^2H and ^{14}N NMR Studies of the Dynamics in the Incommensurate Phases of Betaine Calciumchloride Dihydrate

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Dedicated to Professor Dr. W. Müller-Warmuth on the occasion of his 65th birthday

^2H and ^{14}N NMR spin-lattice relaxation rates were measured in the structurally incommensurately (IC) modulated phases of deuterated and undeuterated betaine calciumchloride dihydrate, respectively. The results are related to the elementary excitations of these phases. The presence of low-frequency phase fluctuations of the modulation wave leads to higher spin-lattice relaxation rates compared with the high-temperature normal phase and the commensurate (C) phases. The corresponding "phason" contributions are found to be nearly constant in the whole IC phases. In the IC phases near the transitions to the C phases the relaxation rates decrease due to the formation of the soliton lattice. This interpretation is in agreement with the results of previous dielectric measurements.

Key words: Nuclear-spin-lattice relaxation; Betaine calciumchloride dihydrate; Incommensurate phases; Phason modes; Incommensurate-commensurate phase transitions.

Introduction

Several compounds consisting of an amino acid and an inorganic component show interesting features associated with structural phase transitions. Examples are the ferroelectrics triglycine sulphate (TGS), trissarcosine calciumchloride (TSCC) and betaine arsenate (BA). Betaine calciumchloride dihydrate (BCCD, chemical formula $(CH_3)_3NCH_2COO \cdot CaCl_2 \cdot 2H_2O$) is an outstanding member of this family. It is distinguished by its exceptionally rich phase diagram including many structurally commensurately (C) and incommensurately (IC) modulated phases in accordance with the "incomplete devil's staircase" behaviour predicted by some microscopic models [1, 2, 3].

The phase sequence of BCCD starts with the transition from the orthorhombic normal (N) phase with space group P*nma* to an incommensurate phase (IC1) at $T_{i1} = 164$ K which is stable down to $T_{c1} = 128$ K [4]. A second IC phase occurs between $T_{i2} = 124$ K and $T_{c2} = 115$ K (IC2). In these phases, the modulation wavevector $\boldsymbol{q}_i = \delta(T) \cdot \boldsymbol{c}^*$ is an irrational fraction of the reciprocal lattice vector $\boldsymbol{c}^*$. Between 128 K and 124 K it locks in at the commensurate value $\delta = 2/7$ (7/2C phase). The 4C phase ($\delta = 1/4$) below 115 K extends over a range of about 40 K and is followed by further commensurate phases which are of less importance in the present context. The last phase transition into the ferroelectric low-temperature phase is found at 46 K [4]. Remarkably, the phase transition temperatures are nearly the same in the deuterated system (DBCCD, $T_{i1} = 166$ K, $T_{c1} = 133$ K, $T_{i2} = 130$ K, $T_{c2} = 120$ K) [5] where the crystal water molecules are substituted by D_2O.

Previous ^2H NMR studies of DBCCD were concerned with molecular motions and local structure in the N phase [6, 7]. The critical behaviour at the N-IC phase transition was investigated by precise ^{35}Cl and ^2H NMR measurements [8]. In particular, it was shown that the NMR spin-lattice relaxation rate is well-suited to investigate the order parameter dynamics in the static limit in BCCD above $T_{i1} = 164$ K.

In a recent work [9] it was demonstrated that generally T_1 measurements can give valuable insight in the dynamics of IC systems, and the formalism developed was applied to the results obtained for the IC phase of Rb_2ZnCl_4. In the following it will be demonstrated that corresponding ^2H and ^{14}N relaxation measurements are appropriate for investigating the elementary excitations in the IC phases of BCCD.

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Theory

A structurally incommensurately (IC) modulated phase can be described by a lattice with the symmetry of the N phase which is distorted by a modulation whose wavelength does not fit to the periodicity of the underlying lattice. The corresponding incommensurate wavevector $\boldsymbol{q}_i$ is an irrational fraction of the reciprocal lattice vectors, e.g. $\boldsymbol{q}_i = \delta \cdot \boldsymbol{c}^*$ with $\delta \neq m/n$ as in the case of BCCD. The order parameter (OP) of the N-IC phase transition is two-dimensional and can be represented in a complex notation as

$$Q = \varrho\, e^{i\phi} \tag{1}$$

with amplitude ϱ and phase ϕ [10]. From general symmetry consideration follows that the OP potential is degenerate with respect to ϕ, what leads to soft phase fluctuations in the whole IC phase [10, 11]. In other words, the free energy of the IC phase is invariant to a shift of the initial phase of the incommensurate modulation wave.

