Neutron scattering study of the incommensurate and commensurate phases of Rb_2ZnBr_4

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Measurements are presented of the diffuse scattering corresponding to order-parameter fluctuations in the incommensurate phase ($200 \lesssim T < 355$ K), and the commensurate phase ($T \lesssim 200$ K) of Rb_2ZnBr_4. The diffuse-scattering distribution is ellipsoidal in shape with the principal axis along the modulation wave vector. The order-parameter fluctuations are quasielastic in both the incommensurate and the commensurate phase. Below the lock-in transition the diffuse-scattering distribution narrows in the *b* direction, which is the direction of spontaneous polarization in the commensurate phase. In addition to this quasielastic diffuse scattering, normal acoustic-phonon branches are observed originating from the satellites. A Landau free-energy model is presented which is in nearly quantitative agreement with the measured temperature dependence of the modulation wave vector. The Landau free energy predicts the existence of a dielectric polarization wave in the incommensurate phase which has the periodicity of the third harmonic of the primary modulation wave. We have calculated the effect of an applied electric field on the diffraction pattern in the presence of the polarization wave. Measurements of the field dependence of the intensity of first- and higher-order satellites agree with the calculation; i.e., the intensity of the first- and third-order satellites is virtually independent of the field whereas the intensity of the second-order satellite is enhanced by the field.

I. INTRODUCTION

The compound Rb_2ZnBr_4 belongs to the class of modulated dielectrics. Related crystals with incommensurate phases are: $(NH_4)_2BeF_4$,[1] K_2SeO_4,[2] and Na_2CO_3.[3] There has been a previous neutron-diffraction study of the incommensurate transition at $T_i = 355$ K ($\alpha \to \beta$ transition).[4] The dielectric behavior both at T_i and the commensurate transition at $T_c = 200$ K ($\beta \to \gamma$ transition) has also been investigated.[5] In the present paper results of a neutron-scattering study are presented with emphasis on the commensurate transformation.

Comparing the above-mentioned modulated crystals one may conclude that Rb_2ZnBr_4 is closely related to K_2SeO_4, since the wave vector $\vec{q}_0$ is close to $\frac{1}{3}\vec{c}^*$ in the incommensurate phase. (Note that we use space-group *Pcmn* for the high-temperature symmetry.) Also, it has a commensurate phase with $\vec{q}_0 = \frac{1}{3}\vec{c}^*$ whereas $(NH_4)_2BeF_4$ locks-in to $\frac{1}{2}\vec{c}^*$ and Na_2CO_3 shows even less resemblance since this crystal is monoclinic and its wave vector has components both along $\vec{c}^*$ and $\vec{a}^*$. On the other hand, the dynamical behavior of Rb_2ZnBr_4 is entirely different from that of K_2SeO_4. The overdamped soft mode in Rb_2ZnBr_4 near T_i is similar to what is found in $(NH_4)_2BeF_4$.[1] The soft mode in K_2SeO_4 is very well defined and its frequency above T_i was unambiguously determined[2]; in both Rb_2ZnBr_4 and $(NH_4)_2BeF_4$ the corresponding branch is stable. Therefore it seems clear that the structural similarity of modulated crystals does not guarantee similarity in dynamical behavior. Still, a comparison on a phenomenological basis (i.e., Landau theory) can be useful to see which properties are determined by symmetry. One such property is the ferroelectric polarization which appears as a secondary effect on locking-in. Except for Na_2CO_3 the above-mentioned modulated crystals are also known to have a low-temperature ferroelectric commensurate phase.

In Sec. II. details of the experimental procedure will be given. The results will be presented in Sec. III, and in Sec. IV a model of the free energy is discussed as well as the results of a diffraction experiment in an electric field.

II. EXPERIMENTAL DETAILS

Experiments were done on triple-axis spectrometers at Brookhaven National Laboratory and ECN (Netherlands Energy Research Foundation) (Petten). Pyrolytic-graphite crystals were used as monochromator and analyzer. Horizontal collimation was tight in most measurements: 20 min both before and after monochromator and analyzer. The incoming energy was 14 MeV and the beam was filtered by pyrolytic graphite in order to prevent second-order scattering from the monochromator. The crystals used in the experiments were grown by evaporating an aqueous solution at a temperature of 40 °C. The crystals had a volume of 3 and 10 cm^3. They were mounted in a helium gas-filled container or directly in the vacuum chamber of a cryostat. For the measurements in an electric field a smaller crystal in the form of a 1-mm-thick plate perpendicular to the b-axis was used. Electrodes were formed by painting silver paste on the surfaces.

