Far-infrared and Raman studies of the incommensurate structure $\text{Rb}_2\text{ZnBr}_4$.
(A superspace approach)

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(Received 28 December 1981)

The temperature dependence of the optical vibration spectrum of the modulated structure $\text{Rb}_2\text{ZnBr}_4$ has been studied with Raman and far-infrared (FIR) spectroscopy in the normal, incommensurate, and different commensurate phases. The observed activation of new modes confirms the predicted change in selection rules as derived from superspace symmetry. A physical interpretation of the results is given by means of a harmonic oscillator model with modulated spring constants in which the superspace translation symmetry of the vibration modes is taken into account. The FIR response of such a system has been derived. At lower temperatures probably three commensurate phases seem to appear which are driven by a temperature-dependent modulation amplitude.

I. INTRODUCTION

Recently, the appearance of incommensurate ($I$) crystal phases has attracted a great deal of interest.1 These phases are characterized by the simultaneous occurrence of two or more periodicities which are incommensurate with respect to each other. This $I$ phase often occurs as an intermediate phase between a high-temperature normal ($N$) and a low-temperature commensurate ($C$) phase, both having ordinary crystal structures.

The incommensurability implies a loss of translation symmetry in at least one direction of the crystal lattice, excluding any three-dimensional space-group symmetry. It has been shown by de Wolff2 and Janner and Janssen3 that the symmetry of these systems can be described by crystallographic space groups in more than three dimensions, the so-called superspace groups. Until now this higher dimensionality of the symmetry group became apparent only in x-ray and neutron-diffraction data3 and the morphological forms of incommensurate crystals.4 However, this superspace symmetry should also lead to interesting consequences in the studies of the vibrational spectra as well. Therefore, we have performed far-infrared (FIR) and Raman experiments on $\text{Rb}_2\text{ZnBr}_4$, known to have an $I$ phase between 200 and 355 K.5 In the same way as the usual space-group symmetry determines the selection rules for the optical activity of a normal crystal, superspace symmetry determines the behavior of the active modes of incommensurate crystals. Accordingly, at the transition temperature to the $I$ phase, a change in the optical selection rules is to be expected, even if the average crystal structure stays the same. Apart from soft-mode effects6 this had not been observed spectroscopically until recently when Raman experiments on $\text{Na}_2\text{CO}_3$ (Ref. 7) and $\text{Rb}_2\text{ZnBr}_4$ (Ref. 8) showed the activation of extra internal modes. In this paper we will present a theoretical and experimental study of the Raman and FIR spectra of $\text{Rb}_2\text{ZnBr}_4$ confirming this change in selection rules as derived from superspace symmetry. A physical interpretation of these results can be given by means of a harmonic oscillator model which incorporates the superspace translational symmetry of the problem. To study the dielectric response of such an incommensurate system, the effects of the incommensurability on the local electrical fields should also be taken into account. A first step is made to generalize the existing theory in this respect. These results show the relevance of the superspace approach in Raman and FIR spectroscopy also. Some preliminary results of these studies have been published before.8

The transition to a $C$ phase below 200 K is not accompanied by observable changes in the selection
rules. This might be in agreement with the idea that superspace symmetry is relevant for certain commensurate superstructures as well.\textsuperscript{9–11} At still lower temperatures, the Raman and FIR spectra are strongly temperature dependent and show additional phase transitions at 113 and 56 K. Besides, it also appears that these low-temperature phases are connected to the modulation.

This paper is organized in the following way: In Sec. II the experimental details are described, and in Sec. III, the FIR and Raman selection rules are derived using the superspace group of Rb$_2$ZnBr$_4$. The physical interpretation as well as the temperature dependence of the modes in the $I$ phase are discussed in Sec. IV. The experimental results from the $N$ and $I$ phase are treated in Sec. V, and those of the different $C$ phases in Sec. VI. A summary of all results is given in Sec. VII. The details of our harmonic oscillator model and the dielectric response of that system are treated in Appendixes A and B.

II. EXPERIMENTAL DETAILS

The single crystals of Rb$_2$ZnBr$_4$ were grown at room temperature from an aqueous solution of RbBr and ZnBr$_2$ in a 2:1 molar ratio. Crystals obtained in this way were colorless though not completely transparent. The orientation of the crystallographic axis was determined from the morphology and by x-ray measurements on the basis of a high-temperature space group $Pcmn$.\textsuperscript{5} For the FIR transmission experiments, different thin plates were cut perpendicular to the $a$ or to the $c$ axis, whereas transparent regions were chosen for the Raman scattering. To study the FIR transmission above room temperature the samples were electrically heated in an evacuated furnace equipped with standard FIR light pipes. The temperature was measured with a Cu-Constantan thermocouple.

The measurements between 5 and 300 K were performed in the chamber of a gasflow cryostat filled with He gas where the temperature was measured with a Au 0.03 at. % Fe-Cr thermocouple. As FIR sources, a Michelson and Lamellar interferometer were used and as a detector a He-cooled silicon bolometer. For the Raman experiments the crystals were placed in a specially designed variable temperature cryostat with working temperature between 5 and 700 K. As thermometers a Au 0.03 at. % Fe-Cr thermocouple and a platinum resistor (Pt-100) were used. An Ar$^+$ laser ($\lambda=514.5$ nm) served as the exciting radiation source. The scattered light was analyzed at a right angle with a double-grating monochromator after which the signal was recorded with the usual photoncounting techniques.

III. FAR-INFRARED AND RAMAN SELECTION RULES IN THE INCOMMENSURATE PHASE

In this paper we limit ourselves to the situation of a one-dimensional displacive modulation, characterized by a periodic distortion with a wave vector $\vec{q}=\vec{q}_c(1-\delta)$ which does not fit on the underlying lattice periodicity of a basic structure obtained by disregarding that distortion; $\delta<<1$ denotes the relative deviation from a commensurate wave vector $\vec{q}_c=\vec{k}/p$, where $\vec{k}$ is a vector of the reciprocal lattice $\Lambda^*$ of the basic structure and $p$ an integer.

The normal modes of a crystal can be classified according to irreducible representations of its space group which are characterized by a set of wave vectors, the star of $\vec{k}$ given by $\{ R\vec{k} \mid R \in$ point group $\}$.\textsuperscript{12} Since potentially infrared or Raman-active vibrations correspond to the totally symmetric representation of the translation group for which $\vec{k}=0$, we only need to consider the representations of the factor group one gets by considering the space group modulo the lattice translations.

