature dependence of the order parameter in the IC phase below  $T_i$  and the critical contribution to the relaxation time  $T_1$  in the N phase close to  $T_i$  are fully consistent with the results of the renormalization group theory, i.e., with critical exponents predicted by the three-dimensional (3D) XY model. Only in the study  $^{35}\text{Cl}$  NQR study of the longitudinal relaxation time  $T_1$  of BCPS performed by Decker and Petersson<sup>15</sup> is there a clear indication that the expected critical exponent for the 3D XY model,  $\zeta = 2\gamma - 3\nu$ , can be derived experimentally. It is the aim of this study to further contribute to a deeper understanding of these questions.

We expect further useful information by applying NMR

measurements on the  $^{35}\text{Cl}$  nuclei which have been found to be very sensitive local probes for the study of IC-modulated systems.<sup>20,21</sup> Because of the large nuclear quadrupole interaction of  $^{35}\text{Cl}$  nuclei in BCPS, however,  $^{35}\text{Cl}$  NMR measurements were very difficult. The problem in the case of BCPS in that respect is that the quadrupole frequency for the chlorine nuclei (ca. 35 MHz) is comparable in size with the Larmor frequencies of 48.99 MHz for  $^{35}\text{Cl}$  and 40.78 MHz for  $^{37}\text{Cl}$  in a magnetic field of 11.744 T. Hence, also for relatively high external magnetic fields an exact calculation of the  $^{35}\text{Cl}$  NMR spectra was necessary and it was impossible to realize the necessary linear coupling between the order parameter and quadrupole coupling tensor.

Nevertheless, in this paper it can be shown that spin-lattice relaxation time measurements  $T_1(T)$  are suitable to detect critical fluctuations. Therefore, we shall restrict our study of the  $^{35}\text{Cl}$  NMR spin-lattice relaxation to an investigation of the critical dynamics in the normal phase near the phase transition into the IC phase at  $T_i$ .  $^{35}\text{Cl}$  spin-lattice relaxation time measurements at various dc magnetic fields would also allow us to check whether slow or fast order parameter fluctuations occur in the vicinity of the N-IC transition as it has been described in details in Ref. 22. In Sec. II we outline the conditions for the NMR experiments. Section III deals with the temperature dependence of the  $^{35}\text{Cl}$  NMR spectra and the line shape associated with the IC modulation. Measurements of the spin-lattice relaxation time are reported in Sec. IV which provide information about the dynamical properties of the crystal and the critical fluctuations close to  $T_i$ .

## II. EXPERIMENTAL DETAILS

$^{35}\text{Cl}$  NMR experiments were run on the central transition lines using dc magnetic fields of  $B_0 = 7.05$  T and 11.7 T. Since crystal impurities result in a broadening of the lines, a high-quality single crystal was used so that we obtain a NMR linewidth of about 1 kHz far from the transition which is much narrower in comparison to those values previously reported in the NQR studies.<sup>6,9-14</sup> The NMR probe is equipped with two goniometers with two perpendicular rotation axes. The first goniometer allows one to rotate the sample tube with the crystal about an axis perpendicular to  $B_0$  and the other one to adjust the crystal around the second axis of rotation. Thus, it is possible to achieve exactly the desired orientation of the probe. Previous angular-dependent  $^{35}\text{Cl}$  NMR measurements<sup>23</sup> have shown that the two non-equivalent  $^{35}\text{Cl}$  sites in the unit cell of the paraelectric phase are also reflected by the two  $^{35}\text{Cl}$  NMR lines seen in Fig. 1. Because of the large  $^{35}\text{Cl}$  quadrupole resonance frequency for BCPS comparable to the Larmor frequency, in this paper it was also shown that only central transitions can be measured and that an exact diagonalization of the spin Hamiltonian is necessary for the treatment of the spectra. The  $^{35}\text{Cl}$  NMR measurements were performed at the orientation of the sample where we obtain an orientational degeneracy of the two lines resulting in one single sharp resonance line. This situation occurs if the crystallographic axes [100] and [010] are oriented perpendicular and parallel to the direction of the

