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Pseudocritical NMR frequency shift above the normal-incommensurate phase transition

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Abstract. The NMR satellite frequencies were measured as a function of temperature in the normal high-temperature phase for ^{87}Rb in Rb_2ZnBr_4 and Rb_2ZnCl_4 and for ^{35}Cl in betaine calciumchloride dihydrate. Approaching the respective normal-incommensurate phase transition an anomalous shift of the NMR frequency is observed for the first two cases. This effect is ascribed to the increasing order parameter fluctuations. The experimental data are compared to calculations which relate the observed behaviour of the NMR frequencies to the non-classical critical behaviour of the substances under investigation.

PACS. 64.70.Rh Commensurate-incommensurate transitions – 68.35.Rh Phase transition and critical phenomena – 76.60.Gv Quadrupole resonance

1 Introduction

Some insulating crystals transform from a high-temperature normal (N) phase into a one-dimensionally structurally incommensurately (IC) modulated phase at a certain temperature T_i. In the IC phase at least one physical quantity is periodically modulated in such a way that the corresponding wavevector $\mathbf{q}_i$ is not a rational multiple of a reciprocal lattice vector. Since an IC modulation leads to marked changes of the local environment of the atoms within the crystal a locally measuring examination method like quadrupolar perturbed nuclear magnetic resonance (NMR) is a powerful tool for investigating IC systems. This has been proved by lots of publications (see *e.g.* [1–5]). Often, the critical temperature dependence of the order parameter (OP) amplitude (*i.e.* the amplitude of the IC modulation) was observed resulting in the determination of its critical exponent. Measuring *e.g.* the ^{87}Rb-NMR satellite spectra in rubidium tetrabromozincate and rubidium tetrachlorozincate (Rb_2ZnBr_4, Rb_2ZnCl_4, abbreviated as RZB, RZC, respectively) below T_i [6] the critical exponents β and $\bar{\beta}$ could be determined in full agreement to the values predicted by the 3d-XY model [7] appropriate to N-IC phase transitions where the OP is a two-component one. The same holds for the exponent β determined from ^{35}Cl-NMR in BCCD (betaine calciumchloride dihydrate) [8,9]. The facts that $\bar{\beta} \neq 2\beta$ and that both deviate from the mean-field value $\bar{\beta} = 2\beta = 1$ indicate in a convincing manner that fluctuations of the OP are important for these N-IC phase transitions. Measurements of the ^{87}Rb-NMR spin-lattice relaxation time T_1 in the N phases of RZB/RZC [8,10] and corresponding measurements of ^{35}Cl-NMR in BCCD [8] demonstrate, moreover, that these fluctuations are also important in the temperature region above T_i independent from the fact that for $T > T_i$ the mean value of the OP vanishes. The corresponding critical exponents fit nicely to the predictions of the 3d-XY model, too. In particular it could be shown that above T_i the critical region is broad with a width of at least 40 K. In the present work the pseudocritical temperature dependence of certain NMR line frequencies above T_i is reported for the first time: The so-called NMR satellite frequency shows an anomalous behaviour in the N phase on approaching T_i. The effect will be related to the OP fluctuations in a manner similar to that applied to the explanation of the behaviour of T_1.

2 Experimental results

We investigated the NMR satellite transitions of ^{87}Rb (Larmor frequency $\nu_L = 98.2$ MHz) in RZB/RZC and ^{35}Cl ($\nu_L = 29.4$ MHz) in BCCD. The high-temperature N phases of these substances belong to the orthorhombic space group Pcmn (RZB, RZC) and Pnma (BCCD) with four formula units per unit cell. The eight Rb nuclei within the unit cell of RZB/RZC are located in the m_y-mirror plane and can be subdivided into two kinds which are not chemically equivalent, henceforth denoted as Rb(1) and Rb(2). In BCCD, however, the eight Cl nuclei are chemically equivalent so that in special crystal orientations (one of the orthorhombic crystal axes parallel to $\mathbf{B}_0$) the satellite frequencies of all Cl nuclei degenerate. In these special orientations the distance of the two frequencies of one pair of satellite lines is proportional to one main diagonal element of the electric field gradient tensor (EFG) given