III. RESULTS

A. Temperature dependence of $\vec{q}_0$

In a previous study of the incommensurate phase of Rb_2ZnBr_4,[4] no temperature dependence of the modulation wave vector $\vec{q}_0$ was found above room temperature. From Fig. 1, it is seen that below 210 K $\vec{q}_0$ increases steeply and at about 190 K a jump is observed to the commensurate value $\vec{q}_0 = \frac{1}{3}\vec{c}^*$.

Upon heating the crystal again a large hysteresis appears in the length of $\vec{q}_0$. We classify the transition as first order in view of the large jump of $\vec{q}_0$. In the incommensurate phase a secondary hysteresis is seen which is most striking close to the commensurate transition. The exact extent of the hysteresis is sample dependent. In one crystal, it was even found that about 15% of the sample did not become commensurate at all, even at helium temperature. A photograph of the diffracted beam showed that the undercooled incommensurate phase occupied a well-defined small region within the otherwise commensurate sample. In this experiment, the crystal was mounted in the cryostat by gluing it directly to an aluminun post. We checked that the undercooling was not due to the way of mounting the crystal, by repeating the experiment with the crystal wrapped in

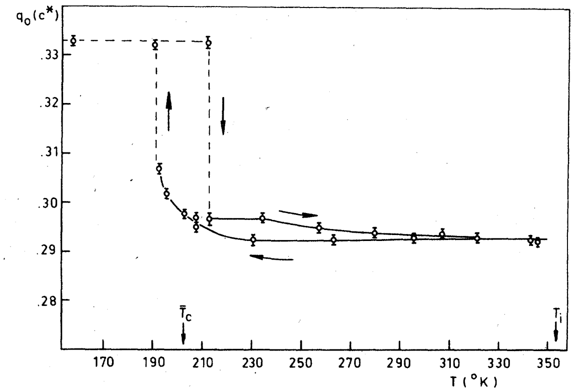

FIG. 1. Temperature dependence of the modulation wave vector $\vec{q}_0$.

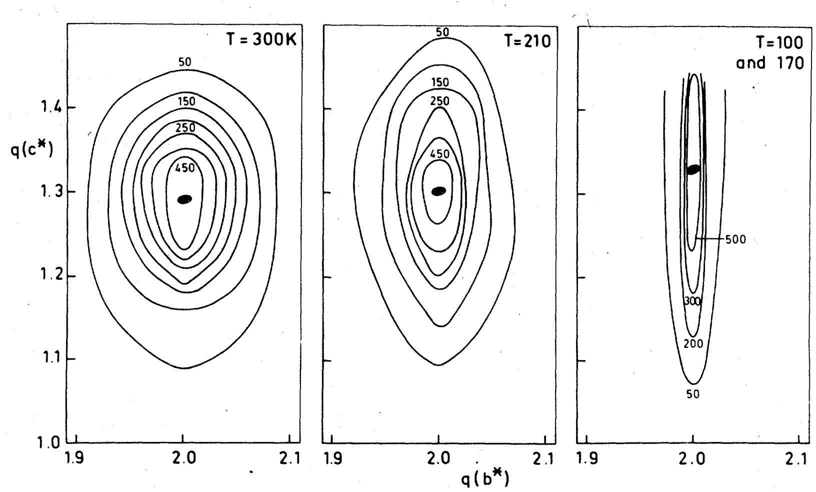

FIG. 2. Intensity contours of diffuse scattering at several temperatures. The contours are obtained by smoothing the raw data of which examples are shown in Fig. 3. The background intensity has been subtracted. The ellipse at the satellite position represents the resolution function. The peak intensity of the satellite is about 3 $\times 10^5$ in the units that were used in the figure (counts/2 min.).

aluminum foil, which was glued to the post. Apparently, the wave vector is partly determined by irreversible stresses and pinning effects which differ from crystal to crystal, and in cooling and heating runs.