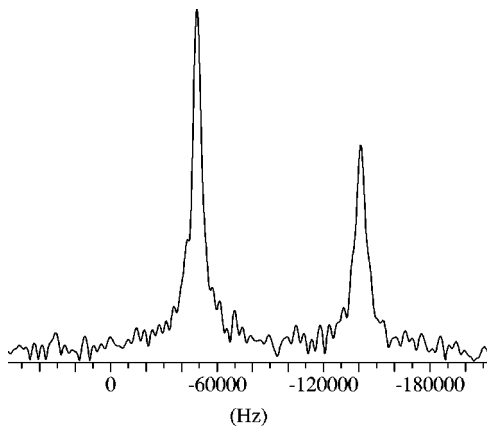


FIG. 1. <sup>35</sup>Cl NMR spectrum of the central lines in the single-crystal bis(4-dichlorobiphenyl)sulphone at room temperature. The measurements were run at the Bruker MSL 500 NMR spectrometer ( $B_0 = 11.744$  T) at a frequency of 42.3 MHz. The crystallographic [100] is held perpendicular to the static magnetic field  $B_0$ . The existence of the two lines is in good agreement with the crystal symmetry and with the two nonequivalent positions of the two chlorine atoms of the considered molecule.

dc magnetic field  $B_0$ , respectively. Thus the signal-to-noise ratio is appreciably improved.

The temperature dependence of the <sup>35</sup>Cl NMR central lines frequencies is measured using a solid echo  $\pi/2$ - $\tau$ - $\pi/2$  pulse sequence in order to circumvent problems with the dead time because of the very broad NMR lines in the incommensurate phase. An inversion recovery pulse sequence  $\pi$ - $\tau$ - $\pi/2$  has been applied to measure  $T_1$  in the normal phase. An Oxford Instruments gas-flow cryostat with liquid-nitrogen vapors associated with an ITC4 temperature controller, characterized by a temperature stability of 0.1 K, was employed in cooling down the temperature from room temperature to 140 K. Independently of the temperature control unit of the Oxford cryostat, the sample temperature was measured by a calibrated Pt 100 sensor placed close to the crystal. The measuring time for each experiment is about 30 min so that the temperature gradient across the sample is minimized.

### III. <sup>35</sup>Cl NMR SPECTRA

<sup>35</sup>Cl NMR central line measurements were carried out in single-crystal samples of BCPS from room temperature down to 140 K. In the normal phase the <sup>35</sup>Cl NMR line shape is nearly Lorentzian. The experimental results show precursor effects within the range 185–150 K on approaching the normal-incommensurate phase transition. A progressive broadening from 1 kHz to about 5 kHz of the linewidth above  $T_i$  can be observed below 170 K. This can also be seen if the height of the line is compared for different temperatures. Between room temperature and 185 K the NMR line height  $I(T)$  increases while it decreases below 185 K. This diminution can be associated with a broadening<sup>10</sup> of the resonance line, which is due to an increase of the fluctuations in the EFG on approaching  $T_i$ , which were also observed in the relaxation times  $T_1(T)$ . The <sup>35</sup>Cl NMR central line fre-

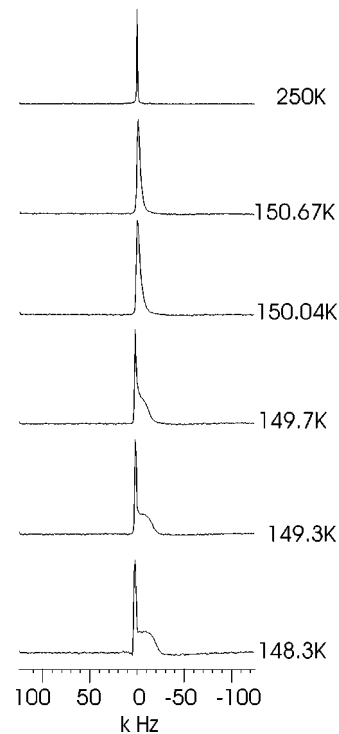


FIG. 2. <sup>35</sup>Cl NMR line shape of the central transition in bis(4-dichlorobiphenyl)-sulphone at different temperatures. The measurements were run at the Bruker MSL 300 NMR spectrometer ( $B_0 = 7.046$  T) and require a broad variation of the frequency offset (up to about +7MHz) relative to the Larmor frequency of 29.395 MHz. The crystallographic axis [010] is held parallel to the static magnetic field  $B_0$ . We note a progressive line broadening of the central line and an important broadening with two edge singularities characteristic of an incommensurate phase transition at  $T_i = 149.7$  K.