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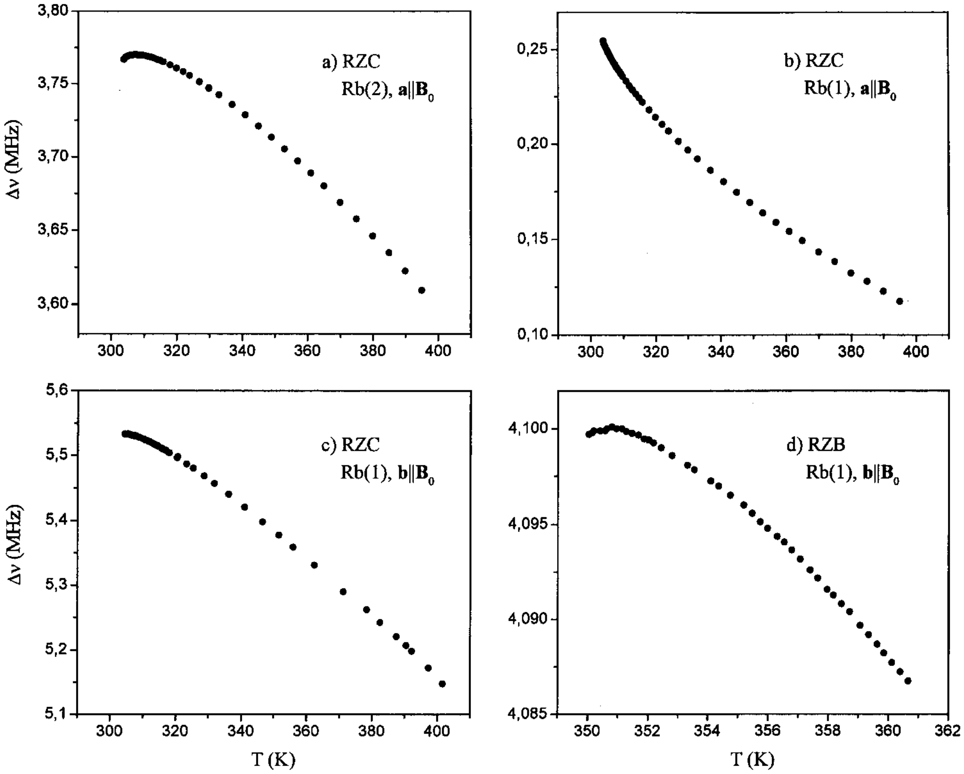

Fig. 1. Temperature dependence of the ^{87}Rb-NMR satellite frequency distance $\Delta\nu$ in the N phase of RZB and RZC in special crystal orientations as indicated. The N-IC phase transition temperature T_i was fixed at $T_i = 303.9$ K (RZC) and $T_i = 350.0$ K (RZB).

in the crystal reference frame. Therefore, we indicate the EFG components by frequencies as usual.

In Figure 1 the frequency distance $\Delta\nu$ of the satellite pair of Rb(1) in RZC in the crystal orientation $\mathbf{b}||\mathbf{B}_0$, of Rb(1) and Rb(2) in the crystal orientation $\mathbf{a}||\mathbf{B}_0$, and of Rb(1) in RZB in the crystal orientation $\mathbf{b}||\mathbf{B}_0$ is plotted as a function of temperature. Since at T_i the NMR line shows a sharp transition to the distribution of NMR lines typical for the IC phase, T_i was determined with an accuracy better than 0.1 K by observing the NMR spectra. As can be seen in Figure 1 far away from T_i the curve describing the temperature dependence of $\Delta\nu$ is nearly linear whereas on approaching T_i a strong bending can be observed. In the following it will be shown that this bending originates from the OP fluctuations. Among other things the quantitative analysis rests on the well-known description of the EFG tensor in IC systems [4] and on the fact that the non-classical critical behaviour of these substances can be described over a broad range of temperatures by the appropriate critical exponents.