Superspace group symmetry plays an analogous role for the vibrations of an incommensurate crystal. Though in this case the three-dimensional lattice translations are no more present, one can again classify the vibrational modes by ordinary three-dimensional $\vec{k}$ vectors namely those of the reciprocal basic lattice $\Lambda^*$\textsuperscript{13}. Because superspace groups modulo the internal translations are isomorphic with three-dimensional space groups, all the necessary representations are known. However, instead of restricting $\vec{k}$ vectors to a Brillouin zone, we now must consider $\vec{k}=\vec{k}$ (mod $\pi\Sigma^*$), where $\pi\Sigma^*$ is the projection on the usual space of the reciprocal lattice $\Sigma^*$ of the superspace group. $\Sigma^*$ consists of vectors $\vec{s}^*=\{\vec{s}^*,\vec{s}^*_f\}$ with $\vec{s}^* = \vec{k} + v\vec{q}$, $\vec{k} \in \Lambda^*$ the reciprocal basic lattice (see below), $v$ is an integer and $\vec{s}^*_f = v\vec{b}^*_f$, where $\vec{b}^*_f$ is a unit vector of the internal reciprocal space.\textsuperscript{4} (This in fact means that the electromagnetic radiation will also couple to $\vec{k}=v\vec{q}$ modes.) The character of the representation is calculated with the help of formula (5.7) from Ref. 13:
\( \chi(g_E, R_I) \)
\[ = \chi_{R_E} \sum_{\mathbf{b}_i^*} \exp(i(\mathbf{k} - v\mathbf{q})\mathbf{u}_j - iv\mathbf{b}_i^* \cdot \mathbf{v}_j) . \]
\( \mathbf{R}_j \mathbf{b}_i^* = \mathbf{b}_i^* \)
\( j \neq j' \)

Here the elements of the superspace group are denoted by pairs of Euclidean transformations \((g_E, g_I)\), where \(g_E\) acts on the three-dimensional "external" or "positional" space and \(g_I\) on the one-dimensional internal space. \( \chi_{R_E} \) is the character of the point-group operation of the space-group element \( g_E \); \( v \) and \( R_I \) are the translation and the homogeneous part, respectively, of \( g_I = \{ R_I \mid \mathbf{v}_I \} \).

\( \text{Rb}_2\text{ZnBr}_4 \) has an I phase between \( T_I = 355 \) and \( T_c \approx 200 \text{ K} \) characterized by \( q = \gamma c^* \approx 0.3 c^* \) and a modulation amplitude along the \( b \) axis (here \( a \approx b \sqrt{3} \)). The \( N \) phase has space group \( \text{Pcmn}(D_{2h}^7), Z = 4 \), and the I phase has presumably the superspace group \( \text{Pcmn}^+ \). The corresponding point groups are isomorphic with \( \text{mmm} \). As a coordinate system in superspace we choose the basis \( \mathbf{a}, \mathbf{b}, \mathbf{c}, \) and \( \mathbf{b}_1 \) where the first three span the basic lattice and \( \mathbf{b}_1 \) is a unit vector in the internal space. Then the superspace group is generated by the lattice
\[ (1,0,0,0),(0,1,0,0),(0,0,1,-\gamma),(0,0,0,1) \]
and the operations
\[ \{ R_E = m_x R_I = 1 \mid v = (1/2, 0, 1/2, -1/2 - \gamma) \} , \]
\[ \{ R_E = m_y R_I = 1 \mid v = (0, 1/2, 1/2, 1/2 + \gamma) \} , \]
\[ \{ R_E = m_z R_I = -1 \mid v = (1/2, 1/2, 1/2, -1/2) \} . \]

The different normal modes belong to either of two classes. The first class belongs to \( \mathbf{b}_1^* = v \mathbf{b}_1^* = 0 \) and its character can be calculated with Eq. (1) yielding
\[ \chi(E, c_2^2, c_2^2, c_2^2, i_c, \sigma_x, \sigma_y, \sigma_x) \]
\[ = \begin{cases} (36, 0, 0, 0, 0, 0, 12, 0) \ (4a) \\ (12, 0, 0, 0, 0, 0, -4, 0) \ (4b) \end{cases} \]
for the translational and librational modes, respectively. For the \( v \neq 0 \) class, Eq. (2) gives correspondingly:
\[ \chi = (24, 0, 0, 0, 0, 0, 8(-1)^v, 0) . \]

In the \( N \) phase, the characters are the same as in Eq. (4) so that the new active modes in the I phase will follow from Eq. (5). Since to a good approximation the modulation can be assumed to be sinusoidal,\(^{15}\) the main contribution will come from \( v = 0 \) and \( v = \pm 1 \).

Table I gives the factor group analysis of the normal modes in the \( N \) and the I phase for \( v = \pm 1 \), showing that the extra activated modes are classified as
\[ 16A_g + 26B_{1g} + 16B_{2g} + 26B_{3g} \]
(Raman) and
\[ 15B_{1u} + 25B_{2u} + 15B_{3u} \]
(FIR) active.

IV. THE OPTICAL VIBRATION SPECTRUM
OF AN INCOMMENSURATE CRYSTAL

A. Introduction

To study the vibration spectrum of a crystal one has to consider the displacement field \( \mathbf{u}_{\alpha j} \), being the displacements from the equilibrium position of particle \( j \) in the cell labeled by \( \alpha \). This labeling reflects the presence of translational symmetry and the latter allows solving of the equations of motion for \( \mathbf{u}_{\alpha j} \) in the usual normal modes by reducing the particles to be considered to the finite number of those in the unit cell. This same simplification is not possible for an incommensurate crystal which has a unit cell of infinite volume in the three-dimensional space, so one has to deal with an infinite number of particles.

To tackle this problem, one has started to study one-dimensional models\(^{16-18}\) in which modulated potentials or spring constants are used to simulate the incommensurate situation. However, the physics of all these models is probably too rich to be of practical use for the interpretation of experimental results as those presented here. Besides that, the simplification due to the presence of superspace symmetry cannot easily be made explicit. Therefore, we constructed a simple harmonic oscillator model with modulated spring constants to describe the vibration modes of an incommensurate crystal like \( \text{Rb}_2\text{ZnBr}_4 \), taking the superspace translational symmetry of the problem into account. The aim is twofold: (1) To identify the new modes predicted...
TABLE I. Factor group analysis of Rb$_2$ZnBr$_4$ in the $N$ (Pcmn, $v=0$) and $I$ phase (P$^{\text{cmn}}$, $v=1$). $N$, $A$, $T$, $R$, and $I$ are numbers of normal modes, acoustical, translational optical, librational optical, and internal modes.

<table>
<thead>
<tr>
<th>$D_{1h}$</th>
<th>$N$</th>
<th>$A$</th>
<th>$T$</th>
<th>$R$</th>
<th>$I$</th>
<th>Raman</th>
<th>FIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>13  + 16$\nu$</td>
<td>6 + 6$\nu$</td>
<td>1 + 4$\nu$</td>
<td>6 + 6$\nu$</td>
<td>$\alpha_{xx},\alpha_{yy},\alpha_{zz}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>8   + 26$\nu$</td>
<td>3 + 12$\nu$</td>
<td>2 + 2$\nu$</td>
<td>3 + 12$\nu$</td>
<td>$\alpha_{zz}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>13  + 16$\nu$</td>
<td>6 + 6$\nu$</td>
<td>1 + 4$\nu$</td>
<td>6 + 6$\nu$</td>
<td>$\alpha_{xx}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{3g}$</td>
<td>8   + 26$\nu$</td>
<td>3 + 12$\nu$</td>
<td>2 + 2$\nu$</td>
<td>3 + 12$\nu$</td>
<td>$\alpha_{xy}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$A_u$</td>
<td>8   + 26$\nu$</td>
<td>3 + 12$\nu$</td>
<td>2 + 2$\nu$</td>
<td>3 + 12$\nu$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td>13  + 16$\nu$</td>
<td>1 + $\nu$</td>
<td>5 + 5$\nu$</td>
<td>1 + 4$\nu$</td>
<td>6 + 6$\nu$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>8   + 26$\nu$</td>
<td>1 + $\nu$</td>
<td>2 + 11$\nu$</td>
<td>2 + 2$\nu$</td>
<td>3 + 12$\nu$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>13  + 16$\nu$</td>
<td>1 + $\nu$</td>
<td>5 + 5$\nu$</td>
<td>1 + 4$\nu$</td>
<td>6 + 6$\nu$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

by group theory, and (2) to explain their temperature dependence. In our model the modulation will be expressed by a periodic variation of the spring constants.$^{17}$

We consider a crystal with a one-dimensional displacive modulation with wave vector $\mathbf{q}$ along the $\mathbf{c}$ axis. The symmetry-adapted displacement field of such a crystal has the form

$$\bar{u}^{nlm}(\tau) = \bar{u}_{j}(qnc + \tau)e^{i(k_{c}ma + k_{b}lb + k_{n}nc - \omega t)},$$

with

$$\bar{u}_{j}(\tau) = \sum_{v} \bar{u}_{j}^{v} e^{iv\tau}, \quad v \in \mathbb{Z}.$$  \hspace{1cm} (6b)

This corresponds to a Bloch ansatz taking into account the superspace translational symmetry of the dynamical system which implies in particular the periodicity in the internal coordinate $\tau$ as expressed in Eq. (6b), based on the periodicity of the modulation wave and of the spring constants, respectively.