quencies in the normal phase show a weak linear temperature dependence comparable to that observed in the <sup>35</sup>Cl NQR measurements.<sup>15</sup> It can be related to vibrations in the crystal. Detectable changes in the angle between the principal axis of the EFG coinciding with the C-Cl bond and the static magnetic field that might result in larger frequency shifts in our <sup>35</sup>Cl NMR measurements cannot be concluded from the <sup>35</sup>Cl NMR measurements in the N phase. The change in the NMR absorption line shape on going into the IC phase is illustrated in Fig. 2. According to our experience, the most reliable criterion to derive the transition temperature from the <sup>35</sup>Cl NMR spectra is to analyze the changes in the line shape. This contrasts to the behavior of the spin-lattice relaxation time  $T_1$  around  $T_i$ . There is no clear relation between the phase transition temperature and a possible minimum of  $T_1$ . For instance, the values of  $T_1$  are expected to become independent of the temperature already above  $T_i$  if the frequency of the order parameter fluctuations is less or comparable to the Larmor frequency used in the NMR measurements. Below the phase transition temperature  $T_i$  the relaxation time  $T_1$  may stay constant if its value is dominated by phason fluctuations. In the present <sup>35</sup>Cl NMR spectra distinct changes in the line shape at  $T_i$  were observed which allow us to derive clearly a value of  $T_i = 149.7$  K for the determination of the phase transition temperature. For temperatures below 149.7

K the NMR spectrum is characterized by a broad line with two edge singularities, as expected in an incommensurate phase. It is not the aim to discuss in detail the difference of this temperature value in comparison to other measurements (e.g., a value of 148.2 K in the NQR measurements in Ref. 15) but to use the clear changes in the NMR line shape and very accurate measurements of the temperature differences  $T - T_i$  for a precise calibration of the temperature-dependent  $T_1$  values. Further, we have to note that a good crystal allows us to gain an improvement in the signal-to-noise ratio<sup>7</sup> and a greater sharpness of the resonance lines (linewidth of about 1–5 kHz). Consequently, we may obtain a better accuracy in the determination of the phase transition temperature from our <sup>35</sup>Cl NMR measurements in comparison with the data reported in the literature.<sup>6,9–15</sup>

#### IV. <sup>35</sup>Cl NMR SPIN-LATTICE RELAXATION AND CRITICAL DYNAMIC

As well known, the spin-lattice relaxation is given by the return of the nuclear spin magnetization  $M_z(t)$  back to its thermal equilibrium value after a preceding radio frequency (rf) excitation. In particular, one obtains for the relaxation of a central line<sup>24</sup> for a spin system with a quantum number  $I = 3/2$ ,

$$M_z(t) = M_0 [1 - (e^{-2W_1 t} + e^{-2W_2 t})], \quad (1)$$

after a preceding 180° pulse, i.e., with the initial condition  $M_z(t=0) = -M_z(t \rightarrow \infty) = -M_0$ .  $W_\mu$  stands for the probability of a quantum transition  $\Delta m = \mu$ ,  $\mu = 1, 2$  induced by fluctuations of the electric field gradient (EFG) tensor components  $V_{ij}$  ( $i, j = x, y, z$ , laboratory frame). Note that  $W_\mu = 0$  for  $\mu > 2$ . For a nucleus with  $I = 3/2$  as <sup>35</sup>Cl, it is found that<sup>25,26</sup>

$$W_1 \propto J(V_{xz}^2; \omega_L) + J(V_{yz}^2; \omega_L), \quad (2)$$

$$W_2 \propto J\left[\frac{1}{4}(V_{xx} - V_{yy})^2; 2\omega_L\right] + J(V_{xy}^2; 2\omega_L), \quad (3)$$