The normal modes of the OP are the longitudinal and transversal components P_1, P_2 of the OP defined by [11]

$$P_1(t) + iP_2(t) = Q(t)\, e^{-i\phi_0} \tag{2}$$

with the mean values $\langle P_1 \rangle = \langle \varrho \rangle = \varrho_0$, $\langle P_2 \rangle = 0$ and $\langle \phi \rangle = \phi_0$. Their fluctuating parts

$$\delta P_1(t) = \delta\varrho(t) - \tfrac{1}{2}\varrho_0\, \delta\phi^2(t) \pm \ldots \tag{3a}$$

and

$$\delta P_2(t) = \varrho_0\, \delta\phi(t) \pm \ldots \tag{3b}$$

couple to the low-frequency phase fluctuations in second or first order, respectively. According to a linear approximation they are termed "amplitudon" and "phason" modes.

Quadrupolar perturbed NMR has been proved to be a sensitive and powerful tool for investigating structural phase transitions with respect to their typical static and dynamic anomalies [12, 13]. Here the electric field gradient (EFG) tensor at the site of the observed nucleus is used to probe local properties. In the incommensurate phase, the complete and general coupling between the EFG at lattice site $\boldsymbol{T}$ and the order parameter is given by a symmetry-adapted EFG Fourier series [14], what has been demonstrated experimentally [15, 16]. On the basis of this general model, a consistent description of the spin-lattice relaxation rate $1/T_1$ (i.e. of the transition probabilities W_μ) has been derived recently and proved by ^{87}Rb relaxation measurements on Rb_2ZnCl_4 [9]. Since the spin-lattice relaxation rate is a local physical quantity, it can be shown to be spatially modulated according to

$$W_\mu(v) = D_\mu\left(\frac{J_1(\mu\omega_L) + J_2(\mu\omega_L)}{2}\right) + E_\mu\left(\frac{J_1(\mu\omega_L) - J_2(\mu\omega_L)}{2}\right)\cos(2v + \psi_\mu) \tag{4a}$$

with the modulation phase $v = \boldsymbol{q}_i \cdot \boldsymbol{T}$ and with the spectral densities

$$J_{1,2}(\mu\omega_L) = \int_{-\infty}^{+\infty} \langle \delta P_{1,2}(0)\, \delta P^*_{1,2}(t) \rangle\, e^{-i\mu\omega_L t}\, dt \tag{4b}$$

of longitudinal and transversal OP fluctuations. The parameters D_μ, E_μ, and ψ_μ can be derived from the amplitudes and phases of the EFG Fourier series [9].

Since the "phason" or transversal OP fluctuations in the whole IC phase conserve the critical state of the soft mode at T_i [11], the respective spectral density $J_2(\mu\omega_L)$ should be nearly temperature independent, apart from the "soliton regime" above T_c. In contrast to this, the longitudinal OP fluctuations harden below T_i, leading to a rapid decrease of the spectral density $J_1(\mu\omega_L)$ at lower temperatures. A more extensive discussion of spin-lattice relaxation in incommensurate systems is given in [9].

On approaching the IC-C phase transition at $T = T_c$, the phase v of the modulation wave is deformed from a linear to a stepwise function of $\boldsymbol{T}$ along the modulation direction [10]. The steps, called solitons or discommensurations (DCs), are separated by plateaus of increasing breadth with nearly the same properties as in the subsequent commensurate phase (C regions). Correspondingly, the phase fluctuations concentrated in the C regions become significantly harder on approaching T_c. On the contrary, the increase of the soliton lattice constant is associated with a further softening of those phase fluctuations localized in the DCs which finally vanish below the IC-C transition [11, 17]. For a system with a ferroelectric C phase the softening of the soliton lattice can be observed by dielectric measurements [18, 19].