Referring to the relative strong binding forces within the ZnBr$_4$ tetrahedra we will study the “lattice” modes and the internal tetrahedron vibrations separately. The details of the model are contained in the appendices; here we will give the main results.

B. The lattice modes in the $I$ phase

We will consider the crystal as being built up of chains of dipoles consisting of the Rb ions and the ZnBr$_4$ ions, connected by a spring constant $\alpha$. The coupling with the rest of the lattice goes via two kinds of nearest-neighbor interactions: One between the ions in the chain and one between the ions of neighboring chains, represented by the spring constants $\beta$ and $\xi_{ij}$ respectively (see Fig. 1), where $i$ labels the chain and $j$ denotes the direction of the coupling. Further, we take modulated spring constants for the nearest-neighbor interactions along the $c$ axis which is a necessary and sufficient assumption to simulate the modulation (see also Refs. 17 and 18).

\[
\beta_c^m = \beta_c + \delta \cos(qnc + \tau), \quad (7a) \\
\xi_{bc}^m = \xi_{bc} + \rho \cos(qnc + \tau), \quad (7b)
\]

where $\delta$ and $\rho$ may depend on the modulation amplitude, whereas the internal dipole spring constant $\alpha$ is considered as left unperturbed by the modulation. The equations of motion result in an infinite set of coupled Fourier components $u_{ij}^{x}$ of Eq. (6b) with a parametric dependence on the variable $\tau$ which describes the dependency on the internal di-pelecatic}

FIG. 1. Part of the structure of Rb$_2$ZnBr$_4$ consisting of chains of Rb and ZnBr$_4$ ions (below) and the schematic picture of our dipole model for a chain along the $b$ axis; the different spring constants are as explained in the text.
mension. Taking only one component labeled by \( v \) and neglecting coupling with \( v' \neq v \) we get the following results for the square of the eigenfrequencies \( (k_x=k_y=0) \):

\[
\omega_{2o}^2 = \omega_0^2 - \frac{8 \xi}{m_0+m_1} \sin^2 \left( \frac{vq + k_z}{2} \right) c + \cdots ,
\]

\[
\omega_{2o}^2 = \frac{8 \xi}{m_0+m_1} \sin^2 \left( \frac{vq + k_z}{2} \right) c + \cdots \tag{8a}
\]

for the optical and acoustical branches, respectively, with \( \omega_0 \) the normal optical frequency and where the ellipses represent higher-order terms in \( \xi/\omega_0^2 \). In the \( N \) phase the term with \( v=0 \) is not coupled to the others (no modulation) and at \( k_z=0 \) we have the ordinary optical (\( \omega_0 \)) and acoustical (\( \omega_a=0 \)) solutions; in the \( I \) phase new modes are expected because of the presence of \( v \neq 0 \) terms, consistent with the selection rules as derived above.

This zeroth-order approximation shows the predicted activation of new modes but by neglecting any coupling, the effects of the temperature-dependent spring constants \( \delta \) and \( \rho \) have been dropped out. In the next degree of approximation we consider the modes \( v \) and \( v \pm 1 \) as decoupled from the remaining ones, and take \( v=0 \), yielding

\[
\omega_{2o}^2 = \omega_0^2 + \rho^2 X , \tag{9a}
\]

\[
\omega_{2o}^2 = 0 , \tag{9b}
\]

\[
\omega_{2o}^2(v= \pm 1) = \omega_0^2 - \frac{8 \xi}{m_0+m_1} \sin^2 \left( \frac{qc}{2} \right) + \cdots , \tag{9c}
\]

\[
\omega_{2o}^2(v= \pm 1) = \frac{8 \xi}{m_0+m_1} \sin^2 \left( \frac{qc}{2} \right) + \cdots \tag{9d}
\]

where \( X \) is a positive number depending on the masses and spring constants. In this order, this gives the following interesting result: The original \( v=0 \) mode is perturbed through \( \rho^2 \), but the new modes remain unaffected. Where the above derivation holds for the chains along the \( a \) and \( b \) direction, a similar result is obtained for the \( c \) direction where now \( \omega_c^2 \) is perturbed by \( \delta ^2 \) only.

C. The internal modes in the \( I \) phase

The effect of the modulation on the internal \( \text{ZnBr}_4 \) modes can be derived in a similar way. As a model we assume the crystal to be made from chains of tetrahedra and represent each tetrahedron by a sphere of mass \( m_1 (\equiv 4 \text{ m}_{\text{Br}}) \), containing a particle of mass \( m_0 (\equiv 4 \text{ m}_{\text{Zn}}) \), connected by a spring constant \( \alpha \). In the chain we consider two kinds of nearest-neighbor interactions: one between inside and outside and one between outside particles of different spheres, represented by the spring constants \( \beta \) and \( \gamma \), respectively. The coupling between neighboring chains is represented by a spring constant \( \xi_{ij} \) where \( i \) denotes the direction of the chain and \( j \) that of the coupling (see Fig. 2). Again, we take modulated spring constants for the nearest-neighbor interactions along the \( c \) axis:

\[
\beta_c = \beta_c + \delta \cos(nqc + \tau) , \tag{10a}
\]

\[
\gamma_c = \gamma_c + \epsilon \cos(nqc + \tau) , \tag{10b}
\]

\[
\xi_{ic} = \xi_{ic} + \rho \cos(nqc + \tau) , \tag{10c}
\]

where \( \delta \), \( \epsilon \), and \( \rho \) may depend on the modulation amplitude, and where \( \tau \) is the internal coordinate (the index \( i \) stands for \( a \) or \( b \)). For the corresponding displacement field \( \vec{u}_i \) (\( j=0 \) or \( 1 \)) we look for “normal mode” solutions of the form of Eq. (6). In zeroth order (taking only one component \( \vec{u}^c \) into account) we get, apart from the acoustical modes, the following solutions:

\[
\omega_i^2 = \omega_0^2 + \frac{4 \xi_{ic}}{m_1} \sin^2 \left( \frac{vqc}{2} \right) + \cdots \tag{11a}
\]

\[
\omega_c^2 = \omega_0^2 + \frac{4 \gamma_c}{m_1} \sin^2 \left( \frac{vqc}{2} \right) + \cdots , \tag{11b}
\]

with \( \omega_o = (\alpha + 2 \beta_i)/\mu \) and \( \mu = m_1 m_0/(m_1 + m_0) \), and where the ellipses represent higher-order terms in \( \xi_{ic}/\omega_0^2 \) and \( \gamma_c/\omega_0^2 \), respectively. In the \( N \) phase only the term \( v=0 \) is relevant (no modulation), and we have three optical modes with different frequencies depending on \( \beta_i \); in the \( I \) phase new modes are expected because of the presence of