where

$$J(V_{ij}^2; \mu\omega_L) = \int_{-\infty}^{+\infty} \langle \delta V_{ij}(0) \delta V_{ij}(t) \rangle e^{-\mu\omega_L t} dt \quad (4)$$

is the spectral density of the EFG fluctuations  $\delta V_{ij}$  at the frequencies  $\mu\omega_L$  ( $\mu = 1, 2$ ). In the relaxation process considered here, a direct process is dominant if an overdamped or relaxatory soft mode is present contributing to the spectral density  $J(V_{ij}^2; \mu\omega_L)$ . This situation is relevant for the critical fluctuations (collective lattice motion) in the N phase close to the phase transition into the IC phase at  $T_i$ . The alternative two-phonon (Raman) relaxation process can be relevant for the noncritical background relaxation.<sup>20</sup> As there is a dominant linear coupling of the EFG to the order parameter,<sup>27</sup> the corresponding spectral densities in Eqs. (2) and (3) are simply proportional. Thus, in a general situation one expects a biexponential relaxation function  $M_z(t)$  [see Eq. (1)]. A single-exponential decay with a longitudinal relaxation time

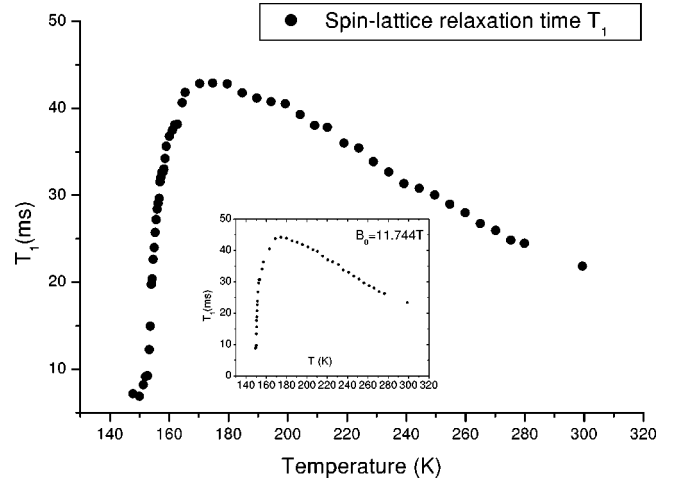


FIG. 3. Temperature dependence of the <sup>35</sup>Cl NMR spin-lattice relaxation time  $T_1$  in single-crystal BCPS above the structural normal to incommensurate phase transition measured in the crystal orientation  $b \parallel B_0$  at the central line. The measurements were run at the Bruker MSL 300 NMR spectrometer and in the inset at the Bruker MSL 500 NMR spectrometer.

$T_1$  may be observed if the transition probabilities are equal,  $W_1 \approx W_2$ , in case of fast motions. In our subsequent discussion only such situations will be considered where a single-exponential behavior is observed with the relaxation rate  $1/T_1 = 2W_1$ , i.e., possible deviations from a single-exponential behavior are beyond the limits of experimental accuracy.

Measurements of the temperature dependence of the <sup>35</sup>Cl NMR spin-lattice relaxation time  $T_1$  were carried out between room temperature and 140 K on single-crystal samples. The temperature dependence of the relaxation time  $T_1$  in BCPS is presented in Fig. 3. The values  $T_1$  show three temperature regions characterized by different dynamic processes. From room temperature down to about 185 K, the relaxation time  $T_1$  increases with decreasing temperature and reaches a maximum value of about 45 ms. On further decreasing the temperature the relaxation time  $T_1$  starts to decrease dramatically on approaching  $T_i$  (Fig. 3). Similarly as reported in Refs. 15 and 18 the relaxation time  $T_1$  shows an unusual behavior below  $T_i$ . The values continue to slightly decrease even below  $T_i$  down to about  $T_i - 4$ . The background (noncritical) relaxation time above ca. 185 K can be interpreted in terms of quadrupole relaxation induced by lattice vibrations through a two-phonon Raman process. On the basis of the Debye model, the following relation was proposed by Van Kranendonk:<sup>28</sup>

$$\frac{1}{T_{1bg}} = T^2 \left( a - \frac{b}{T^2} \right) \quad (5)$$

for

$$T > \frac{1}{2} \Theta_D, \quad (6)$$

where  $\Theta_D$  is the Debye temperature of the crystal [ $\Theta_D = 70$  K (Ref. 17) for the BCPS crystal]. Between 185 K and