Experimental Details

The samples of deuterated and undeuterated BCCD were cut from single crystals grown from

aqueous solutions [20]. In both cases, the size of the samples was about $7 \times 7 \times 10\ mm^3$. The crystals were oriented with the crystallographic $\boldsymbol{b}$ axis parallel to the external magnetic field $\boldsymbol{B}_0$ by means of a special mechanical device. For this purpose, the sensitive ^{35}Cl NMR spectra were used as a reference. The temperature was controlled in a cryostat by evaporating liquid nitrogen. In previous measurements the temperature gradient of this device was found to be less than 0.1 K [8]. In the case of the ^{14}N NMR measurements, the temperature was measured additionally by a calibrated silicon diode placed close to the sample (the temperatures belonging to the ^2H NMR data were corrected accordingly).

The spin-lattice relaxation rates were measured using a Bruker CXP 300 NMR spectrometer operating at ^2H and ^{14}N Larmor frequencies of 46.05 MHz and 21.66 MHz, respectively. In all cases, the spectra had a width of less than 200 kHz and were excited completely. Due to the long relaxation times the saturation recovery pulse sequence was applied with 12 pulses of length 5.3 μs and with 20 pulses of length 7.0 μs, respectively. In order to improve the signal-to-noise ratio, between 10 and 20 scans (^2H) and between 50 and 120 scans (^{14}N) were taken for each signal. Typically 10 signals with different magnetization recovery times were used to obtain the spin-lattice relaxation rates.

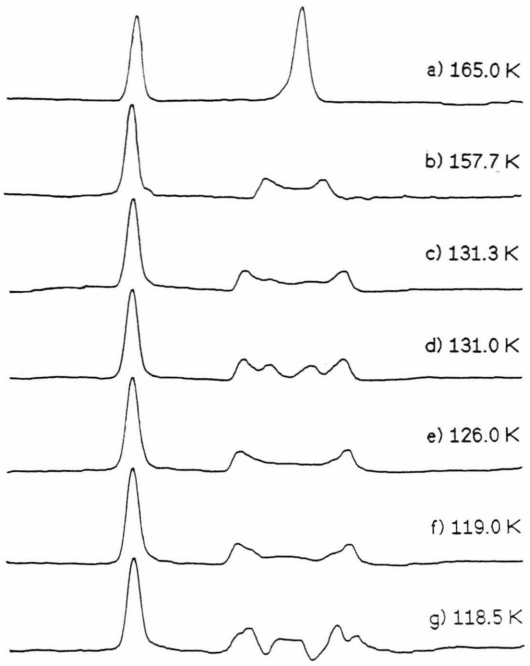

Fig. 1. Upper-frequency part of the ^2H NMR spectra measured on DBCCD in the crystal orientation $\boldsymbol{b} \parallel \boldsymbol{B}_0$ at different temperatures. The total width of the spectra shown is 125 kHz (the frequency increases from the right to the left). The spectra were taken in the N (a), IC 1 (b, c), 7/2 C (d), IC 2 (e, f), and 4 C phase (g) at the given temperatures. The ^2H spin-lattice relaxation rates were measured for the higher-frequency line (left-hand side) which exhibits no splitting (see text).

Results and Discussion

The ^2H NMR spectra of DBCCD measured in the crystal orientation $\boldsymbol{b} \parallel \boldsymbol{B}_0$ are shown in Figure 1. In the upper spectra (Figs. 1 a to 1 c) the splitting of one of the lines (N phase) into a frequency distribution with two edge singularities typical for IC systems can be observed. The singularity distance is equal to the amplitude of the first harmonic for the EFG component V_{yy} and thus proportional to the order parameter [14, 21]. Its temperature dependence led to the critical exponent $\beta = 0.35 \pm 0.02$ of the OP in accordance with the ^{35}Cl NMR results [8]. The shape of the frequency distribution in both IC phases (Figs. 1 b and 1 e) is in agreement with that expected for a sinusoidal IC modulation [22]. Deformations are observed only in small temperature regions of about 0.5 K above the IC-C phase transitions (Figs. 1 c and 1 f). In view of the spectra found in the C phases (Figs. 1 d and 1 g) this can be interpreted as the effect of the formation of the soliton lattice [23]. Because of the small frequency resolution in the ^2H NMR spectra, however, these measurements are not very sensitive to soliton effects, and we therefore refrain from a quantitative discussion.

