NMR Evidence for Universal Nonclassical Critical Behavior of Incommensurately Modulated Crystals

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Nonclassical universal critical behavior is revealed in several one dimensionally modulated incommensurate (IC) crystals by means of quadrupolar perturbed NMR. In the IC phase the temperature dependence of the NMR line shape leads to the same critical order parameter exponent β for all systems. Above the phase transition a nonclassical exponent was found for the critical contribution to the spin-lattice relaxation. All results agree with the theoretical predictions of the 3D XY model.

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Some insulating crystals undergo a phase transition at a temperature T_i from a high-temperature normal (N) phase to a structurally incommensurately modulated (IC) phase [1]. In these systems at least one local property is modulated in such a way that the modulation wave vector $\mathbf{q}_i$ is irrational with respect to the reciprocal lattice of the N phase.

Quadrupolar perturbed nuclear magnetic resonance (NMR) has been proved to be a very sensitive and accurate tool for investigating IC phases and in particular their static critical behavior [2–7]. In many cases the electric field gradient tensor (EFG) at the site of the nucleus under investigation is strongly affected by the IC modulation. As a result, well-known frequency distributions occur in the NMR spectra with singularities at the two edges which are typical for IC phases. In general this effect is about 1 or 2 orders of magnitude more pronounced for first-order quadrupolar effects (e.g., satellite line splitting) than for second-order ones (e.g., shifts of the central and satellite lines).

In previous NMR works [2–6] a universal nonclassical critical behavior showing up in the exponents β and $\bar{\beta}$ was found for the IC phases in some crystals of the A_2BX_4 type [Rb_2ZnBr_4, Rb_2ZnCl_4, $(NH_4)_2ZnCl_4$]. The exponents are in excellent accordance with the predictions of the 3D XY model. It is one purpose of the present Letter to show that the critical exponent β determined by NMR for the uppermost IC phase ($T_i = 164$ K) of betaine calcium chloride dihydrate (BCCD) also agrees excellently with this model, although both the structure and the exceptionally rich phase diagram [8,9] of this substance differ considerably from those of the A_2BX_4 systems, thus demonstrating the universal meaning of the critical exponents determined.

A one-dimensional incommensurate periodic modulation of the crystal lattice leads to a corresponding modulation of the EFG. Consequently, the EFG in the IC phase can be described by a symmetry adapted Fourier series [2,3]. For a nucleus at a lattice site underlying no restrictions by symmetry observed in a crystal orientation with the crystallographic $\mathbf{a}_i$ axis parallel to the external magnetic field $\mathbf{B}_0$, the edge singularity distance $\Delta\nu_{IC}$ of a satellite frequency distribution is related to the order parameter amplitude ρ and its temperature dependence by [2,4]

$$\Delta\nu_{IC} \propto |\langle V_{1ii}\rangle| \propto \langle\rho\rangle \propto (T_i - T)^{\beta}. \quad (1)$$

Here V_{1ii} denotes the amplitude of the first harmonic of the Fourier series of the EFG tensor element V_{ii} in the crystal reference frame.

An accurate determination of critical exponents requires a sufficient precise knowledge of the transition temperature T_i. In our experiments a low-temperature helium flow cryostat was used characterized by a very good temperature stability ($\Delta T \approx 0.05$ K over the measuring time) and a very small temperature gradient (< 0.1 K/cm). Samples had a size of about $0.7 \times 0.7 \times 1$ cm^3. The temperature was measured by a calibrated silicon diode (accuracy ± 0.02 K) placed about 1 cm beside the sample.

The ^{35}Cl ($I = \frac{3}{2}$) satellite transitions ($m = \pm\frac{3}{2} \leftrightarrow \pm\frac{1}{2}$) in the uppermost IC phase ($T_i = 164$ K) of BCCD were measured at a static magnetic field $B_0 = 7.0$ T (Larmor frequency $\nu_L = 29.4$ MHz) for crystal orientations specified by $\mathbf{a},\mathbf{b},\mathbf{c} \| \mathbf{B}_0$. In these cases, an eightfold degeneracy of the spectra occurs leading to a remarkable increase of the signal-to-noise ratio. The detectability of the satellite lines in the N and IC phase is a clear indication of the high quality of the crystals. The results for the three crystal orientations are shown in Fig. 1. We obtain critical exponents $\beta = 0.35 \pm 0.01$ ($\mathbf{a} \| \mathbf{B}_0$), $\beta = 0.345 \pm 0.005$ ($\mathbf{b} \| \mathbf{B}_0$), and $\beta = 0.354 \pm 0.005$ ($\mathbf{c} \| \mathbf{B}_0$). This critical behavior according to Eq. (1) is found to hold in the whole IC phase.