$T_i$  the strong decrease of the spin-lattice relaxation time  $T_1$  clearly indicates an additional relaxation mechanism due to the influence of critical fluctuations, i.e., to precursor effects of the structural phase transition at  $T_i$  correlated to long-range fluctuations in the EFG at <sup>35</sup>Cl nuclear sites. Such a behavior might indicate a structural transition driven by a soft mode. The contribution  $1/T_{1cr}$  to the total relaxation rate  $1/T_1$ , which is due to the critical slowing down of the soft mode fluctuations on approaching the N-IC transition from above, can be derived from the experimental with a sufficiently high accuracy if the background contribution is taken into account. On the assumption that the critical and noncritical mechanisms are independent, we can write

$$\frac{1}{T_{1cr}} = \frac{1}{T_1} - \frac{1}{T_{1bg}} = \frac{1}{T_1} - T^2 \left( a - \frac{b}{T^2} \right), \quad (7)$$

with  $a$  and  $b$  constant quantities.

In the following we are only interested in an analysis of the temperature dependence of the critical contribution  $1/T_{1cr}$  above  $T_i$ . By assuming a direct relaxation process of the nuclear spin system for the case in which the relaxation mechanism is due to the order parameter fluctuations and by considering the classical limiting case of the fluctuation-dissipation theorem, one can derive the critical contribution from the following formula:

$$\frac{1}{T_{1cr}} \propto W_1 \propto T \sum_{\mathbf{k}} \frac{\chi''(\mathbf{k}, \omega_L)}{\omega_L}. \quad (8)$$

If we consider, moreover, a model system of interacting pseudospins in which the interaction of the spins with the lattice vibrations induces spontaneous flips, the dynamical susceptibility can be written in the form<sup>24,29</sup>

$$\chi(\mathbf{k}, \omega) = \frac{\chi(\mathbf{k}, 0)}{1 + i\omega\tau(\mathbf{k})}, \quad (9)$$

where  $\chi(\mathbf{k}, 0)$  is the static order parameter susceptibility. It depends on the wave vector according to a generalized Ornstein-Zernicke representation<sup>22</sup>

$$\chi(\mathbf{k}, 0) = \frac{\chi(0, 0)}{1 + (\kappa\xi)^{2-\eta}}, \quad (10)$$

where  $k = q - q_i$  is the reduced wave vector,  $q_i$  is the wave vector of the IC modulation wave,  $\xi$  is the correlation length depending critically on the temperature with a critical exponent  $\nu$ , and  $\eta$  is a critical exponent defining a small correction at the phase transition. Thus, replacing the sum in Eq. (8) by an integral we find

$$\frac{1}{T_{1cr}} \propto T \frac{\chi(0, 0)\tau(0)}{\xi^3} \int_0^\kappa \frac{x^2 dx}{(1+x^{2-\eta})+a^2}, \quad (11)$$

where  $a = \omega_L\tau(0)$ ,  $x = k_c\xi$  with  $k_c$  a constant cutoff wave number comparable with the magnitude of the radius of the first Brillouin zone. Supposing the validity of the van Hove

theory for critical dynamics in this present case which assumes that  $\chi(\mathbf{k}, 0)$  and  $\tau(\mathbf{k})$  show the same critical behavior one can write

$$T\chi(k, 0) \propto \frac{\tau(k)}{\tau_0}, \quad (12)$$

where

$$\tau_0 = \tau_\infty \exp\left(\frac{E_a}{k_B T}\right) \quad (13)$$

is the relaxation time in the absence of interaction and  $E_a$  is the corresponding activation energy assuming a dynamics driven by an Arrhenius-type thermally activated process. We can finally write for the critical contribution to the nuclear relaxation rate

