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Structure of the incommensurate phase of Rb_2ZnCl_4 as determined by ^{35}Cl nuclear quadrupole resonance

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^{35}Cl nuclear quadrupole resonance "lines" in the incommensurate phase of Rb_2ZnCl_4 were assigned as singularities in the quasicontinuous spectrum due to the frozen-in displacements. The plane-wave model describes suitably the microscopic structure down to T_c+10 K, when narrow solitons become dominant.

I. INTRODUCTION

Incommensurate (I) systems are characterized by the appearance of a superlattice with a periodicity which is an irrational fraction of the periodicity of the basic crystal lattice. The proper symmetry group of these systems is a superspace group[1] in $3+m$ dimensions, where $m=1$ for a modulation in one direction, $m=2$ for modulations in two directions, etc.

Rb_2Zncl_4 is a typical example of the one-dimensionally modulated incommensurate system. It undergoes two successive phase transitions at $T_I=302$ K and $T_c=192$ K.[2] On cooling through T_I the crystal exhibits instability against a soft mode with a critical wave vector $\vec{q}_\delta$ which condenses out at a general point in the Brillouin zone. The high-temperature (paraelectric) phase is therefore followed by the I phase, characterized by a frozen-in displacement wave with

$$\vec{q}_\delta=\frac{\vec{c}^{\,*}}{3}(1-\delta) \quad . \tag{1}$$

The parameter δ was found[2] to decrease slightly from approximately 0.03 to 0.015 until the lock-in transition at T_c, when it drops discontinuously to zero. The translational periodicity, which was lost in the I phase, is restored and the crystal becomes commensurate (ferroelectric). The three-dimensional unit cell is tripled with respect to the paraelectric phase.

Rb_2ZnCl_4 has been studied extensively by ^{35}Cl nuclear quadrupole resonance[3–6] (NQR) and ^{87}Rb NMR.[7,8] Several important results about the structure of the paraelectric and ferroelectric phase have been deduced,[3] but on the other hand contradictory interpretations were proposed for the incommensurate one. In order to obtain a consistent description of ^{35}Cl NQR spectra we decided to (i) repeat the measurements, (ii) calculate the position of the lines, and (iii) compare the NQR data with the results of other methods.

The present paper is divided into the following sections: Experimental details and results are described in Sec. II. Section III shows how the shape of NQR spectra is calculated within the models of the I phase, while the comparison with the experimental results is given in Sec. IV. Finally, the most important conclusions are summarized in Sec. V.

II. EXPERIMENTAL RESULTS

Our NQR measurements were performed on a DECCA Super Regenerative Spectrometer. The sideband suppression method was used to avoid any confusion with satellites coming from the quenching frequency. The single crystal ($16\times6\times5$ mm^3) was grown by slow evaporation of an aqueous solution of RbCl and $ZnCl_2$ in 2:1 molar mixture. The sample was heated or cooled by a nitrogen-gas flow and the accuracy of the temperature stabilization was ~0.5 K.

Circles on Fig. 1 denote the experimentally measured ^{35}Cl NQR frequencies. In the high-temperature paraelectric phase three sharp lines are observed and they represent signals of four chemically nonequivalent chlorine sites in the unit cell.[3] When cooling below T_I the lines broaden significantly and their intensity decreases. All the same distinct peaks can be observed through the I phase. On further cooling the signals start to grow up again ~10 K above T_c (Fig. 2). In the ferroelectric phase up to 12 lines can be separated,[3,4] thus indicating tripling of the unit cell.

III. LINE-SHAPE CALCULATIONS

NQR studies of the I phases are based on the fact that quadrupolar frequencies reflect microscopic en-