In contrast to the rather small effects reported sometimes for the central lines in other substances, the edge singularity distances observed for the ^{35}Cl satellite lines in the IC phase of BCCD depend very sensitively on the

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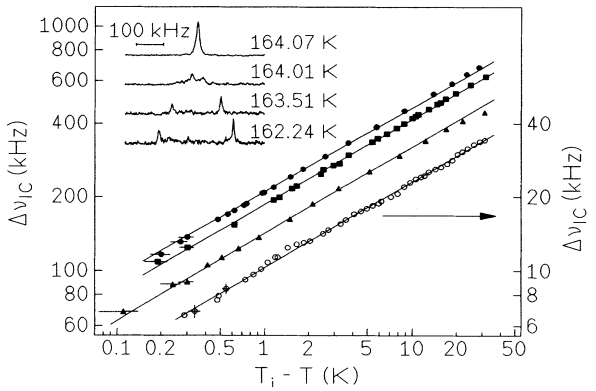

FIG. 1. Temperature dependence of the distance of the edge singularities in the IC phase for the satellite lines of ^{35}Cl in BCCD [$\mathbf{a}\|\mathbf{B}_0$ (■), $\mathbf{b}\|\mathbf{B}_0$ (●), $\mathbf{c}\|\mathbf{B}_0$ (▲), left-hand scale] and of ^{2}H in deuterated BCCD [$\mathbf{b}\|\mathbf{B}_0$ (○), right-hand scale]. The inset shows how the upper ^{35}Cl satellite transforms from the single line in the N phase (top) into the frequency distribution in the IC phase.

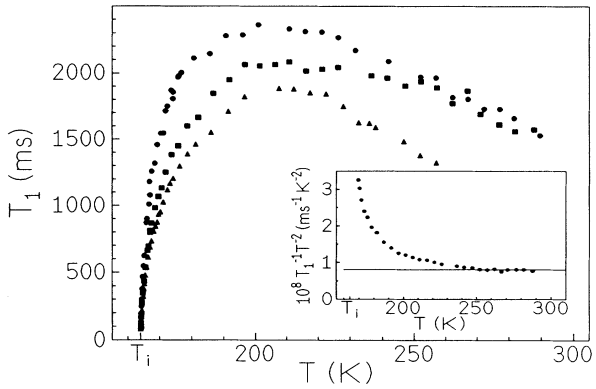

FIG. 2. Temperature dependence of the ^{35}Cl spin-lattice relaxation time T_1 in BCCD above the N-IC phase transition measured in the crystal orientations $\mathbf{a}\|\mathbf{B}_0$ (■), $\mathbf{b}\|\mathbf{B}_0$ (●), and $\mathbf{c}\|\mathbf{B}_0$ (▲) at the central line. In the inset the convergence of $1/(T_1T^2)$ to a constant at higher temperatures is demonstrated exemplarily for the crystal orientation $\mathbf{a}\|\mathbf{B}_0$ (see text).

temperature (see inset of Fig. 1). Thus, by inspecting the NMR spectra T_i can be fixed within a temperature interval of 0.05 K. The value for T_i determined this way is confirmed, moreover, when choosing T_i as a third parameter in a fit of $\Delta\nu_{IC}$ according to Eq. (1). In a temperature range $T-T_i \leq 2$ K close to T_i we find a broadening of the line from 2 to 10 kHz which is very small compared to the edge singularity distance of about 100 kHz measured only 0.2 K below T_i. Thus, this line broadening has no consequences at all for the evaluation of our data, neither for the determination of T_i nor for the determination of the edge singularity distances. This seems to contrast some of the results and conclusions presented in Ref. [10] for the ^{87}Rb central line in Rb_2ZnCl_4.

In addition, ^{2}H ($I=1$) NMR spectra ($\nu_L=46.1$ MHz) of the water molecules in deuterated BCCD were measured in the IC phase in the crystal orientation $\mathbf{b}\|\mathbf{B}_0$ (Fig. 1). The temperature dependence of the corresponding edge singularity distance is also found to follow the power law (1) in the whole IC phase with the same critical exponent $\beta=0.35\pm0.02$.

While the NMR spectrum is determined by the static part of the EFG, its fluctuating part is responsible for the transition probabilities 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 ($\approx 10^8$ Hz). In suitable cases they are strongly affected by order parameter fluctuations [11,12]. It is a further purpose of this Letter to demonstrate that for some incommensurate systems these critical contributions are sufficiently strong to allow a rather precise determination of a corresponding critical exponent above T_i.