$$\frac{1}{T_{1cr}} \propto T^2 e^{E_a/k_B T} \frac{\chi^2(0, 0)}{\xi^3} \int_0^\kappa \frac{x^2 dx}{(1+x^{2-\eta})+a^2}, \quad (14)$$

where the symbols have the usual meaning. We stress that the quantity  $a$  can be considerably changed by varying only the Larmor frequency  $\nu_L = \omega_L/2\pi$ . This situation has been discussed in detail in a previous paper.<sup>22</sup> In particular it has been pointed out that the critical contribution  $1/T_{1cr}$  to the relaxation rate  $1/T_1$  will become temperature independent if the frequency for the critical (order parameter) fluctuations is comparable or less than the Larmor frequency  $\nu_L$ . In this case the relaxation rate  $1/T_{1cr}$  reveals a typical dependence on the Larmor frequency.<sup>22</sup> The present data (Figs. 5 and 6) allow the conclusion that for temperatures  $T \geq T_i$  the critical fluctuation frequencies should not reach this limit and that we have fast fluctuations which are not in contradiction to the large value for the phason gap reported in previous inelastic neutron scattering experiments.<sup>19</sup> Hence, by assuming that the order-disorder fluctuations of the order parameter verify the condition of the fast motion limit,  $\tau(\mathbf{k}) \ll 1/\omega_L$ , for all wave vectors, the critical contribution to the spin-lattice relaxation rate is simply given by

$$\frac{1}{T_{1cr}} \propto T^2 e^{E_a/k_B T} \frac{\chi^2(0, 0)}{\xi^3} \int_0^\kappa \frac{x^2 dx}{(1+x^{2-\eta})}. \quad (15)$$

Since it may be assumed the critical behavior of the quantities  $\xi$  and  $\chi(0, 0)$  to diverge, respectively, as  $(T - T_i)^{-\nu}$  and as  $(T - T_i)^{-\gamma}$  near  $T_i$ , and the integral can be approximated by a constant, Eq. (15) becomes<sup>22</sup>

$$\frac{1}{T_{1cr}} \propto T^2 e^{E_a/k_B T} (T - T_i)^{-\zeta}. \quad (16)$$

The temperature dependence of the critical behavior is reflected by the critical exponent  $\zeta = 2\gamma - 3\nu$ .

The relaxation time  $T_{1bg}$  can be estimated by fitting the experimental values by Eq. (5) at relatively high temperatures ( $T > 185$  K) at which we assume a two-phonon Raman process dominating the background relaxation mechanism. This assumption is confirmed in Fig. 4 by the convergence of  $1/T_1 T^2$  to a constant value for temperatures well above  $T_i$ ,

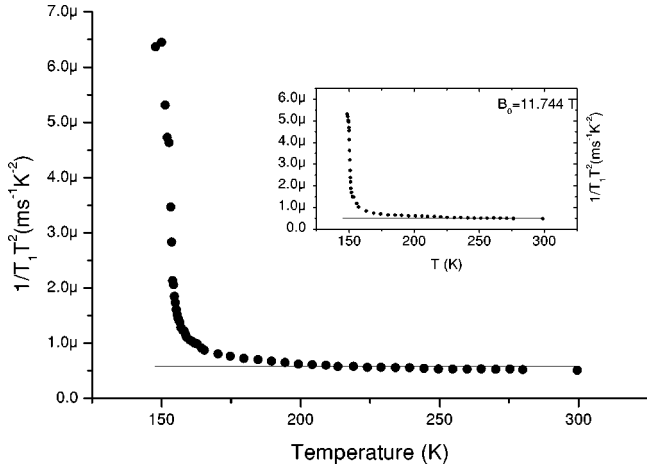


FIG. 4.  $1/T_1 T^2$  plot of the temperature dependence of the  $^{35}\text{Cl}$  NMR spin-lattice relaxation time  $T_1$  in the normal phase. We observe the convergence of  $1/T_1 T^2$  to a constant value  $a$  at the higher temperatures where the background mechanism is dominating. The measurements were carried out at the Bruker MSL 300 NMR spectrometer and in the insert at the Bruker MSL 500 NMR spectrometer.