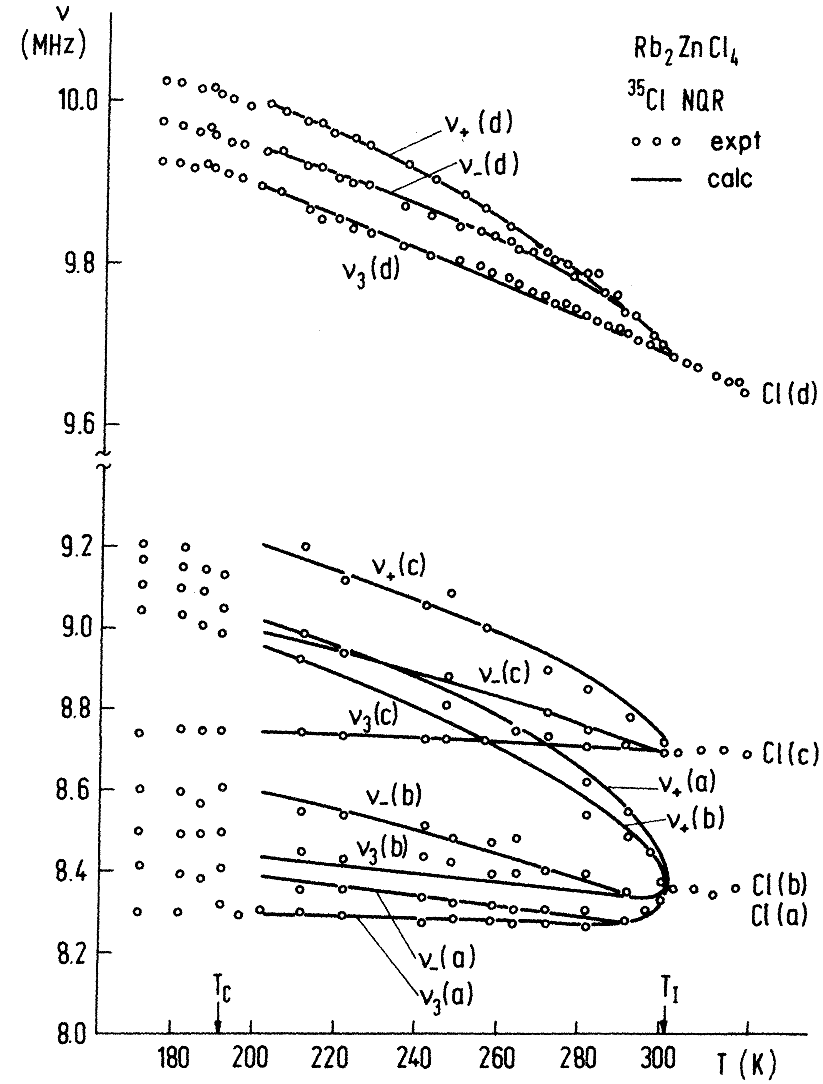

FIG. 1. Comparison between the experimental and calculated NQR "lines" in the I phase of Rb_2ZnCl_4. When cooling through T_I the lines broaden and split, therefore only distinct peaks are plotted (compare with the Ref. 3). All of them can be assigned as singularities in the quasicontinuous NQR spectrum, which results from the frozen-in incommensurate displacements. The calculated curves were obtained within the "plane-wave" model. See the text for details.

vironment of the nucleus. In commensurate systems the number of lines is determined by the (usually small) number of chemically nonequivalent nuclear sites in a unit cell, while in the incommensurate phases the translational periodicity is lost and (roughly speaking) all nuclei become nonequivalent. Someone might conclude that NQR lines would smear out in the I phase and only in the "narrow-soliton" limit[9] sharp signals of commensurate regions might be expected. In the next paragraphs it will be shown that even within the "plane-wave" limit distinct peaks can be obtained in the spectrum.

When cooling through the I phase the nuclei are displaced and their NQR frequencies change. If we denote the noncritical temperature dependence by v_0 and if we suppose that the frequencies v are proportional to the order parameter η, we can write

$$v = v_0 + a_1\eta + \tfrac{1}{2}a_2\eta^2 + \cdots \quad . \tag{2}$$

Here the expansion in powers of the order parameter is used and the coefficients $a_1, a_2, \ldots$ depend on the crystallographic structure, the local symmetry of the