For the particular crystal orientation $\boldsymbol{b} \parallel \boldsymbol{B}_0$ the line on the left-hand side of Fig. 1 accidentally does not show a splitting corresponding to a zero amplitude of the V_{yy} modulation of the respective EFG component. Consequently, the intensity of this line is not diminished below T_i and allows to carry out relaxation measurements with a sufficient signal-to-noise ratio. The results of these experiments are shown in Figure 2. In this case, in the IC phase the magnetization recovery is governed by the whole inhomogeneous relaxation time distribution given by (4 a, b). Consequently, contrary to the situation in the N phase, a non-monoexponential relaxation behaviour should be expected here, though all lines are irradiated in the experiment. Nevertheless, within the frame of experimental accu-

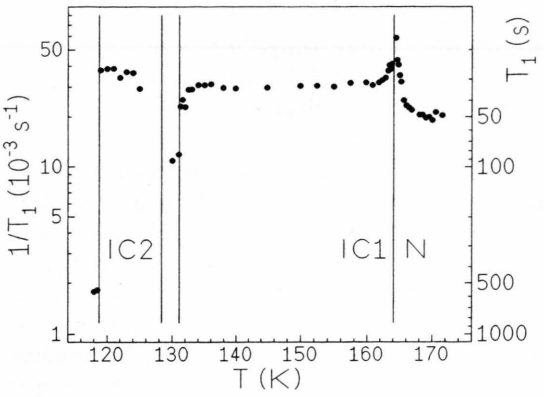

Fig. 2. Temperature dependence of the ^{2}H spin-lattice relaxation rates $1/T_1$ obtained for DBCCD in the crystal orientation $\boldsymbol{b} \parallel \boldsymbol{B}_0$ at the lines with no splitting in the IC phases (cf. Fig. 1) from the magnetization recovery curves ($T > 138$ K) or from their initial slopes ($T < 138$ K). The temperatures given here are corrected with respect to the values of the control device in accordance with the ^{14}N NMR measurements.

racy a monoexponential magnetization recovery was observed. This might be due to relatively small E_μ/D_μ ($\mu = 1, 2$) ratios in (4a). Thus, the relaxation measurements provide an average relaxation rate according to

$$\frac{1}{T_1} = \frac{1}{2\pi} \int_0^{2\pi} (W_1(v) + 2W_2(v))\,\mathrm{d}v$$
$$= D(J_1(\omega_L) + J_2(\omega_L)), \qquad (5)$$

where the fast-motion limit (i.e. $J_{1,2}(\omega_L) = J_{1,2}(2\omega_L)$) is assumed [8] and where $D = (D_1 + 2D_2)/2$. Below 138 K in the IC1 phase and in the whole IC2 phase, however, the magnetization recovery deviates from the single-exponential behaviour measured before. The relaxation rates given in Fig. 2 for these temperatures are derived from the initial slope of the magnetization recovery and should also be in accordance with (5).

The measured $1/T_1$ values exhibit a distinct decrease below T_{i1} by a factor of about 2. This can be understood on the basis of (5) since $J_1(\omega_L) = J_2(\omega_L)$ at T_i and $J_1(\omega_L) \ll J_2(\omega_L)$ in the lower part of the IC phase as a consequence of the hardening of the longitudinal "amplitudon" fluctuations $\delta P_1(t)$. Thus, the value of $1/T_1$ in the subsequent plateaus in the IC1 and IC2 phases is essentially given by

$$\frac{1}{T_1} = DJ_2(\omega_L), \qquad (6)$$

i.e. by the remaining spectral density $J_2(\omega_L)$ of the "phason" modes.