3 Discussion

As usual, the static EFG tensor $\underline{V}$ of a one-dimensionally modulated IC phase can be represented by a Fourier series as [8]:

$$\underline{V} = \underline{V}_N + \sum_{n=0,\pm1,\ldots} \underline{V}_n \exp(inv), \tag{1}$$

where $\underline{V}_N$ is the static EFG tensor of the N phase, v is the continuous internal variable, and $\underline{V}_n$ are complex Fourier amplitudes with $\underline{V}_{-n} = \underline{V}_n^*$. Keeping in mind that in the fast-motion limit the NMR spectrum is determined by the time averaged, *i.e.* the static, value of the EFG it is worthwile to examine the complex Fourier amplitudes somewhat closer. They are coupled to the time dependent OP $Q(t) = Q + \delta Q(t)$ as follows [4]:

$$\begin{aligned}
\underline{V}_0 &= \underline{A}_0\langle Q(t)Q^*(t)\rangle,\\
\underline{V}_1 &= \underline{A}_1\langle Q(t)\rangle,\\
\underline{V}_2 &= \underline{A}_2\langle Q(t)Q(t)\rangle,\\
&\vdots\\
\underline{V}_n &= \underline{A}_n\langle (Q(t))^n\rangle,
\end{aligned} \tag{2}$$

where the $\underline{A}_i$ are constant coupling tensors and the brackets denote the time average as usual. Note that $\langle\delta Q(t)\rangle = 0$ and the static part $Q = \rho_0 \exp(i\varphi_0)$ of $Q(t)$ vanishes above T_i. Therefore, $\underline{V}_0 = \underline{A}_0\langle\delta Q(t)\delta Q^*(t)\rangle$ is the only non-vanishing Fourier amplitude above T_i. Thus, the special EFG main diagonal element V_{ii} under observation is simply given as

$$V_{ii} = V_{N_{ii}} + A_{0_{ii}}\langle\delta Q(t)\delta Q^*(t)\rangle. \tag{3}$$

Since the signs of the coefficients $A_{0_{ii}}$ are principally not subject to any restriction, V_{ii} can be increased or reduced by the OP fluctuations. For temperatures $T \gg T_i$ the OP fluctuations can be neglected, *i.e.* $V_{ii} \approx V_{N_{ii}}$, and the temperature dependence of $\delta\nu$ is more or less linear, *i.e.* $\Delta\nu = c_0 + c_1(T - T_i)$. The second term in (3) accounts for the contribution $\delta\nu_c$ of the OP fluctuations.

Two different ways have been reported [11–13] to treat the second term in (3) on the basis of scaling theory. As a starting point of the first one we write the equipartition theorem as

$$\frac{1}{2}\chi^{-1}(\mathbf{k})\langle\delta Q_{\mathbf{k}}\delta Q^*_{\mathbf{k}}\rangle = \frac{1}{2}k_B T, \tag{4}$$

where $\mathbf{k}$ is the wavevector, $\chi(\mathbf{k})$ is the $\mathbf{k}$-dependent OP susceptibility, and $\delta Q_{\mathbf{k}}$ is the $\mathbf{k}$-dependent Fourier component of the OP fluctuations. Summing over the wavevectors $\mathbf{k}$ (2) and (4) results in

$$\Delta\nu_c \propto T \sum_{|\mathbf{k}|<|\mathbf{k}_c|} \chi(\mathbf{k}), \tag{5}$$

where, k_c is a constant cutoff wavenumber. (Note that the constant of proportionality depends on the orientation of the crystal with respect to $\mathbf{B}_0$.)

Replacing the sum by an integral, assuming isotropy in $\mathbf{k}$-space, and writing for the OP susceptibility a modified Ornstein-Zernicke Ansatz, *i.e.* $\chi(\mathbf{k}) = \chi(\mathbf{k}=0)/(1+(k\xi)^{2-\eta})$, one gets:

$$\Delta\nu_c \propto T\frac{\chi(\mathbf{k}=0)}{\xi^3}\int_0^{k_c\xi}\frac{x^2}{1+x^{2-\eta}}dx. \tag{6}$$

As usual ξ denotes the correlation length, $x = k\xi$, and η is a well-known critical exponent [14]. For temperatures far above T_i where critical effects are negligible, *i.e.* $k_c\xi \ll 1$, (6) reproduces a result well known already for a long time [16].

Using the relation $\frac{x^2}{1+x^{2-\eta}} = x^\eta - \frac{x^\eta}{1+x^{2-\eta}}$, treating one of the occurring integrals as $\int_0^{k_c\xi}\cdots = \int_0^\infty\cdots - \int_{k_c\xi}^\infty\cdots$, and substituting $y = x^{-(1-2_\eta)}$ (6) can be rewritten as

see equation (7) below.