FIG. 2. Schematic picture of our tetrahedron model for a chain along the \( a \) axis; the different spring constants are as explained in the text.
\( v \neq 0 \) terms, consistent with the derived selection rules and the results for the lattice modes. However, in the next approximation (taking the coupling of \( v \) and \( v \pm 1 \) into account) an asymmetry manifests itself for the \( a \) and \( b \) direction on one side, and the \( c \) direction on the other. The results are as follows. For \( v = 0 \):

\[
\omega_{c}^{2} = \frac{\alpha_{c} + 2\beta_{c}}{\mu} + 4\gamma_{c} \sin^{2} \left( \frac{q_{c}}{2} \right) + \rho^{2} X,
\]

(12a)

\[
\omega_{a}^{2} = \frac{\alpha_{a} + 2\beta_{a}}{\mu} + e^{2}X.
\]

(12b)

For \( v = \pm 1 \):

\[
\omega_{a}^{2} = \frac{\alpha_{a} + 2\beta_{a}}{\mu} + \frac{4\gamma_{c}}{m_{1}} \sin^{2} \left( \frac{q_{c}}{2} \right) + \rho^{2} Y,
\]

(12c)

\[
\omega_{c}^{2} = \frac{\alpha_{c} + 2\beta_{c}}{\mu} + \frac{4\gamma_{c}}{m_{1}} \sin^{2} \left( \frac{q_{c}}{2} \right),
\]

(12d)

where \( X \) and \( Y \) depend on \( m_{0}, m_{1} \), and on the spring constants. Again, to this order, this gives the following interesting result: For the \( a \) and \( b \) direction the original \( v = 0 \) mode remains unaffected and the new \( v = \pm 1 \) mode is perturbed via \( \rho^{2} \); The opposite happens for the \( c \) direction, where the \( v = 0 \) mode is perturbed and the new one not.

**D. The dielectric response in the \( I \) phase**

In order to describe the behavior of a dielectric medium under the influence of an electric field we must take into account the polarization giving rise to an effective local field inside the crystal. The relation between this local field and the external applied field is generally given by a tensor and will depend on the lattice symmetry. In addition, in incommensurate crystals one should also consider the implications of the modulation on the local electrical field \( E_{1} \). In Appendix B this is done for our harmonic oscillator model yielding a Fourier decomposition of \( E_{1} \) with respect to the internal coordinate \( \tau \):

\[
E_{1} = \sum_{\nu} E^{v} e^{i
\nu \tau}, \quad \nu \in Z.
\]

(13)

The resulting coupling of \( \nu \) with \( \nu' \neq \nu \) terms can be interpreted as the appearance of an effective field \( E' \):

\[
E' = (1 - \rho^{2} F) E,
\]

(14)

where \( E \) is the external applied field and \( F \) is a frequency-dependent function having a resonance near \( \omega_{0}(v \pm 1) \) (see Fig. 3). Consequently the dielectric response function will not only show resonances near \( \omega_{0}(v) \) but also near \( \omega_{0}(v \pm 1) \). These two resonances are mutually coupled; therefore the changes in \( \omega_{0}(v \pm 1) \) can be observed indirectly at \( \omega_{0}(v) \). This is consistent with the basic fact that in incommensurate crystals, the "normal modes" are not decoupled even without anharmonicity.

**V. EXPERIMENTAL RESULTS IN THE \( N \) AND \( I \) PHASE**

**A. \( N \) phase spectra**

Raman-scattering experiments were done principally in the \( c(bb)a \) geometry, i.e., the \( A_{g} \) modes were studied referred to the point-group symmetry \( mmm \), and FIR transmission experiments were performed on thin plates cut perpendicular to the \( a \) and \( c \) axes. In Fig. 4 the temperature dependence of the observed \( A_{g} \) Raman lines is plotted, together with two of the most interesting \( B_{1g} \) modes. From Table I we see that one expects 13 \( A_{g} \) modes of which all six internal modes and four lattice modes could be distinguished (see also Table II). Figure 5 shows the FIR transmission along the \( a \) and \( c \) axes.
The crystals appear to be practically opaque below 300 cm\(^{-1}\) except at the low-frequency end (below 15 and 30 cm\(^{-1}\)) and a small region around 150 cm\(^{-1}\). Above 300 cm\(^{-1}\) the crystals become transparent with still a double absorption band with minima at 405 and 426 cm\(^{-1}\) for the \(a\) and at 390 and 425 cm\(^{-1}\) for the \(c\) direction, respectively. This is the typical picture of a harmonic oscillator system, with zero transmission between the transverse- and longitudinal-optical modes. In Rb\(_2\)ZnBr\(_4\) the softest direction is along the \(b\) axis (see elastic constants of Ref. 14), and from Table I we see that in the \(N\) phase two \(b\) polarized infrared-active \(B_{2g}\) modes are expected. Neutron scattering experiments yielded one branch at 31 cm\(^{-1}\) of this polarization.\(^5\) Because of the fact that this branch did not show any softening as should be expected and also is observed in isomorphous structures,\(^19\) there must be an even lower branch present here. From our low-temperature measurements it follows that this branch is situated around 22 cm\(^{-1}\) (at least for \(k=0\)). An estimate for the longitudinal frequencies can be made from the Lyddane-Sachs-Teller relation \(\omega_L/\omega_T = \sqrt{\epsilon_p/\epsilon_m}\), yielding \(\omega_L \approx 52\) cm\(^{-1}\) for the 31-cm\(^{-1}\) mode. From Table II it also follows that all the internal tetrahedron modes are infrared active. Because in Rb\(_2\)ZnBr\(_4\) these internal modes have relatively low frequencies (see Table II), there

---

**TABLE II.** Classification and assignment of ZnBr\(_4\) internal modes in the \(N\) phase of Rb\(_2\)ZnBr\(_4\).

<table>
<thead>
<tr>
<th>Mode</th>
<th>Molecular frequency (cm(^{-1}))</th>
<th>Molecular symmetry</th>
<th>Site symmetry</th>
<th>Crystal symmetry</th>
<th>Observed (A_g) modes (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\nu_1)</td>
<td>172</td>
<td>(T_d)</td>
<td>(C_t)</td>
<td>(A_g + B_{3g} + B_{1u} + B_{3u})</td>
<td>182</td>
</tr>
<tr>
<td>(\nu_2)</td>
<td>63</td>
<td>(E)</td>
<td>(A' + A'')</td>
<td>(A_g + B_{4g} + B_{3g} + B_{3u} + A_u)</td>
<td>78</td>
</tr>
<tr>
<td>(\nu_3)</td>
<td>210</td>
<td>(F_2)</td>
<td>(2A' + A'')</td>
<td>(2A_g + B_{4g} + 2B_{3g} + 2B_{3u} + A_u + 2B_{1u} + B_{2u} + 2B_{3u})</td>
<td>203 226</td>
</tr>
<tr>
<td>(\nu_4)</td>
<td>82</td>
<td>(F_2)</td>
<td>(2A' + A'')</td>
<td>(2A_g + B_{4g} + 2B_{3g} + 2B_{3u} + A_u + 2B_{1u} + B_{2u} + 2B_{3u})</td>
<td>90 100</td>
</tr>
</tbody>
</table>
is only a small region of nonzero transmission around 150 cm$^{-1}$, i.e., the frequency region between $v_2$ and $v_4$ internal modes at one side, and the $v_1$ and $v_3$ modes at the other side. (Note that the usual $v_1$ notation is used to indicate molecular vibration modes, not to be confused with our $v$ label of the superspace.) The absorption bands at higher frequencies belong probably to librational modes of the tetrahedra.