IV. DIFFUSE SCATTERING

In the incommensurate phase the $\pm\vec{q}_0$ degeneracy of the soft mode is lifted and the excitations should split into independent fluctuations of the amplitude and the phase of the static wave.[6] These can be distinguished since a phase fluctuation branch is gapless at the modulation wave vector, contrary to the amplitude branch. Extensive measurements were done in order to check this picture of the low-temperature soft excitations. However, we failed to observe a well-defined soft branch in the γ and the β phases. We see only acoustic modes, with an appropriately weak structure factor, originating from the satellite positions. Perhaps, the absence of a propagating soft mode should not be surprising in view of the quasielastic nature of the critical diffuse scattering in the α phase. Just as in the high-temperature phase, quasielastic diffuse scattering was observed below T_i which is rather broad in reciprocal space. In Fig. 2 contour maps are shown of the diffuse intensity in the commensurate phase and in the incommensurate phase. In the incommensurate phase there is a broad distribution which is roughly ellipsoidal in shape with the principal axis along $\vec{q}_0$. On cooling from 300 to 210 K a slight change appears in the width of the distribution. A drastic decrease of the width along $\vec{b}^*$ is seen on passing the commensurate transition, while the width along $\vec{q}_0$ hardly changes. In Fig. 3 scans across the diffuse ridge are shown at about 0.1 $\vec{c}^*$ from the satellite position. They clearly demonstrate the sharpening in the $\vec{b}^*$ direction. The curves show that at lock-in the diffuse intensity is redistributed near the center of the ridge. The integrated intensities of the peaks in Fig. 3 are nearly equal: the peak intensity at 170 K is three times higher and the width is three times narrower than the peaks in the commensurate phase.

V. LANDAU FREE ENERGY

Inasmuch as the experiments did not energy resolve the diffuse scattering, it is by no means clear whether the fluctuations associated with it are best thought of as quasistatic or dynamical. In any case, we assume that these are indeed the order-parameter fluctuations and it is clear that they are very anisotropic, with the correlation range increasing perpendicular to $\vec{q}_0$ near T_c.

For the purposes of this discussion we adopt the

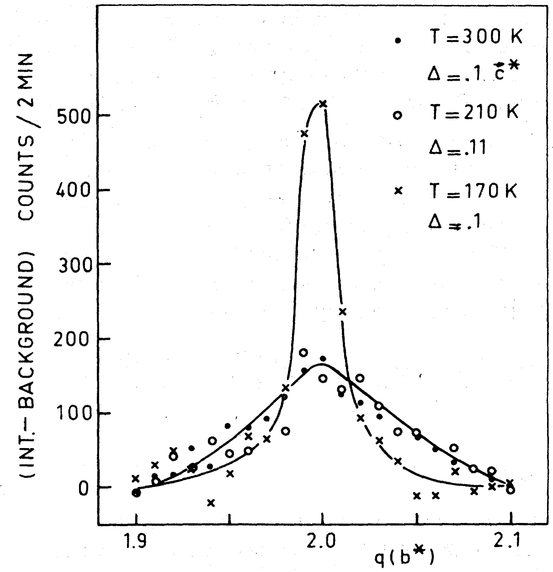

FIG. 3. Scans across the diffuse ridge at several temperatures. The width of the peak at 170 K is nearly resolution limited. The distance from the satellite is given by Δ in units $\vec{c}^*$.

following picture of the incommensurate phase near the lock-in transformation temperature. The phase of the order parameter is modulated in such a way as to produce regions in which the wave vector is locally locked at the commensurate values which are separated by narrower regions in which the phase changes rapidly. These "defect" regions of rapid phase change have been termed discommensurations.[7]

In an ideal material, these defects themselves form a regular array and thus give rise to additional satellite reflections at $2q_0$, $3q_0$,... But it seems probable that strains and impurity pinning centers can partly disrupt this discommensuration lattice to produce diffuse scattering qualitatively similar to that observed.

In connection with the growth in correlation length along $\vec{b}^*$ below T_c, we note that $\vec{b}^*$ is the ferroelectric axis and it is well known[8] that dipolar coupling favors such an anisotropy in correlation lengths. Of course, the present case is complicated by the secondary role of the ferroelectric polarization.

Although the observed diffuse scattering is evidence of large fluctuations in the modulation wave, the sharpness of the satellites shows that the wave has a component with true long-range order. Therefore, it would also appear that the higher harmonics can still be described by the long-range correlated part of the discommensurations.