This relation can be regarded as an improvement of that derived previously [12] for describing the anomalous temperature dependence of the birefringence. For $T \to T_i$ the correlation length and the susceptibility $\chi(\mathbf{k}=0)$ diverge as $(T-T_i)^{-\nu}$ and $(T-T_i)^{-\gamma}$, respectively. (Note that $\chi(\mathbf{k}=0)$ contains a non-critical factor $1/T$ which cancels with the prefactor T.) Consequently, the prefactor $\chi(\mathbf{k}=0)/\xi^3$ approaches zero as $(T-T_i)^{3\nu-\gamma}$. Note that because of scaling relations $3\nu - \gamma = 2\beta$ [14]. Moreover, the integral in (6) and, thus, the term in the brackets in (7) diverge. As has been pointed out by Bruce [13] in a similar context, the behaviour of $\Delta\nu_c$ is a result of a subtle balance between the diverging integral and its vanishing prefactor. To be more specific, we discuss (7). The critical exponent of the first term together with the prefactor is given by $3\nu-\gamma-\nu(1+\eta) = \nu(2-\eta)-\gamma = 0$, because of the well-known scaling relation $\gamma = \nu(2-\eta)$ [14]. Thus, this term is a constant and shows no critical behaviour. The second term in the brackets of (7) is a constant whereas the third one approaches zero. Consequently, close to T_i these two terms together with the prefactor approach zero as a consequence of the critical behaviour. A behaviour of this type is sometimes termed pseudocritical [13].

Since $k_c\xi > 1$, the integrand in (7) can be written as an alternating geometric series. Taking into account the leading term only we obtain for the total effect

$$\Delta\nu = \mu_1 + \mu_2(T-T_i) + \mu_3(T-T_i)^{2\beta} + \mu_4(T-T_i)^\gamma, \tag{8}$$

where the μ_i are constants. Note that very close to T_i the leading exponent is 2β. In practice, however, an influence of the last term cannot be excluded.

The other approach is achieved by reminding the fact that the second term in (3) is proportional to the energy density. Thus, without any further calculation one can write [13]

$$\langle\delta Q(t)\delta Q^*(t)\rangle = E_0 + E_1(T-T_i) + E_2(T-T_i)^{1-\alpha}, \tag{9}$$

where the E_i are constants and α is the specific heat exponent. The same formula is also used to explain the behaviour of the birefringence [12] or the Debye-Waller factors [13] in the vicinity of structural phase transitions. Altogether, the value $\Delta\nu = V_{ii}$ is given by

$$\Delta\nu = \nu_1 + \nu_2(T-T_i) + \nu_3(T-T_i)^{1-\alpha}, \tag{10}$$

where the ν_i are constants. Note that the first two terms contain the linear temperature dependences of both the background contribution of the lattice and the OP fluctuations according to (9).

Equations (8) and (10) principally give rise to different critical behaviour. Whereas the leading exponent near T_i in (8) is 2β, (10) predicts $1-\alpha$. For the 3d-XY-model $2\beta \approx 0.7$ and $1-\alpha \approx 1$. Thus, measurements of the type discussed here should principally be able to distinguish between the two models. In practice, however, the fit parameters in these equations are highly correlated so that both equations can account for the observed behaviour. This is demonstrated in Figure 2, where both fit curves

$$\Delta\nu_c \propto T\frac{\chi(\mathbf{k}=0)}{\xi^3}\left[\frac{1}{1+\eta}(k_c\xi)^{1+\eta} - \frac{\dfrac{\pi}{2-\eta}}{\sin\dfrac{\pi(1+\eta)}{2-\eta}} + \frac{1}{1-2\eta}\int_0^{\left(\frac{1}{k_c\xi}\right)^{1-2\eta}}\frac{1}{1+y^{\frac{2-\eta}{1+\eta}}}dy\right]. \tag{7}$$