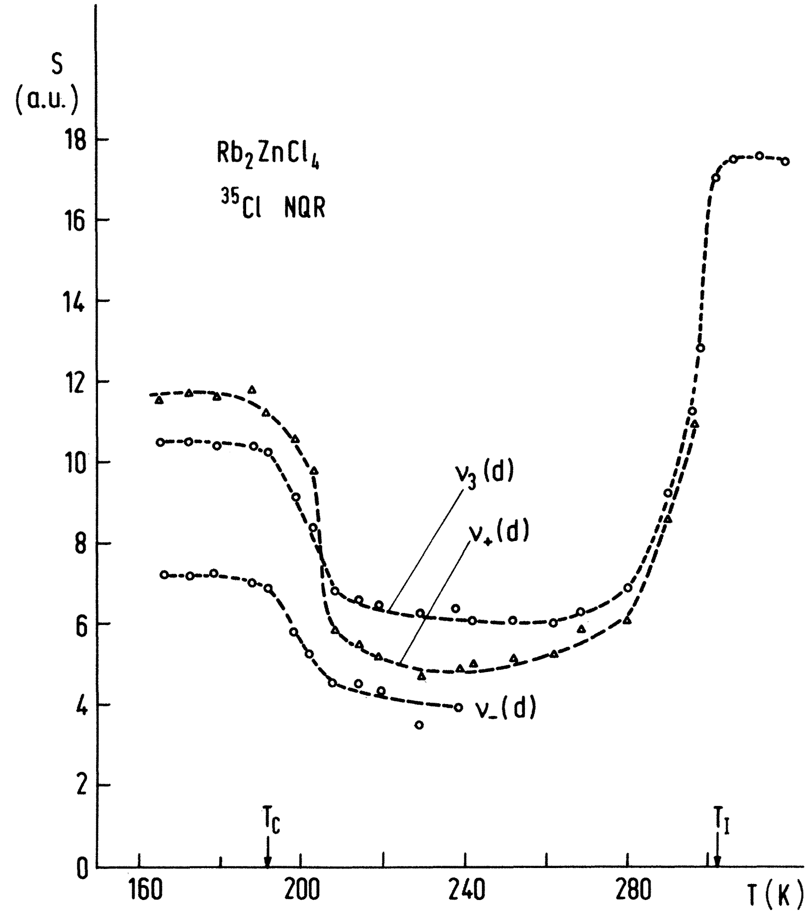

FIG. 2. Temperature dependence of intensities S of the Cl (d) lines. Although the measurements are not accurate, they clearly show that the lines start to grow up significantly above the lock-in transition. The results indicate that the plane-wave model breaks down and that narrow solitons become dominant close to T_c.

basic lattice, directions of the displacements, etc. Taking into account that η is determined by its amplitude A and its phase ϕ

$$\eta = A \cos\phi \tag{3}$$

we find

$$\nu = \nu_0 + a_1 A \cos\phi + \tfrac{1}{2} a_2 A^2 \cos^2\phi + \cdots \quad . \tag{4}$$

The frequency distribution $f(\nu)$ in the I phase is obtained from

$$f(\nu)\, d\nu = \rho(z)\, dz \quad , \tag{5}$$

if we suppose that the density of nuclei per unit length in the direction of the modulation is constant[7]

$$f(\nu) = \frac{\rho_0}{|d\nu/dz|}, \quad \rho(z) = \rho_0 = \text{const.} \tag{6}$$

The derivative

$$\frac{d\nu}{dz} = -(a_1 A + a_2 A^2 \cos\phi + \cdots) \sin\phi \frac{d\phi}{dz} \tag{7}$$

therefore describes the shape of the quasicontinuous spectrum, which has distinct peaks (singularities) whenever $d\nu/dz = 0$.

The spatial variation of the phase $\phi = \phi(z)$ was obtained[9] as a solution of a sine-Gordon equation which leads to a domainlike structure, containing commensurate regions $[\phi(z) = \text{const}]$ separated by solitonlike discommensurations, where the phase changes rapidly for $2\pi/p$ ($p = 3$ in the case of Rb_2ZnCl_4). If the solitons become so broad that the commensurate regions can be neglected, the "plane-wave" relation $\phi = \text{const.}\ z$ turns out to be the best approximation for the microscopic description of the I structure.

In the plane-wave limit the derivative (7) becomes

$$\frac{d\nu}{dz} \propto (a_1 A + a_2 A^2 \cos\phi + \cdots)\sin\phi \quad (8)$$

and neglecting the higher-order terms the line shape is calculated analytically (Fig. 3). The frequency distribution is peaked when $d\nu/dz$ becomes small. The first possibility

$$\sin\phi = 0$$

gives rise to singularities

$$\nu_\pm = \nu_0 \pm a_1 A + \tfrac{1}{2} a_2 A^2 \quad (9)$$

which always appear in the spectrum. They reflect the fact that the density of states has a maximum at the extreme displacements in the incommensurate wave. The next peak at