For a more quantitative description of the lock-in transformation, we follow McMillan[7] and describe the inhomogeneity of the modulated crystal by a spatially varying Landau free energy. The functional form of the free energy is derived as follows: The atomic displacements can be written in terms of a normal coordinate Q_q as; $u_{lk} = \mathrm{Re}(Q_q \exp i\,\vec{q}\cdot\vec{r}_{lk})$. We take as order parameter the normal coordinate of a commensurate distortion Q_{qc}, with $\vec{q}_c = \frac{1}{3}\vec{c}^{\,*}$, which is modulated by the slowly varying function $e^{-i\phi}$. The angle is the phase of the actual modulation wave with respect to the hypothetical commensurate wave. For simple single plane-wave response we have $\phi = \delta z$ $(\delta = |\vec{q}_c - \vec{q}_0|)$. If we neglect for the present coupling to the dielectric polarization, the invariants in the free-energy density are of the form

$$Q^n(Q^*)^{n'},\quad Q\frac{\partial}{\partial z}Q^* - Q^*\frac{\partial}{\partial z}Q,\quad \frac{\partial Q\,\partial Q^*}{\partial z\,\partial z},$$

and

$$Q^m + (Q^*)^{m'},$$

where $n = n'$ and $m = m'$ since the inversion transforms Q into $-Q^*$. The lowest possible value of m is six, in view of translational and rotational invariance requirements. (A translation $\vec{t}$ transforms Q into $e^{i\vec{c}^{\,*}\cdot\vec{t}/3}Q$.) We will ignore in the gradient terms the derivative with respect to the amplitude ρ $(\rho = |Q|)$.

As a result the free energy can be expressed as

$$F - F_0 = \int \tilde{F}\, dz\ ,$$

$$\tilde{F} = \frac{\alpha}{2}\rho^2 + \frac{\beta}{4}\rho^4 + \frac{\gamma_1}{6}\rho^6 + \frac{\gamma_2}{6}\rho^6\cos(6\phi) + \rho^2[\tfrac{1}{2}\gamma(\phi')^2 - \mu\phi']\ . \qquad (1)$$

The coefficient α is temperature dependent; $\alpha = a(T - T_0)$. For $\alpha < \frac{\mu^2}{\gamma}$ the incommensurate distortion becomes stable with $\phi' = \delta_0 = \frac{\mu}{\gamma}$.

The incommensurate phase is allowed to become inhomogeneous by the formation of higher harmonics of the primary wave. The inhomogeneity is caused by the dependence of $\tilde{F}$ on ϕ. For the present discussion only phase fluctuations will be considered,

$$\phi = \delta z + \sum_{n=1}^{\infty} A_n \sin(6n\,\delta z)\ . \qquad (2)$$

The difference between the free energy in Eq. (1) and that of the commensurate state must be minimized in order to find the coefficients δ and A_n

$$\Delta\tilde{F} = \frac{\gamma_2}{6}\rho^6[1 + \cos(6\phi)] + \rho^2[\frac{\gamma}{2}(\phi')^2 - \mu\phi']\ , \qquad (3)$$

where we have used

$$F_{\mathrm{comm}} = \frac{\alpha}{2}\rho^2 + \frac{\beta}{4}\rho^4 + \frac{1}{6}(\gamma_1 - \gamma_2)\rho^6\ .$$

By numerically minimizing the volume integral of $\Delta\tilde{F}$ one finds the amplitudes A_n and the wave vector δ at constant ρ. We performed this calculation using a computer program based on the simplex function minimization procedure.[9] In the expansion in Eq. (2) six Fourier coefficients were retained.

The character of the solutions that result from the minimization depends upon how the amplitude ρ is handled. If, following McMillan, we constrain $\rho^2 \propto a(T - T_0)$, then minimizing with respect to δ produces a second-order lock-in transformation; δ/δ_0 is a smooth function of ρ. If, however, we remove this restriction and minimize Eq. (1) with respect to ρ as well as δ, we find that ρ is no longer equal in the commensurate and incommensurate phases. [Close to T_c two minima in the free energy are ob-