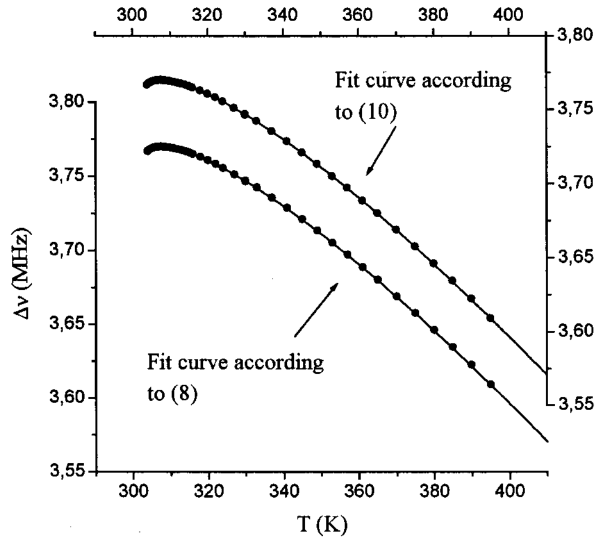

Fig. 2. Data points from Figure 1a together with the fit curves according to (8) (bottom) and (10) (top).

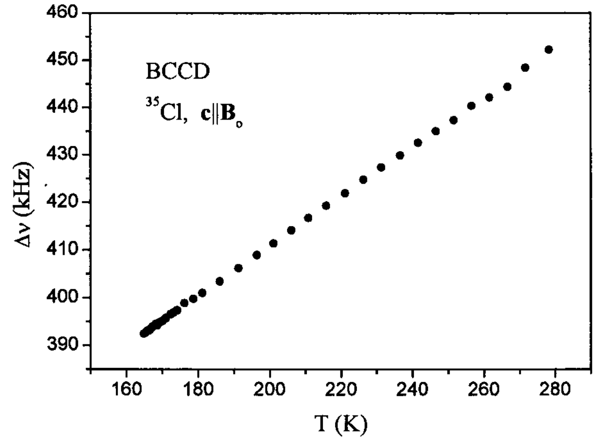

Fig. 3. Temperature dependence of the ^{35}Cl-NMR satellite frequency distance $\Delta\nu$ in the N phase of BCCD. The N-IC phase transition temperature T_i was fixed at $T_i = 164.0$ K.

are shown exemplarily for one set of data points given in Figure 1 (the exponents α, β, and γ have been chosen due to the 3d-XY model and only the constants μ_i and ν_i are fit parameters.). The sum of squared deviations is nearly the same in both cases.

Following the arguments discussed by Bruce [13], (10) should be assumed to be correct, since it simply rests on the first law of thermodynamics. On the other hand it seems to be difficult to name the reasons why the other approach does not give the correct result for $T \to T_i$, *i.e.* $2\beta \neq 1-\alpha$ for non-classical critical behaviour ($2\beta = 1-\alpha$ only for $\gamma = 1$). One reason might possibly be that the type of divergence of the integral in (6) depends strongly on the behaviour of the integrand at large arguments whereas the Ornstein-Zernicke behaviour only holds for small wavenumbers. To make this point clear one may compare (6) to the equation derived previously on the same assumption for the case of the critical spin-lattice relaxation rate [8]

$$\frac{1}{T_{1c}} \propto \frac{\chi^2(\mathbf{k}=0)}{\xi^3} \int_0^{k_c\xi} \frac{x^2}{(1+x^{2-\eta})^2} dx. \qquad (11)$$

In this case the critical divergence of $1/T_{1c}$ is determined only by the prefactor $\chi^2(\mathbf{k}=0)/\xi^3$ because the integral converges in any case and can be approximated by a constant as long as $k_c\xi \gg 1$.

The anomalous shift of NMR frequencies discussed in the present work becomes detectable on the conditions that both the OP fluctuations and the coupling constants are of sufficient strength. Therefore, the effect cannot be observed for all substances. For example it is shown in Figure 3 that it does not occur for the ^{35}Cl-NMR in BCCD despite the fact that the spin-lattice relaxation is strongly influenced by the OP fluctuations for a temperature range of more than 40 K above T_i [8]. Comparison of the T_1 values of ^{87}Rb in RZB/RZC and ^{35}Cl in BCCD at the respective phase transition temperatures shows that the former mechanism is by about a factor of 100 more effective. Since both the line shift and T_{1c} are coupled analogously to the square of the OP the negligible line shift in BCCD becomes plausible.

In the present work we have discussed the shift of the NMR satellite frequency occurring on approaching the N-IC phase transition. This is observable because of the high sensitivity of the satellite transitions in comparison to the so-called central transition. The effect should not be confused with the broadening of NMR lines which is sometimes observed [15]. Both effects have a common root: they are due to a suitable coupling to the OP fluctuations.

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