Because of the extreme sensitivity of the ^{35}Cl satellite line intensity in BCCD to the smallest misorientations of the sample T_1 was measured at the ^{35}Cl central line applying 90°-τ-90° pulse sequences and the same experimental arrangement and crystal orientations as described above. The magnetization recovery showed a weak deviation from a single-exponential behavior. Nevertheless, a well-defined relaxation time could be determined from its initial slope.

Approaching T_i, a drastic decrease of T_1 is observed (Fig. 2). In order to extract the considerable critical contribution to the relaxation rate the relaxation rates caused by independent noncritical processes are to be subtracted. We assume a two-phonon Raman process to be responsible for the background relaxation rate $1/T_1^{bg}$, leading to a temperature behavior $1/T_1^{bg}=AT^2$, where A is a constant [13]. This assumption is confirmed by the convergence of $1/(T_1T^2)$ to a constant value for temperatures well above T_i, where the critical contribution vanishes (an example is given in the inset of Fig. 2). Consequently, the critical contribution to the spin-lattice relaxation rate is given by

$$1/T_1^{crit}=(1/T_1)-AT^2. \tag{2}$$

If this procedure is applied to the T_1 values measured for ^{35}Cl in BCCD in the crystal orientations $\mathbf{a},\mathbf{b},\mathbf{c}\|\mathbf{B}_0$, the critical contributions show the same temperature dependence in a temperature range of about 40 K above T_i (Fig. 3).

Assuming order-disorder fluctuations of the order parameter with relaxation times fulfilling the condition $\tau(\mathbf{q})\ll(2\pi\nu_L)^{-1}$ (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 critical contribution to the spin-lattice relaxation rate is given by [11]

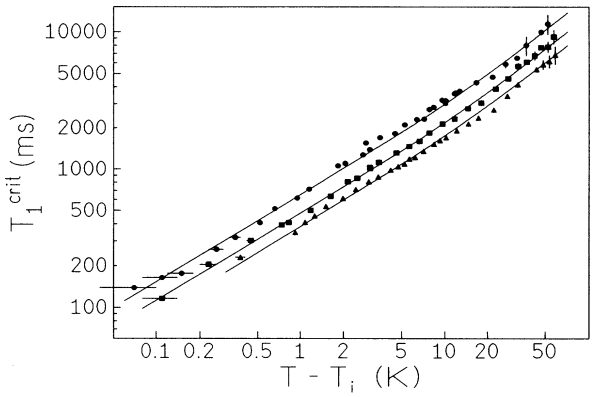

FIG. 3. Temperature dependence of the critical ^{35}Cl spin-lattice relaxation time T_1^{crit} obtained by means of Eq. (2) from the T_1 values measured for BCCD in the crystal orientations $\mathbf{a}\|\mathbf{B}_0$ (■), $\mathbf{b}\|\mathbf{B}_0$ (●), and $\mathbf{c}\|\mathbf{B}_0$ (▲). The fit curves according to Eq. (6) correspond to the parameters given in the text.

$$1/T_1^{crit} \propto T^2 e^{\Delta U/k_B T} \sum_{\mathbf{k}} \chi^2(\mathbf{k}) , \tag{3}$$

where [14]

$$\chi(\mathbf{k}) = \chi(\mathbf{k}=0)/[1+(k\xi)^{2-\eta}] \tag{4}$$

is the order parameter susceptibility depending on the reduced wave vector $\mathbf{k}=\mathbf{q}-\mathbf{q}_i$. In Eqs. (3) and (4) we denote as usual by ΔU the activation energy of the uncoupled dipole system, by ξ the correlation length, and by η the critical exponent which characterizes the long-range behavior of the correlation function. Replacing in Eq. (3) the sum by an integral yields

$$1/T_1^{crit} \propto T^2 e^{\Delta U/k_B T} \frac{\chi^2(\mathbf{k}=0)}{\xi^d} \int_0^{\xi k_c} \frac{x^{d-1}dx}{(1-x^{2-\eta})^2} , \tag{5}$$

where k_c is a constant cutoff wave number whose magnitude is of the order of the radius of the Brillouin zone. Since ξ diverges as $(T-T_i)^{-\nu}$ near T_i, the integral can be represented by a constant. Consequently, Eq. (5) reduces to

$$1/T_1^{crit} \propto T^2 e^{\Delta U/k_B T} (T-T_i)^{-\zeta} , \tag{6}$$

where for the critical exponent ζ of the relaxation rate the relation

$$\zeta = 2\gamma - d\nu = \gamma - 2\beta \tag{7}$$

holds and where the usual definitions of critical exponents and relations among them [14] were used. Thus, although T_1 is principally a dynamical quantity it is related to the static critical behavior as long as the fast motion condition holds.