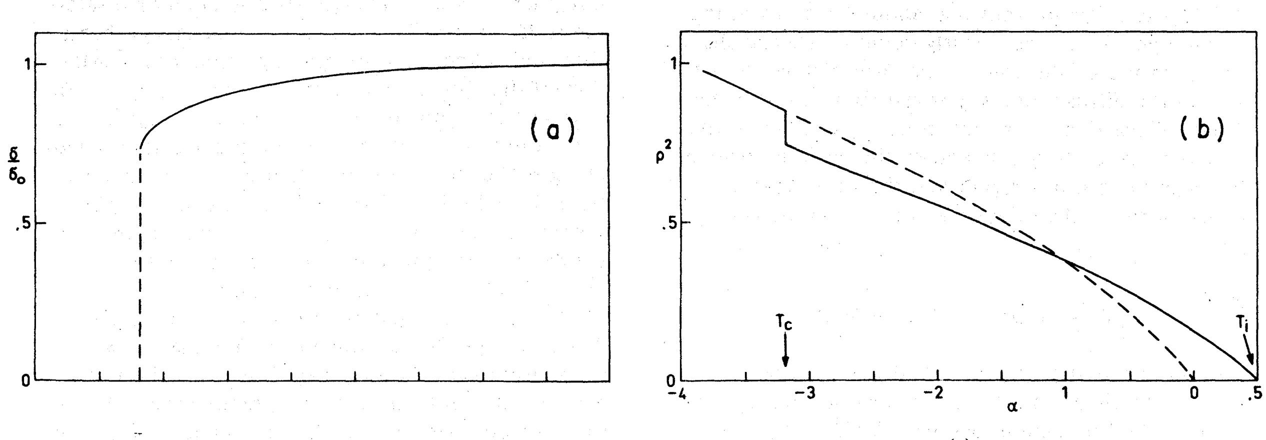

FIG. 4. Results of the minimization of the Landau free energy which is discussed in the text. (a) Temperature dependence of the wave vector in reduced units. At the lock-in transition the wave vector δ jumps to zero. The value of δ/δ_0 was determined from the minimum of the free energy as a function of the wave vector δ. (b) Temperature dependence of the squared amplitude of the displacement wave. The drawn curve gives the result of the minimization of the free energy in the incommensurate phase and the jump of the amplitude at the transition. The dashed curve corresponds to the minimization of the free energy without the gradient terms that give rise to the modulated structure.

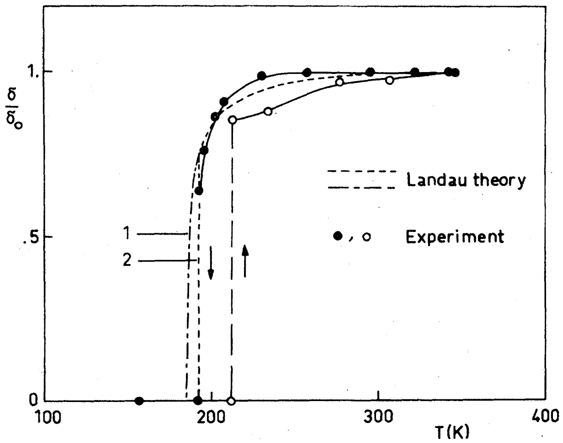

FIG. 5. Temperature dependence of δ/δ_0 as determined in (closed circles) and heating runs (open circles). The minimization of the difference between the free energy in the commensurate phase and the incommensurate phase yields a smooth decrease of δ/δ_0 (dashed-dotted line, numbered 1). Minimizing the full expression of the free energy leads to a first-order transition (dashed line, numbered 2). Above T_c, both minimization procedures yield the same value of δ/δ_0.

tained as a function of δ/δ_0; one at $\delta/\delta_0 \approx 0.05$, the other at $\delta/\delta_0 \approx 0.71$. The minimum near $\delta/\delta_0 \approx 0.05$ shifts toward zero if more Fourier coefficients are retained in Eq. (2), so we take $\delta/\delta_0 = 0$ to be the true position of the minimum.] Not only ρ, but also δ/δ_0 changes discontinuously (to zero) at T_c and the transformation is of first order as observed experimentally. These results are shown in Fig. 4.

Comparison with the experimental values of q_0 is shown in Fig. 5. The values of the coefficients in Eq. (1) have been taken as $\beta = 2$, $\gamma_1 = 5$, $\gamma_2 = 3$, $\mu = 1$, and $\gamma = 2$. Note that the only significant coefficients in the free energy are γ_2/γ_1, β, and the temperature. The other coefficients can be deleted by proper rescaling. From a numerical solution it is impossible to obtain the entire phase diagram that corresponds to the free-energy model. However, we found that the temperature dependence of δ/δ_0 was nearly independent of the choice of the coefficients in Eq. (1). In particular, the jump of δ/δ_0 at the lock-in transition was found to be virtually independent of the coefficients.