where the critical contribution vanishes. The critical relaxation time  $T_{1cr}$  may be evaluated by fitting the measured values by an approximately linear temperature dependence in a double-logarithmic plot at temperatures ( $150\text{ K} < T < 185\text{ K}$ ) at which a critical temperature behavior dominates in the quadrupolar relaxation mechanism. Thus, the critical temperature dependence of  $T_{1cr}$  can be represented by a critical exponent  $\zeta$  according to  $T_{1cr} \propto (T - T_i)^\zeta$ . We omit the prefactor  $T^2 \exp(Ea/kT)$  which has a negligible effect on the fit value of  $\zeta$  in a temperature interval of about 10 K above  $T_i$ . Accordingly to Fig. 5 this relation is verified in a critical temperature region of about 10 K above  $T_i$  with the exponent  $\zeta = 0.67$ . No deviation from the power law even close  $T_i$  has

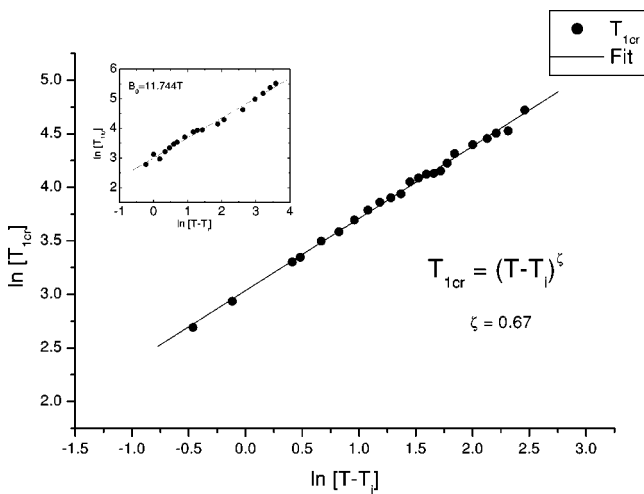


FIG. 5. Double-logarithmic plot of the temperature dependence of the  $^{35}\text{Cl}$  NMR critical spin-lattice relaxation time  $T_{1cr}$  near  $T_i$ . The measurements were carried out at the Bruker MSL 300 NMR spectrometer and in the inset at the Bruker MSL 500 NMR spectrometer.

been observed. Consequently, in BCPS there is no transition to the slow-motion limit which, for instance, is well known to occur in other systems.<sup>22</sup> This value for the experimental critical exponent  $\zeta = 0.67$  can be compared with the theoretical exponent ( $\zeta = 0.663$ ) derived from a comprehensive field-theoretical model<sup>30</sup> that goes beyond the mean-field approach for the IC phase. Dynamic scaling arguments associated with critical exponents calculated within the renormalization-group theory for the 3D XY model in three dimensions have been used to derive the temperature dependence of the NMR relaxation rate in the high-temperature phase close to  $T_i$ . For the fast-motion limit the relaxation rate is given by the following expression<sup>30</sup>

$$\frac{1}{T_1} \propto \xi^{z-1-\eta} = \left( \frac{T - T_i}{T} \right)^{-\nu(z-1-\eta)} \quad (17)$$

or

$$\frac{1}{T_1} \propto \left( \frac{T - T_i}{T} \right)^{-0.663}, \quad (18)$$

where the values  $\nu = 0.6695$ ,  $z = 2.024$ , and  $\eta = 0.033$  were applied. This result fits very nicely with our experimental data. However, the theoretical critical exponent  $\zeta = 2\gamma - 3\nu = 0.625$ , derived from Eq. (16) by using the static critical exponent values of  $\gamma$  and  $\nu$  from the 3D XY model, slightly differs from the exponent ( $\zeta = 0.663$ ).<sup>30</sup> Moreover, it has been shown that this conventional prediction<sup>31</sup> may be justified from the dynamical scaling hypothesis, i.e., a value  $\zeta = \gamma + (z-3)\nu = 2\gamma - 3\nu$ , by assuming the van Hove approximation for the dynamical critical exponent  $z = 2 - \eta = \gamma/\nu \approx 2$ , instead of  $z = 2 + c\eta$  with  $c = 0.726$  from the scaling prediction.<sup>30</sup> Thus, the conventional theory can be considered to be a good approximation<sup>32</sup> of the time-dependent Ginzburg-Landau model,<sup>30</sup> since the value of the deviation of the dynamical critical exponent ( $z = 2 + c\eta$ ) to the value