On approaching the IC1-7/2C phase transition, the relaxation rate decreases once more. This is due to the formation of the soliton lattice and the associated hardening of the phase fluctuations in the C regions. Since the remaining discommensurations cover only a relatively narrow range compared with the C regions, the averaging according to (5) practically does not take into account the softening of the phase fluctuations (i.e the increase of relaxation rates) in the DCs. The latter can only be observed in frequency-resolved T_1 measurements [9]. Nevertheless, the decrease of the averaged "phason"-induced relaxation rate is an indication of dynamical soliton effects. This behaviour is restricted to an interval of about 3 K above T_{c1}, in agreement with previous dielectric dispersion measurements [24]. Closely above the transition to the 4C phase, however, several narrow C phases are expected to occur, resulting in a more difficult situation for the IC2-4C than for the IC1-7/2C phase transition.

On entering into the C phases a jump in the relaxation rates is found due to the vanishing of phase fluctuations. This jump is clearly smaller for the 7/2C phase than that for the 4C phase. This difference might be due to the influence of the dynamics of remaining solitons in the 7/2C phase which have here the character of domain walls. This interpretation is in accordance with dielectric measurements in these temperature regions [24, 25]. Note that the very high T_1 values given for the 4C phase are just estimates from the initial part of the magnetization recovery curve.

Contrary to the ^{2}H nuclei of the crystal water molecules, the ^{14}N nuclei of the betaine units are situated in m_y mirror planes of the high-temperature structure [26]. Thus, in the IC phase the first harmonic of the modulation of the EFG element V_{yy} vanishes [14]; instead one has a much smaller V_{yy} modulation by the second harmonic. This modulation results in a width of the IC frequency distribution which is smaller than the natural ^{14}N NMR linewidth in BCCD. Thus, the expected line splitting below T_i actually cannot be observed in the experiment. Consequently, the same situation occurs as in the ^{2}H measurements in the IC phases discussed before: On the one hand, one has a sufficient line intensity for performing relaxation experiments efficiently, on the other hand, the magnetization recovery includes the whole relaxation rate distribution according to (4) and is therefore not expected to be monoexponential. This behaviour is actu-

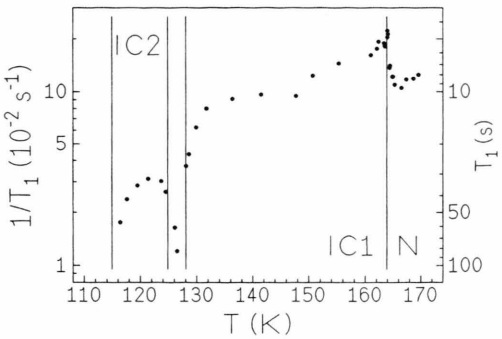

Fig. 3. Temperature dependence of the ^{14}N spin-lattice relaxation rates $1/T_1$ obtained for BCCD in the crystal orientation $\boldsymbol{b} \parallel \boldsymbol{B}_0$ from the initial slopes of the magnetization recovery curves. In this orientation, the ^{14}N NMR spectrum in the N phase consists of a single line pair which practically does not split below T_{i1} (cf. text).

ally found. The relaxation rates shown in Fig. 3 correspond to the initial slope of the magnetization recovery curve and should be given by (5).

In agreement with the ^2H results of Fig. 2, the temperature dependence of the ^{14}N relaxation rates in the IC1 phase exhibits a decrease by a factor of 2 in a range of about 10 K below T_{i1}. In the subsequent temperature region of the expected $1/T_1$ "plateau", however, the observed values in fact indicate a tendency to lower on decreasing temperature. This might be due to the influence of a temperature-dependent background rate. As demonstrated in Fig. 3, the "phason"-induced relaxation rates of the IC1 phase exceed those of the IC2 phase. This result is not yet understood and in contrast to the ^2H relaxation data.

On approaching the IC1-7/2C phase transition, the same behaviour as in the case of the ^2H experiments is found: The relaxation rate decreases in a temperature interval of about 3–4 K above T_{c1}. This is observed analogously above the IC2-4C and, moreover, below the 7/2C-IC2 transitions. The results seem to confirm the above interpretation in terms of soliton effects near the IC-C phase transitions. Besides, the jumps of the ^{14}N relaxation rates to lower values on entering from the incommensurate phases into the 7/2C phase are also in accordance with the ^2H measurements.

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