In Rb_2ZnBr_4 the incommensurate phase is stable over a large temperature range 150 K which should be related to a low value of γ_2/γ_1. However, such a large temperature interval raises some doubt as to the validity of Landau theory where only α depends on T (and in a simple linear way). In this respect we note that the overall temperature dependence of q_0 is well described by the Landau theory. Particularly just below T_i, q_0 is independent of temperature, which agrees with the calculation. In the related compound K_2SeO_4, the incommensurate phase exists in a much smaller temperature region ~ 30 K but the wave vector changes linearly with temperature in this range.[2] At least to some extent, this must be due to the intrinsic temperature dependence of δ, which is also manifest in the position of the minimum of the phonon dispersion above T_i. In Rb_2ZnBr_4 the coefficients γ and μ are presumably independent of temperature.

From a theoretical point of view the question of whether the lock-in transformation is first or second order is subtle. Nakanishi and Shiba[10] have also noted that if ρ is assumed spatially uniform, but its amplitude fixed by explicit minimization, that the lock-in transformation is first-order, contrary to McMillan's result. However, these authors went on to show that if one admits grad ρ terms in $\tilde{F}$ so that ρ as well as ϕ become spatially modulated, then one regains a second-order phase transformation. At least one other possibility exists as an explanation of the observed first-order nature of the transformation. Shiba and Ishibashi[11] have considered the effect of the coupling to the dielectric polarization and conclude that if grad P terms in $\tilde{F}$ are important that [at least for $(NH_4)_2BeF_4$] the lock-in transformation is first order. Clearly, further work is necessary to resolve this question.

VI. ELECTRIC-FIELD DEPENDENCE OF SATELLITE INTENSITIES

In a previous paper[5] it was shown how the dielectric behavior of Rb_2ZnBr_4 can be understood from the inhomogeneity of the incommensurate phase. In particular, it was suggested that an applied electric field $\vec{E}$ would cause a modification of the phase modulation $\phi(z)$ from that given in Eq. (2). Physically, this comes about because whereas in the absence of a field equal regions of positive and negative polarization alternate, in the presence of the field the regions of favorable polarization grow at the expense of the unfavorable ones. The coupling of the polarization with Q induces the additional modulation of $\phi(z)$. In fact, it can be shown that in the presence of an applied field that $\phi(z)$ becomes $\tilde{\phi}(z)$, which can be written

$$\tilde{\phi}(z) = \phi(z) + \sum_m B_m \sin(3m\delta z) \quad . \tag{4}$$

This modification $\phi \rightarrow \tilde{\phi}$ is reflected in the satellite intensities, which are proportional to $|F(\vec{Q})|^2$, where

$$F(\vec{Q}) = \sum_{lk} b_k \exp i[\vec{Q}\cdot(\vec{r}_{lk} + \vec{u}_{lk})] \quad . \tag{5}$$

We write

$$\vec{u}_{lk} = \mathrm{Re}(\rho\vec{e}_k e^{i\tilde{\phi}(z_{lk})}) = \mathrm{Re}\left[\rho\vec{e}_k e^{i\phi(z_{lk})}\left(1 + i\sum_m B_m \sin(3m\,\delta z_{lk}) + \cdots\right)\right]$$

$$\cong \vec{u}^{\,0}_{lk} + \mathrm{Re}\tfrac{1}{2}(\rho\vec{e}_k)\sum_m B_m(e^{i(3m+1)\delta z_{lk}} + e^{-i(3m-1)\delta z_{lk}}) , \tag{6}$$

where $\vec{u}^{\,0}_{lk}$ are the displacements at $\vec{E}=0$. Except very close to lock-in, the correction terms in Eq. (4) are dominated by $m=1$, and it follows immediately that the intensities most changed are those with reduced wave vectors $\vec{q}=(\frac{1}{3}-2\delta)\vec{c}^{\,*}$ and $\vec{q}^{\,*}=(\frac{1}{3}+4\delta)\vec{c}^{\,*}$.