$$\nu_3 = \nu_0 - \frac{a_1^2}{2a_2} \quad (10)$$

is found, if the condition

$$a_1 A + a_2 A^2 \cos\phi = 0 \quad (11)$$

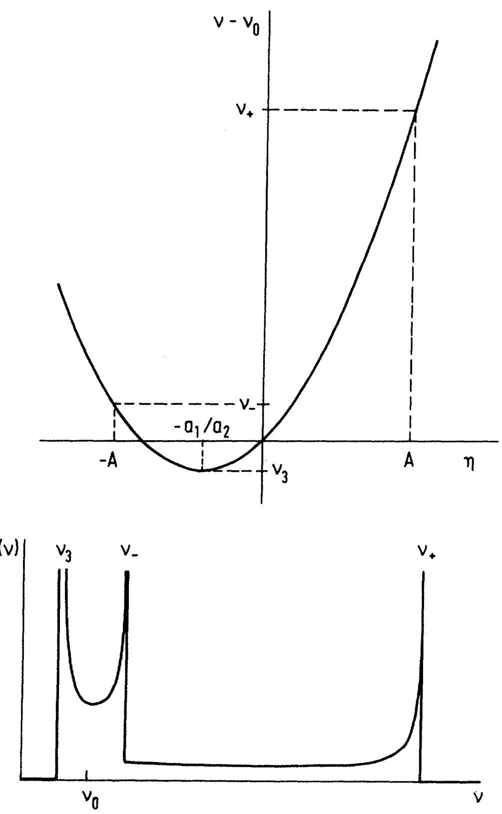

FIG. 3. Illustration to the line-shape calculation in the I phase. The relation between the frequency ν and the order parameter η is expanded up to the second order. When cooling through the I phase the amplitude A of the order parameter increases. When $A \leq |-a_1/a_2|$ only the edge singularities $\nu_\pm$ are observed in the spectrum, but at lower temperatures ν_3 also appears. The theoretical line shape for $A = 2.5 a_1/a_2$ is shown on the figure.

is satisfied. This singularity (ν_3) is a consequence of the nonlinearity in the relation between the NQR frequency and the order parameter. It is easy to show that $\nu_4, \nu_5, \ldots$ are obtained, if higher-order terms are included in the expression (8). These singularities are shifted for a constant value with respect to ν_0 and they do not depend on the order parameter, therefore NQR measurements of the noncritical temperature dependence are sometimes possible even in the I phase.

On the other hand the difference

$$\nu_+ - \nu_- = 2a_1 A \propto (T_I - T)^\beta \quad (12)$$

is proportional to the amplitude A of the order parameter η and by plotting $\nu_+ - \nu_-$ vs $T_I - T$ in a logarithmic scale the value of the critical exponent β is obtained, if higher-order terms in (8) can be neglected.

Close to T_c the solitons were found to become narrower[8] and $\phi(z)$ is constant segmentally. The expression (7) becomes zero also for $|d\phi/dz| = 0$, therefore additional peaks are expected to grow on the expense of the other spectral components. They represent signals of the commensurate regions and they are continued into the "ferroelectric" lines below the lock-in transition.

IV. DISCUSSION

It was shown in Sec. III, that different types of NQR "lines" can be observed in the I phase of Rb_2ZnCl_4 and they can be easily recognized, if the resolution and sensitivity of the spectrometer are excellent: (i) The "edge singularities" ($\nu_\pm$) depend critically on the order parameter and their positions change characteristically on cooling through the I phase. (ii) $\nu_3, \nu_4, \nu_5, \ldots$ arise from the nonlinearity in the relation between the NQR frequency and the order parameter and (if they appear) they continue the noncritical behavior. (iii) "Commensurate" lines grow up close to T_c at the same position as the low-temperature "ferroelectric" ones.

The quasicontinuous ^{35}Cl NQR spectra spread over a wide frequency range (up to 0.7 MHz) in the present experiment therefore is not possible to compare the theoretical line shape (Fig. 3) with the experimental results. Since the broad background is unobservable, only the singularities are detected to check our model.

Figure 1 shows that the plane-wave approximation describes suprisingly well the spectra of the bulk of the I phase. To calculate the positions of ν_+, ν_- and ν_3 for chlorine sites a, b, and c we used the expansion of the frequency up to the second order in powers of η [see Eq. (2)] and taking into account $A \propto (T_I - T)^\beta$, we had to vary parameters a_1, a_2, and

β till the curves on Fig. 1 were obtained. They suitably connect all experimentally obtained NQR lines.

For the chlorine site d the linear term was found to be approximately zero ($a_1 \approx 0$) due to the local symmetry,[10] therefore the expansion (2) was extended up to the fourth order.