B. Soft mode

The transition from the $N$ to the $I$ phase is thought to be driven by a soft optical mode at $k = \mathbf{q}$ which is neither FIR nor Raman active. We have shown previously that this soft mode can yet be observed in a FIR transmission experiment by making use of the coupling between $k = 0$ and $k = \mathbf{q}$ modes$^{20}$ (see Fig. 6). This can also be understood from our analysis in Sec. IV, which within our approximations also applies to commensurate modulated phases. Below $T_I$ this soft mode gives rise to two new types of modes, the so-called amplitudon and phason modes, originating from fluctuations of the amplitude and phase of the modulation, respectively. The amplitudon mode behaves as a normal soft mode. In Fig. 4 a temperature-dependent mode of the required polarization is observed in the Raman spectrum around 15 cm$^{-1}$ in the $I$ phase; however, due to the crossing with a mode at around 13 cm$^{-1}$ and the weakness of the signal on approaching $T_I$, it was not possible to measure its exact temperature dependence unambiguously. This same problem was also reported by Takashige et al.$^{21}$ and is contrary to that observed for $K_2SeO_4$, where the amplitudon mode strength increases on approaching $T_I$. The phason mode has probably zero frequency in the whole $I$ phase and can only be seen from a broadening of the Rayleigh peak in the Raman spectra, as is indeed observed near the lock-in transition in $K_2SeO_4$. Unfortunately, this was not possible in our present Raman experiments.

C. New activated Raman modes in the $I$ phase

In Fig. 4 the following three new modes can be seen from the Raman experiments: (1) at 206 cm$^{-1}$, (2) at 83 cm$^{-1}$, and (3) a very weak one at 44 cm$^{-1}$ (see also Fig. 7). In addition, a number of modes [(1) and (2) as well as the mode at 226 cm$^{-1}$] increases in frequency with decreasing temperature. These results are in agreement with the predicted selection rules and the analysis given in terms of our model in Sec. IV. The two modes at 203 and 226 cm$^{-1}$ in the $N$ phase originate from the internal $v_3$ tetrahedron mode, which is a three-fold degenerate mode for a free ZnBr$_4$ ion, with all Br ions moving in phase against the Zn ion with a frequency of 210 cm$^{-1}$. This mode can be analyzed with our harmonic oscillator model: Placed in the crystal the degeneracy ($\alpha$ uniform) will be removed by the anisotropic coupling constant $\beta$, $\omega_1^2 = (\alpha + 2\beta)/\mu$. In the $A_g$ representation only $\omega_a$ and $\omega_c$ can be observed. Regarding the mutual distances of the tetrahedra along both directions and the elastic constants$^{14}$ it follows that $\beta_c > \beta_a$ so that $\omega_c > \omega_a$. Therefore the three highest frequency modes in the $I$ phase can be assigned as $\omega_c(v=0) = 226$ cm$^{-1}$, $\omega_a(v=\pm 1) = 206$ cm$^{-1}$ (Fig. 4) and $\omega_a(v=0) = 203$ cm$^{-1}$.
FIG. 7. Part of the $A_g$ Raman spectra of Rb$_2$ZnBr$_4$ at temperatures above (369 K) and below (322 and 285 K) $T_J$, showing activation of new mode (1). From Fig. 4 we see that the first two, i.e., the $c$ polarized $v=0$ mode and the $a$ polarized $v=\pm 1$ mode both shift as a function of temperature, in agreement with the conclusions of Eq. (12). The $B_{1g}$ mode at 80 cm$^{-1}$ is presumably a $\nu_2$ internal mode so that the new one at 83 cm$^{-1}$ will be a $\nu_2 (v=\pm 1)$ mode. Again in qualitative agreement with Eq. (12), the latter also increases in frequency with decreasing temperature. The mode at 44 cm$^{-1}$ might be a $v=\pm 1$ lattice mode. The observed temperature dependences entering through the modulation-dependent spring constants [8, $\epsilon$, and $\rho$; see Eqs. (7) and (10)] reflect the change of the modulation amplitude, because in Rb$_2$ZnBr$_4$ the temperature dependence of the modulation wave vector $\vec{q}$ is negligible.\textsuperscript{5} If the observed shift of the $\omega_a (v=\pm 1)$ mode is described phenomenologically by

$$\omega_a (v=\pm 1) = \omega_a [1 + \alpha (T - T_1)]^\beta,$$

one gets as fitting parameters $\alpha=5.2 \times 10^{-3}$ and $\beta=0.37\pm 0.03$, for $\omega_a = \omega_a (T = T_1) = 206$ cm$^{-1}$, which is in excellent agreement with recent NMR experiments\textsuperscript{25} yielding for the modulation amplitude $u = u_a (T_1 - T)^\beta$ with $\beta=0.35$. The fact that the modulation has the biggest effect on the internal modes is consistent with recent x-ray studies\textsuperscript{26} showing that the modulation mainly consists of large rotations of the ZnBr$_4$ tetrahedra.

FIG. 8. Low-frequency part of the FIR transmission showing the activation of the original acoustic frequencies in the optical spectra. In the spectra measured along the $c$ axis, the resonance at 11 cm$^{-1}$ in the $N$ phase, splits up in two below $T_J$. At the inset in the right top corner the dispersion curves are shown as measured by de Pater et al.\textsuperscript{5}

D. New activated FIR modes in $I$ phase

In Fig. 8 details of the low-frequency part of the FIR transmission spectra are plotted, showing the activation of $v=\pm 1$ acoustical modes around 12 cm$^{-1}$ in accordance with the conclusions of Sec. IV, Eqs. (9) and (14). As expected, the observed effect is small because the polarization vectors are still mainly acousticalike, despite the mixing with $K=0$ modes. The frequencies are in good agreement with the neutron experiments of de Pater et al.\textsuperscript{5} (shown in the inset) and from those we can conclude that the lowest mode originates from the $a$ polarized transversal mode ($T_a$) and the other from the $b$ polarized transversal mode ($T_b$). Possible effects at higher frequencies could not be observed because there the FIR transmission is already zero so that additional absorption cannot be seen.

VI. EXPERIMENTAL RESULTS IN THE COMMENSURATE PHASES

A. The lock-in transition

The transition from the $I$ to the $C$ phase at $T_c=200$ K does not cause drastic changes in the
optical spectra. All the temperature-dependent modes, including the soft-amplitudon mode, go continuously through this transition point with the exception of the $B_{1g} (v = \pm 1)$ mode around 83 cm$^{-1}$ (see Fig. 4). The latter increases linearly with decreasing temperature, but with a discontinuous change of the slope at $T_c$: 0.03 cm$^{-1}$/K above and 0.05 cm$^{-1}$/K below $T_c$. This temperature dependence resembles that of a phason-like excitation; in the same geometry Inoue et al. observed the soft phason in K$_2$SeO$_4$. However, we were unable to see this soft mode.