The fits according to Eq. (6) lead to the parameters $\Delta U/k_B = 600$ $K \pm 100$ K and $\zeta = 0.625 \pm 0.025$ for all three curves in Fig. 3. Note that the factor $T^2\exp(\Delta U/k_B T)$ has a negligible effect on the fit value of ζ in a temperature interval of about 10 K above T_i.

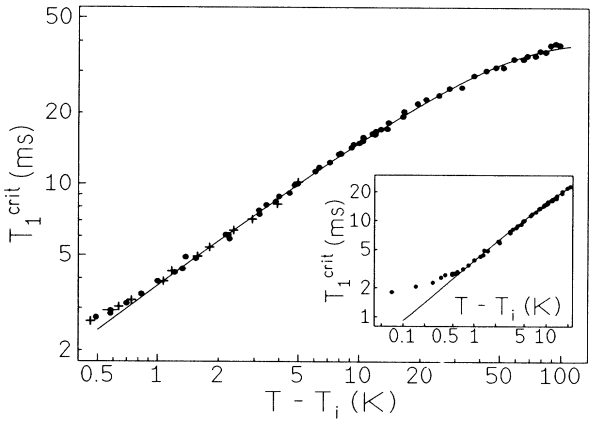

FIG. 4. Same as in Fig. (3) but for the ^{87}Rb satellite transition in RZC (crystal orientation $\mathbf{b}\|\mathbf{B}_0$) for Larmor frequencies $\nu_L = 98.2$ MHz (●) and 51.9 MHz (+). The inset shows for $\nu_L = 98.2$ MHz (●) the deviation from the fit curve [Eq. (6)] very close to T_i (see text).

A critical contribution to the relaxation rate can be observed for the ^{2}H spin-lattice relaxation time in deuterated BCCD, too. Since this effect is comparatively small, a quantitative analysis as described above is not possible.

Moreover, we succeeded in measuring the temperature dependence of T_1 of the ^{87}Rb ($I = \frac{3}{2}$) upper frequency satellite line in high quality crystals of Rb_2ZnCl_4 (RZC) in the orientation $\mathbf{b}\|\mathbf{B}_0$ at two different Larmor frequencies $\nu_L = 98.2$ and 51.9 MHz above T_i (304 K). Because of symmetry the magnetization recovery was single exponential in this special case. The behavior of T_1 agrees qualitatively with that found for the ^{35}Cl relaxation in BCCD. Consequently, a procedure for separating the critical contribution $1/T_1^{crit}$ similar to that described above [cf. Eq. (2)] was applied. The fit of these data (Fig. 4) according to Eq. (6) results in the same critical exponent $\zeta = 0.625 \pm 0.025$ as found for BCCD and in a more or less indeterminable value for $\Delta U/k_B$. The experimental accuracy of these results allows us to exclude the mean-field value $\zeta = 0.5$ reported previously [15,16]. Very close to T_i, however, a systematic deviation of the measured T_1 values from the fit curve is observed (inset of Fig. 4). This result can be explained by assuming that the fast-motion condition $\tau(\mathbf{q}_i) \ll (2\pi\nu_L)^{-1} \approx 10^{-9}$ s is violated and thus Eq. (6) becomes invalid. This assumption is supported by taking into account the explicit temperature dependence of $\tau(\mathbf{q}_i)$ derived recently from ultrasonic data on RZC [17]. On the contrary, the fact that T_1 does not depend on the Larmor frequency for $T - T_i > 1$ K demonstrates the validity of the fast-motion condition.

Our T_1 measurements have shown that (i) the T_1 anomalies which are observed above T_i allow us to determine a universal nonclassical critical exponent ζ for that temperature range and (ii) the extension of the critical region above T_i is of the same order of magnitude as that

observed in the IC phase.

In conclusion, our results demonstrate that for substances different in composition and structure but equally characterized by the occurrence of a one-dimensional incommensurate modulation the NMR investigations of critical phenomena lead both in the IC phase and in the N phase to the same critical exponents β and ζ, respectively, as required by the universality hypothesis. Comparing the values of β and ζ found experimentally with those obtained theoretically [18], an excellent agreement with the predictions of the 3D XY model ($\beta=0.345$, $\zeta=2\gamma-d\nu=0.625$) is ascertained. This model is characterized by a two-dimensional order parameter with three-dimensional interactions and consequently applies to the case of a one dimensionally incommensurately modulated lattice. The independent experimental determination of the exponents β and ζ with sufficient high accuracy allows the calculation of the remaining critical exponents by applying the well-known relations among them [14] so that now a complete set of critical exponents is available.

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