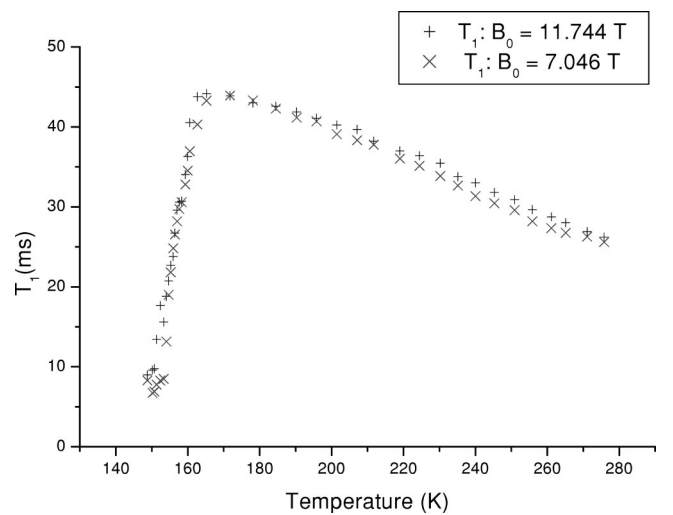


FIG. 6. Comparison of the two temperature dependences of the  $^{35}\text{Cl}$  NMR spin-lattice relaxation time  $T_1$  measured at the Bruker MSL 300 and 500 NMR spectrometers, respectively. The temperature dependences of the  $^{35}\text{Cl}$  NMR spin-lattice relaxation time  $T_1$  are independent of the static magnetic field in the critical region.

from the conventional van Hove model ( $z=2-\eta$ ) is numerically small,  $\eta(c+1)=0.056$ . Accordingly, extremely accurate measurements are necessary to detect these deviations. As long as the accuracy of both the theoretical and experimental data is not considerably improved, a comparison with the different theoretical predictions is not easy because of the uncertainties in the values of the static critical exponent  $\eta$ . Moreover, it has been shown in Ref. 22 that deviations from the value  $\zeta=2\gamma-3\nu$  may also occur far above  $T_i$  when  $x=\kappa\xi$  [see Eq. (10)] becomes appreciably smaller than 1. Consequently, possible deviations may be understood, in this context, as the limits of experimental accuracy achieved in this study (see Fig. 6).

## V. CONCLUSION

BCPS presents a normal crystalline phase above the temperature  $T_i=149.7$  K at which the crystal undergoes a structural phase transition to an incommensurate phase. The molecular dynamics of the crystal in the paraelectric phase is approximately described by the rigid molecule model. The appreciable temperature dependence of the quadrupole splitting in a wide range above the phase transition is consistent with the twisting of the phenyls rings. For the temperatures

between 185 K and  $T_i$ , the crystal experiences structural instabilities which produce fluctuations in the EFG at the <sup>35</sup>Cl nuclei sites which were detected in a wide temperature range. The results of the relaxation time as a function of temperature, angular orientation, and resonance frequency were interpreted in terms of quadrupole relaxation induced by lattice vibrations through a Raman two-phonon mechanism above  $T=185$  K. It was suggested that the critical contribution is associated with frequency lowering of a soft mode. The effects on the NMR parameters (critical temperature dependence of  $T_1$  and line broadening) have been attributed as precursor effects which appear in the proximity of the normal-incommensurate structural phase transition. The exponents  $\zeta$  derived from the <sup>35</sup>Cl NMR  $T_1$  experimental data and recent <sup>35</sup>Cl nuclear quadrupole resonance measurements<sup>15</sup> are in very good agreement. Furthermore, they fit very nicely to the 3D XY model and, thus, indicate a universal behavior.

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