The smoothness at this lock-in transition shows that despite the first-order character of this transition, several quantities change continuously at $T_c$. This is in agreement with the experimentally confirmed soliton model in which the transition is seen as a growth of commensurate domains at the expense of the incommensurate boundaries.

The fact that the selection rules do not change at $T_c$ might indicate that in this respect the commensurability of the modulation is not a fundamental property, and that the superspace approach can also be used in the C phase. This means that, though not strictly necessary there, the superspace approach can also be a helpful tool to analyze commensurate structures as well, as it might contain more structural information than the ordinary space group of the same crystal (see, for example, Refs. 9 and 11).

B. Second commensurate transition

Recently there have been indications for a new phase transition in Rb$_2$ZnBr$_4$ at $T_0 = 113$ K. In Fig. 9, parts of the Raman spectra are plotted showing the appearance of new modes below $T_0$ at 60, 80, and 90 cm$^{-1}$. In Fig. 10 the temperature dependence of the activated $v = \pm 1$ acoustical modes in the FIR spectra along the $c$ axis is plotted, showing a minimum of the lowest mode at $T = T_0$ whereas the two $v = \pm 1$ modes coincide at lower temperatures. These results indicate a phase transition driven by a $k \neq 0$ soft mode: In the C phase all $k = 0$ optical modes are Raman as well as FIR active, but no soft mode was found here in either of the spectra. Besides, all representations are one-dimensional in this orthorhombic phase so that a mode splitting due to the removal of degeneration is not possible. Supplementary dielectric constant measurements have shown that the peak in $\varepsilon(0)$ only occurs in the $a$ direction. Therefore we conclude that these effects are probably caused by a mode softening at the Brillouin-zone boundary of an $a$ polarized optical mode. This is also confirmed by Raman experiments at low temperatures of Francke et al. indicating a mode softening but only far below $T_0$. However, their extrapolation to $T_0 = 140$ K seems to be too high. Because the experimental results indicate a second-order character (see Fig. 9 and Ref. 30), we propose a possible
transition to a phase with space group $P\bar{1}$, though there are no structural data present to confirm this hypothesis.

C. Third commensurate transition

Previously we have reported a new phase transition around 50 K accompanied by a change of the FIR selection rules. This was further supported by dielectric constant measurements showing a peak along the $a$ axis from which it was concluded that the transition takes place at 56 K. Additional $\varepsilon(0)$ measurements show also a peak in the $c$ direction. A careful study of the low-frequency part of the FIR transmission spectra gave the following result: At 22 cm$^{-1}$ there is a very strong optical mode which strongly broadens with increasing temperature with a discontinuous change at 56 K (see Fig. 11). This mode is strongly active in the spectra measured along the $c$ axis but weaker in those along the $a$ axis. Therefore we conclude that this mode has a polarization in the $a,b$ plane. Comparing these FIR data with the temperature dependence of the Raman lines in Fig. 4, it appears that an extrapolation of the linear shift of the amplitudon mode exactly coincides with this strongly temperature-dependent FIR active mode. This mode at 22 cm$^{-1}$ can thus be assigned to the amplitudon mode, and consequently this low-temperature phase seems to be directly coupled to the modulation wave. Because

the latter consists of large rotations of the ZnBr$_4$ tetrahedra, this will also cause displacements in the $a$ direction.

VII. SUMMARY

In this paper we have studied the specific features of the optical spectra of an incommensurate crystal, using Rb$_2$ZnBr$_4$ as an example. The Raman and FIR selection rules for the $I$ phase are derived from the superspace group symmetry and the predicted activation of new modes is experimentally confirmed. The physical origin of these new modes as well as their temperature dependence can be explained with a simple harmonic oscillator model using modulated spring constants and superspace symmetry adapted normal modes. The dielectric response of such a system is also derived and is in agreement with the experiments. The change from an incommensurate to a commensurate modulation does not seem to have much effect on the vibration modes. At lower temperatures there appear to be two more phase transitions of which the lowest at 56 K can be related to the amplitudon mode.

APPENDIX A: HARMONIC OSCILLATOR MODEL FOR AN INCOMMENSURATE CRYSTAL

We consider the crystal as being built up of chains of dipoles represented by a particle of mass $m_0$ and one of mass $m_1$, connected by a spring constant $\alpha$ and mutually coupled via the spring constants $\beta^m$ in the chain and $\xi_{ij}$ between the chains, where $i$ labels the chain in consideration and $j$ denotes the direction of the coupling (see Fig. 1). We must distinguish chains parallel and perpendicular to the modulation wave vector $\mathbf{q} / / \mathbf{c}^*$, and assume modulated spring constants along the $c$ direction:

$$\beta^c = \beta_0 + \delta \cos(qnc + \tau),$$

$$\xi_{c} = \xi_0 + \rho \cos(qnc + \tau),$$

where $\rho$ and $\delta$ may depend on the displacive modulation amplitude and thus are temperature dependent, and $\tau$ is the internal coordinate. The dipoles are labeled with $m$ and $n$, where $m$ is the running index for the $a$ or $b$ and $n$ for the $c$ axis. The equations of motion for the displacements $u_i^{nm}$ then become for $i=a$ or $b$.
whereas for the c direction $\xi_{ic}$ becomes $\xi_{al}$. To solve these equations we look for "normal mode" solutions of the form of Eq. (6). Substitution in Eq. (A2) and taking terms with the same factor $e^{ivv}$ yields the following infinite set of coupled equations:

\[
\begin{align*}
A_vu^{v-1} + D_vu^v + B_vu^{v+1} &= 0, \quad v \in \mathbb{Z}, \quad (A3)
\end{align*}
\]

where $u$ stands for

\[
\begin{bmatrix}
\bar{u}_0 \\
\bar{u}_1 \\
\end{bmatrix}.
\]

In the following we will only consider the $a$ direction (and drop the index $i$ for convenience), giving the results of the $b$ and $c$ chains which are derived in a similar way at the end. Setting $k_x = k_y = 0$ for the optical modes, the matrices $A, D, and B$ are given by

\[
\begin{align*}
A_v &= \frac{\mu}{2} \begin{bmatrix}
1 + e^{iqc} & -f(v + 1) \\
-f(v + 1) & 1 + e^{-iqc}
\end{bmatrix}, \\
D_v &= \begin{bmatrix}
 a - m_0 \omega^2 & -a + 4\xi \sin^2 \left( \frac{(k_x + v QC) c}{2} \right) \\
-a + 4\xi \sin^2 \left( \frac{(k_x + v QC) c}{2} \right) & a - m_1 \omega^2
\end{bmatrix}, \\
B_v &= \frac{\rho}{2} \begin{bmatrix}
1 + e^{iqc} & -f(v - 1) \\
-f(v - 1) & 1 + e^{-iqc}
\end{bmatrix},
\end{align*}
\]

where $a = \alpha + \beta + 2\xi$ and

\[
f(v \pm 1) = e^{-i \theta (v \pm 1) + k_x c} + e^{i \theta (v \pm 1) + k_x c}.
\]

In zeroth order we consider only one Fourier component labeled by $v$ and neglect coupling with other components $v' \neq v$, i.e., we take $A_v = B_v = 0$. The eigenfrequencies are calculated from $\det |D_v| = 0$ yielding

\[
\begin{align*}
\omega^2_0 &= \frac{a}{\mu} - \frac{8\xi}{m_0 + m_1} \sin^2 \left( \frac{(v QC + k_x) c}{2} \right) + \cdots, \\
\omega^2_0 &= \frac{8\xi}{m_0 + m_1} \sin^2 \left( \frac{(v QC + k_x) c}{2} \right) + \cdots, \quad (A5a, A5b)
\end{align*}
\]

for the optical and acoustical branches, respectively, with $\mu = m_0 m_1 / (m_0 + m_1)$ and where the ellipses represent higher-order terms in $\xi / (a / \mu)$.