In order to check this result an experiment was done in an electric field. The field is along the $\vec{b}$ direction (which is the direction of spontaneous polarization in the γ phase) and the temperature was T_c+4 K and $\delta=0.02\vec{c}^{\,*}$. The field alternates at 50 Hz and we indicate the strength by the maximum value of the reflection peak. The result is plotted in Fig. 6. The second-order satellite is enhanced by the field, in agreement with the model calculation. The third-order satellite depends only slightly on the field. The main reflections and first-order satellites are virtually independent of the field. Also, it was found that the position of satellites and main reflections was independent of the field in both the β phase and the γ phase. No Bragg peaks were observed at $\vec{q}=\frac{1}{3}\vec{c}^{\,*}$ in the β phase from which we conclude that the field does not give rise to coherently scattering commensurate regions.

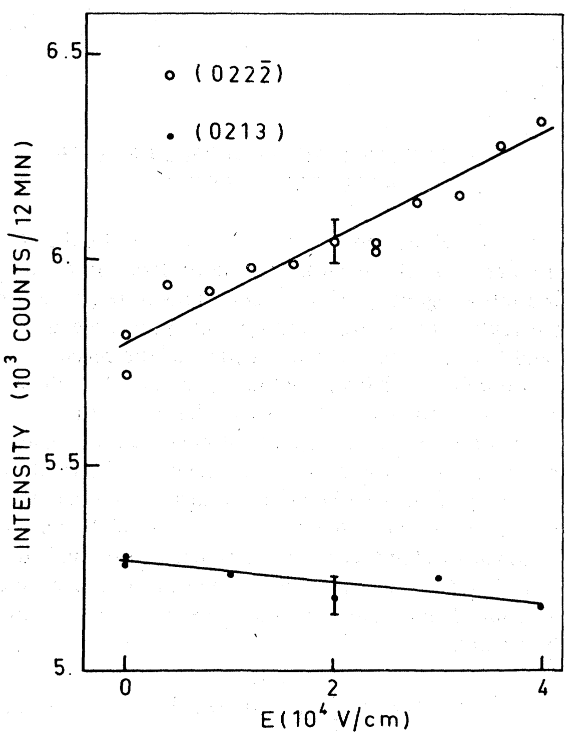

FIG. 6. Field dependence of the intensity of a second-order and third-order satellite. The field alternates at 50 Hz. The field strength is indicated in the figure by the maximum value of the field. The indices of a satellite are $(hklm)$, where m stands for the mth order satellite of main reflection (hkl).

The above results support the picture of a modulated crystal as a "wavy" ferroelectric, particularly near the commensurate transition. Assuming that the linear behavior in Fig. 6 is also valid at low fields ($1\ \mathrm{V\,cm^{-1}}$), it can be concluded that the dielectric behavior is governed by the appearance of a 3δ polarization wave. Close to the transition the lock-in energy becomes more important than the energy which is needed to distort the wave. A weak field stabilizes the locked-in domains, leading to a large response. The peak in the dielectric constant[5] can thus be understood from the deformation of the polarization wave by the applied electric field.

VII. CONCLUSIONS

In Rb_2ZnBr_4 the soft mode is overdamped above T_i, and so are the phase and amplitude fluctuations below T_i. Still, a description of the fluctuations of the order parameter in terms of phase fluctuations is useful for an interpretation of the broad diffuse-scattering distribution around satellite reflections. The higher harmonics of the modulation wave can be visualized as inhomogeneity of the crystal over distances of about $2\pi/3\delta$; in the present crystal this is about 150 Å just above T_i. The inhomogeneous state of the crystal is described by a local free-energy expansion. The numerical solution of the free-energy model gives good agreement with the observed temperature dependence of the modulation wave vector and the first-order character of the transition. The first-order lock-in transition was obtained because the amplitude of the primary wave was allowed to be discontinous at the transition temperature.

We have done diffraction experiments in an electric field supporting the conclusion that the dielectric response at low fields involves an additional modulation of the incommensurate displacements, but with a period which is twice that of the original ($\vec{E}=0$) modulation. Certainly, it is worthwhile to do similar experiments on the related modulated ferroelectrics in order to obtain a better insight into the relation of primary- and secondary-order parameters in this class of improper ferroelectrics.

Note added in proof. In a recent paper [J. Phys. Soc. Jpn. 45, 1777 (1978)], Gesi and Iizumi study the temperature dependence of the incommensurate satellite in Rb_2ZnBr_4. Their data look very similar to those given in Fig. 1 of this paper, but they interpret the data as indicating an additional incommensurate-incommensurate transformation at a temperature $\sim T_c + 10$ K. Further measurements would be necessary to clarify whether this is a universal or sample dependent feature.

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