The value of the critical exponent $\beta = 0.36 \pm 0.04$ agrees with the $d = 3$, $n = 2$ Heisenberg model ($\beta = 0.35$) which applies to the simple case of incommensurate phase transitions.[11] Our results confirm that the whole I phase is indeed critical in the one-dimensionally modulated Rb_2ZnCl_4 crystal. The value of β is in accordance with the results of other methods in similar systems: (i) ^{87}Rb NMR gave $\beta = 0.36 \pm 0.02$ for Rb_2ZnCl_4 and Rb_2ZnBr_4.[8] (ii) Neutron scattering results gave $\beta = 0.37 \pm 0.03$ for Rb_2ZnCl_4 (Refs. 2 and 12) and $\beta = 0.4 \pm 0.05$ for K_2SeO_4.[13] (iii) In EPR of Mn^{2+} doped Rb_2ZnCl_4 the value $\beta = 0.36 \pm 0.04$ was obtained.[14] (iv) Ultrasonic measurements on Rb_2ZnCl_4 gave the values $\beta = 0.31$ or 0.32 depending on the acoustic modes which were considered.[15]

It should be noted that properties of the basic lattice were also studied in our experiment. From the positions of the singularities v_3 [see Eq. (10)] we determined the noncritical temperature dependences (v_0) which continue the paraelectric behavior. All of them show a slight increase on cooling through the I phase: dv_0/dT lies between -0.2 and -1 kHz/K for the chlorine sites a, b, and c and $dv_0/dT = -2.0$ kHz/K for the chlorine site d. There was no step observed at the transition temperature T_I.

The plane-wave picture starts to break down about 10 K above T_c.[8] Resolution and sensitivity of the superregenerative NQR spectrometer were not sufficient to recognize unambiguously the "commensurate" lines which are expected to appear close to T_c, therefore only an indirect proof for the "narrow-soliton" structure will be given. Figure 2 shows the temperature dependence of the intensities of the Cl (d) lines, which are most easily observed in the I phase, because the quasicontinuous spectrum spreads over a frequency range not exceeding 100 kHz. Just below T_I the line splits and on further cooling more and more of the signal is lost in the unobservable background. This behavior is saturated when the frequency separation between $v_+(d)$ and $v_3(d)$ becomes nearly temperature independent. About 10 K above T_c the intensity starts to grow up quickly. The soliton density n_s decreases as[8,16]

$$n_s \propto (T - T_c)^{1/2}$$

therefore their contribution to the broad background becomes smaller. The intensity of the "commensurate" lines—which nearly coincide with the singularities—must increase significantly (see Fig. 2).

Although it is known that cw detection deteriorates the line shape of NQR signals, the result was found to be so clear and reproducible that it cannot be treated as an experimental artifact. We believe that pulsed NQR measurements might provide detailed information about the microscopic structure of the I phase close to T_c.

The conclusions about narrow solitons agrees with the previous intuitive proof,[3] but the proposal that the incommensurate phase has the "ferroelectric" structure slightly modulated by a long wave with the period $1/\delta$,[5] was not confirmed. Our measurements and calculations show that the basic crystal lattice is equal to the high-temperature (paraelectric) one, while the displacements form a nearly "plane-wave" superlattice down to $T - T_c \sim 10$ K, where they gradually change into a domainlike structure. This picture agrees with the ^{87}Rb NMR measurements on Rb_2ZnBr_4 (Ref. 17) and Rb_2ZnCl_4.[7]

The soliton density has been also studied in $2H$-$TaSe_2$ which appears to be an ordinary metal at high temperatures only. In the temperature range between 90 and ~ 120 K incommensurate charge-density waves are present. Measurements of the ^{77}Se Knight shifts were interpreted within the "narrow-soliton" picture through the whole I phase.[18] Fukui *et al.*[19] have also observed that the low-temperature ESR lines are continued into the I phase of the partially polymerized bis (p-toluene sulfonate) ester of 2,4-hexadiyne-1,6-diol crystal. Their results were not explained within the plane-wave model.

The last two incommensurate systems deserve further studies to confirm whether they form a domainlike structure even far from T_c.

CONCLUSIONS

Measuring and analyzing ^{35}Cl NQR spectra we derived or verified the following conclusions about the incommensurate phase of Rb_2ZnCl_4: (1) Bulk of the I phase consists of very broad solitons which are suitably approximated by the plane-wave model. (2) The temperature variation of the amplitude of the order parameter is described by the critical exponent $\beta = 0.36 \pm 0.04$. (3) The whole I phase is critical in the present system. (4) The noncritical temperature dependence of NQR frequencies continues the paraelectric behavior without any significant step at T_I. The frequencies slightly increase when cooling through the I phase. (5) Narrow solitons are present only close to the lock-in transition ($T - T_c \lesssim 10$ K).

Note added in proof. After sending the manuscript another paper on the same subject appeared [I. P. Aleksandrova, A. K. Moskalev, and I. A. Belobrova, J. Phys. Soc. Jpn. Suppl. B 49, 86 (1980) (proceedings of the second Japanese Soviet Symposium on Ferroelectricity, Kyoto, 1980)]. It gives a similar description of the incommensurate phase, but line positions are calculated within the mean-field approximation ($\beta = 0.5$).

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