In the $N$ phase the ordinary solutions for $k_x = 0$ are given by the term $v = 0$ and we have

\[
\begin{align*}
\omega^2_0 &= \frac{a}{\mu}, \\
\omega^2_0 &= 0. \quad (A6a, A6b)
\end{align*}
\]

In the $I$ phase new modes are expected because of the presence of $\nu \neq 0$ terms, consistent with the selection rules as derived above. For $v = \pm 1$ they are

\[
\begin{align*}
\omega^2_0(v = \pm 1) &= \frac{a}{\mu} - \frac{8\xi}{m_0 m_1} \sin^2 \left( \frac{QC}{2} \right), \\
\omega^2_0(v = \pm 1) &= \frac{8\xi}{m_0 + m_1} \sin^2 \left( \frac{QC}{2} \right). \quad (A6c, A6d)
\end{align*}
\]

This zeroth-order approximation shows the predicted activation of new modes, but by neglecting any coupling the effects of the temperature-dependent modulation constants $\delta$ and $\rho$ have been dropped. In the next approximation we consider the set of three modes $v$ and $v \pm 1$ as decoupled from the remaining ones. The determinantal equa-
tion yielding the eigenfrequencies now gets the form

$$\Delta = \begin{vmatrix} D_{v-1} & B_{v-1} & 0 \\ A_v & D_v & B_v \\ 0 & A_{v+1} & D_{v+1} \end{vmatrix} = 0,$$

(A7a)

which can be written as

$$\Delta = \Delta_{v-1} \Delta_{v}^{(1)} \Delta_{v+1}^{(1)} = 0,$$

(A7b)

where

$$\Delta = \Delta_{-1} \left[ \Delta_{0} \Delta_{-1} - \rho^{2} \omega^{2} \begin{vmatrix} \frac{qc}{2} (m_{1} + m_{0}) \left( \frac{m_{1} + m_{0}}{m_{1}} \right) \omega^{2} - \xi_{ee}^{2} \sin^{2} \left( \frac{qc}{2} \right) \right. \right] \right].$$

(A8)

Because

$$\Delta_{0} = \omega^{2} \left[ m_{2} + m_{0} \omega^{2} - \left( \alpha + \beta + 2 \xi \right) \left( m_{1} + m_{0} \right) \right],$$

the term $\omega^{2}$ can also be taken out of the term in large bold parentheses, leading finally to the following result.

(a) For $\rho = 0$ we get the solutions obtained from the unperturbed determinants $\Delta_{0}$ and $\Delta_{-1}$ (= $\Delta_{1}$) as in Eq. (A6).

(b) For $\rho \neq 0$ we see that $\Delta_{1} = 0$ and $\omega^{2} = 0$ remain good solutions for the first-order perturbation and that only the original $v = 0$ optical mode is perturbed. The latter can be calculated leading to

$$\omega_{0}^{2}(T) = \omega_{0}^{2}(T_{f}) + \rho^{2}X,$$

(A9)

where $\omega_{0}(T_{f})$ is the value at the transition temperature $T_{f}$, and $X$ is a positive number depending on $m_{10}$, $m_{1}$, and $\alpha$. From Eq. (A9) we see that in the $I$ phase $\omega_{0}^{2}$ becomes temperature dependent via $\rho^{2}$, causing a positive shift in frequency.

The solutions for the $b$ direction are exactly the same while those for the $c$ direction are as follows. For $v = 0$,

$$\omega_{0}^{2} = \frac{a}{\mu} + \delta^{2}Y,$$

(A10a)

$$\omega_{0}^{2} = 0.$$  

(A10b)

For $v = \pm 1$,

$$\omega_{0}^{2}(v \pm 1) = \frac{a}{\mu} - \frac{4\beta(\alpha + 2\xi)\sin^{2}(qc/2)}{(m_{0} + m_{1})(\alpha + 2\xi + \beta)},$$

(A10c)

$$D_{v}^{(1)} = D_{v} - A_{v}D_{v-1}B_{v-1},$$

(A10d)

$$A_{v}^{(1)} = A_{v},$$

(A10e)

$$B_{v}^{(1)} = B_{v},$$

$$(\alpha, \beta, \xi)$$

etc. As discussed above in the present case $v = 0$ and $v = \pm 1$ are the relevant ones. After some algebra, $\Delta$ appears to factorize in the following way:

Because

$$\Delta_{0} = \omega^{2} \left[ m_{2} + m_{0} \omega^{2} - \left( \alpha + \beta + 2 \xi \right) \left( m_{1} + m_{0} \right) \right],$$

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(A10b)

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$$\omega_{0}^{2}(v \pm 1) = \frac{a}{\mu} - \frac{4\beta(\alpha + 2\xi)\sin^{2}(qc/2)}{(m_{0} + m_{1})(\alpha + 2\xi + \beta)},$$

(A10c)

$$D_{v}^{(1)} = D_{v} - A_{v}D_{v-1}B_{v-1},$$

(A10d)

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$$\omega_{0}^{2}(v \pm 1) = \frac{a}{\mu} - \frac{4\beta(\alpha + 2\xi)\sin^{2}(qc/2)}{(m_{0} + m_{1})(\alpha + 2\xi + \beta)},$$

(A10c)
for $i=c$

$$\omega_c^2 = \frac{\alpha_c + 2\beta_c}{\mu} + \frac{4\gamma_c}{m_1} \sin^2 \left( \frac{qc}{2} \right) + \cdots.$$  \hfill (A12b)

where the ellipses represent higher-order terms in $\xi_c/\omega_c^2(v=0)$ and $\gamma_c/\omega_i^2(v=0)$, respectively. As for the lattice modes, we see that in the $I$ phase for $v\neq 0$ new modes can become active in the optical spectrum. However, in the next approximation, taking the coupling of $v$ and $v \pm 1$ into account, an asymmetry shows up for the $a$ and $b$ direction on one side and the $c$ direction on the other side. Calculating the matrices $A_v$ and $B_v$, it appears that for $i=a$ and $b$,

$$A_0 = A_1 = B_{-1} = B_0 = 0.$$  \hfill (A13)

This implies that the first-order perturbation will not affect $\omega_i(v=0)$ but only $\omega_i(v=\pm 1)$, whereas for the $c$ direction the $v=0$ mode is perturbed. The determinantal equations get the form: For $a,b$:

$$\Delta_0^a \Delta_1^a = \Delta_0^b \Delta_1^b - \rho^2 X,$$  \hfill (A14a)

for $c$:

$$\Delta_{-1} \Delta_1^c = \Delta_{-1} \Delta_1^c - e^2 Y,$$  \hfill (A14b)

where $X$ and $Y$ are functions of the force constants and masses. This means that for the internal modes we have the following results:

(a) For $\rho = \epsilon = 0$ we have the unperturbed determinants $\Delta_0$ and $\Delta_1$ giving the solutions of Eqs. (A12a).

(b) For $\rho \neq 0$, $\epsilon \neq 0$ we see that for the $a, b$ direction $\Delta_0=0$ remains and that the $v=\pm 1$ mode is unaffected and the original $v=0$ mode gets perturbed. From Eqs. (A14a) we can deduce: For $v=0$,

$$\omega_a^2 = \frac{\alpha_a + 2\beta_a}{\mu},$$  \hfill (A15a)

$$\omega_b^2 = \frac{\alpha_b + 2\beta_b}{\mu} + e^2 X';$$  \hfill (A15b)

for $v=\pm 1$,

$$\omega_a^2 = \frac{\alpha_a + 2\beta_a}{\mu} + \frac{4\xi_a}{m_1} \sin^2 \left( \frac{qc}{2} \right) + \rho^2 X',$$  \hfill (A15c)

$$\omega_b^2 = \frac{\alpha_b + 2\beta_b}{\mu} + \frac{4\gamma_b}{m_1} \sin^2 \left( \frac{qc}{2} \right).$$  \hfill (A15d)

APPENDIX B: DIELECTRIC RESPONSE OF AN INCOMMENSURATE CRYSTAL

To study the optical properties of our incommensurate system we must consider the response to the ac electric field associated with the electromagnetic radiation. In the long-wavelength approximation, we now must include charges $z$ and $z_1 = -z$ on the ions in our model resulting in a term $\pm z E_i$ on the right-hand side of the equations of motion. $E_i$ is the local electric field acting on the ion, and depends on the applied external field and the internal dipole field. We will ignore the atomic polarization and only consider the dipole moment due to the displacement of the charged ions by the electric field. The resulting electric dipole field is given by

$$\vec{E}_p(\vec{n}) = \frac{z}{c^2} \sum_{\vec{n} \neq \vec{n}^0} \frac{\vec{u} - \vec{u}^0}{|\vec{n} - \vec{n}^0|^3},$$  \hfill (B1)

where $\vec{z}$ is $2z$ or $-z$ for the longitudinal or transversal modes, respectively, and $c$ the lattice constant along the $c$ chain. To calculate the lattice summation of Eq. (B1) we must insert the displacement field of the modulated crystal [Eq. (6)]. Doing this and making a Fourier decomposition with respect to $\tau$, one arrives at the following expressions for the local electric field $E_i$:

$$E_i = E_0 + \tilde{E}_p(n^0) = \sum_v \tilde{E}_v(n^0, \tau) e^{i\omega_\tau},$$  \hfill (B2a)

with for $v=0$

$$\tilde{E} = E_0 + z(\vec{u} - \vec{u}^0)e^{i(\vec{k} \cdot \vec{n})} S'(0 | \vec{k}^2, \vec{\tau})' (B2b)$$

and for $v\neq 0$

$$\tilde{E}_v = z(\vec{u} - \vec{u}^0)e^{i(\vec{k} \cdot \vec{q} + v^2 \tau)} S'(0 | \vec{k} + v\vec{q}, \vec{\tau})',$$  \hfill (B2c)

where $S'$ is the lattice sum

$$S'(\vec{R}, \vec{k}, m) = \sum_{\vec{n} \neq \vec{R}} \frac{e^{i(\vec{k} \cdot \vec{n})}}{|\vec{n} - \vec{R}|^{2m}}.$$  \hfill (B2d)

Putting this into the equations of motion [Eq. (8)] we now get the following infinite set of coupled equations: For $v=0$,

$$A_s u^{-1} + B_0 u^0 + B_0 u^1 = \left[ \begin{array}{c} -z \\ z \end{array} \right] E_0,$$  \hfill (B3a)
for $v\neq 0$,

$$A_v u^{v-1} + \tilde{D}_v u^{v} + B_v u^{v+1} = 0,$$  \hspace{1cm} (B3b)

where $\tilde{D}_0$ and $\tilde{D}_v$ now contain the local field term $S'$; they are the same as in Eq. (A4a) if one just replaces $a$ by $a + S'$. From Eq. (B3a) we see that only the $v=0$ term is directly driven by the frequency of the external field whereas the $v\neq 0$ terms require the frequencies of the modes, i.e., they are suppressed except for the resonances. We can make use of this fact to solve these inhomogeneous equations if we also assume that $\omega(v=0)\neq \omega(v=\pm 1)$, i.e., $\Delta_0 \neq \Delta_1$. In that case we can consider two regimes, one for $\omega \approx \omega_0$ [$= \omega_0(v=0)$] and one for $\omega \neq \omega_0$. As before we will consider $v=0$ and $v=\pm 1$. From Eq. (A4a) it follows that $B_1 = A_{-1} = 0$ so that in the regime $\Delta_0 \neq 0$ we can solve $u^1$ and $u^{-1}$ leading to the following set of equations:

$$-\tilde{D}_1^{(1)} u^1 + Cu^{-1} = Z,$$ \hspace{1cm} (B4a)

$$C u^1 - \tilde{D}_1^{(1)} u^{-1} = Z^*,$$ \hspace{1cm} (B4b)

where $C$ stands for $A_1 \tilde{D}_0^{-1} A_0$ and $Z$ for

$$A_1 \tilde{D}_0^{-1} \begin{pmatrix} -z \\ z \end{pmatrix} E.$$

Because $\tilde{D}_1^{(1)}$ is real, it follows that $u^1 u^* = u^{-1} u^*$. Because $C \ll \tilde{D}_1^{(1)}$ we will neglect this coupling term between $u^1$ and $u^{-1}$. In this way we get for $u^1$:

$$u_0^1 = -\frac{\alpha E}{\Delta_1^{(1)}/m_1 \omega^2},$$ \hspace{1cm} (B5a)

$$u_1^1 = \frac{\alpha E}{\Delta_1^{(1)}/m_0 \omega^2},$$ \hspace{1cm} (B5b)

with

$$\alpha = \frac{\delta(m_1 - m_0)(1 + e^{i\phi})}{2 \Delta_0/\omega^2}.$$

The tilde used with the determinants denotes that they contain the dipole term $S'$. Inserting Eq. (B5) into the inhomogeneous Eq. (B3a) yields

$$\tilde{D}_0 u^0 = (1 - \rho^2 F) \begin{pmatrix} -z \\ z \end{pmatrix} E,$$ \hspace{1cm} (B6a)

with

$$F = \frac{2 \cos^2(qc/2)(m_1^2 - m_0^2)}{(\Delta_0^2/\omega^2)(\Delta_1^{(1)}/\omega^2)}.$$ \hspace{1cm} (B6b)

For $\rho = 0$ (no coupling), this leads to the classical result:

$$u_0^0 = \frac{(z/m_0)}{\omega^2 - \omega_0^2} E, \hspace{1cm} u_1^0 = -\frac{(z/m_1)}{\omega^2 - \omega_0^2} E.$$ \hspace{1cm} (B7a)

For $\rho \neq 0$ the coupling can be understood as an effective field $E' = (1 - \rho^2 F)E$, which is no longer a constant for $k = 0$ but shows resonances near the frequency $\omega(v = \pm 1)$ (see Fig. 3). As a result, the dielectric response function $\chi \propto u/E$ will not only show resonances near $\omega_0$ but also near $\omega(v = \pm 1)$. In an analogous way the same procedure can now be repeated for $\omega(v + 1)$ to make the derivation self-consistent. The $\omega_0$ mode will then be affected by $\omega(v + 1)$ and the other way around. The interesting consequence of this mutual coupling is that changes in the mode $\omega(v \pm 1)$ can be observed indirectly at $\omega_0$. This is consistent with the basic fact that in incommensurate crystals the "normal modes" are not decoupled even without anharmonicity.

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