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EVIDENCE OF SUPERSPACE SELECTION RULES IN INCOMMENSURATE STRUCTURES

BY RAMAN SPECTROSCOPY ON Rb_2ZnBr_4

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(Received 18 November 1981 by A.R. Miedema)

Raman spectra of the modulated structure Rb_2ZnBr_4 show the appearance of new and temperature dependent modes in the incommensurate phase, in accordance with the predicted change in selection rules as derived from superspace symmetry. The results can be interpreted with the help of a harmonic oscillator model in which the superspace symmetry of the normal mode solutions is taken into account.

Since the discovery of the existence of solids with incommensurate structure (e.g. crystals with an arrangement of atoms where at least in one direction the translation symmetry of the crystal lattice is lost, therefore excluding any conventional space group symmetry), the rather fundamental problem has risen if and how the usual concepts of solid state physics intimately related to symmetry (like Brillouin zones, normal modes, crystal fields, selection rules etc.) can be generalized and how this will be manifested in the physical properties. This problem is particularly intriguing because of the widespread occurrence of incommensurate systems: ionic and molecular crystals, metals, semiconductors, superconductors, organic and magnetic systems, ferroelectrics etc., indicating that incommensurability is a very general phenomenon. Until now these problems have been discussed mainly in connection to X-ray or neutron-diffraction experiments^{1,2}, and to the morphology of incommensurate crystals³.

In this paper, we will show experimentally and theoretically how the Raman scattering, an other phenomenon closely related to the symmetry of the crystal involved, is influenced by the incommensurability. We will show that the mathematical method of the superspace symmetry gives the full and adequate machinery to calculate explicitly the selection rules for Raman and far-infrared spectroscopy on incommensurate structures. In addition we will illustrate how the underlying physical principles can be understood on the basis of a simple text-book spring model of an incommensurate crystal, in surprisingly excellent agreement with our experimental results.

As a specific example we have chosen Rb_2ZnBr_4 , known to have a normal (N-) phase above a temperature $T_I = 355$ K, and an incommensurate (I-) phase between T_I and $T_C = 200$ K⁴. Single crystals of Rb_2ZnBr_4 were grown by slow evaporation from an aqueous solution and transparent re-

gions were chosen for the experiment. The samples were placed in a flow cryostat and radiated with an Ar⁺ laser at 514.5 nm where after the scattered light was analysed with a double grating monochromator and a photoncounter in a conventional way. At the transition to the I-phase a change in the optical selection rules occurs (i.e. new Raman lines appear), despite the fact that the average structure of the crystal stays unchanged. Figure 1 shows the temperature dependence of the position of the Raman lines and a part of the spectra, showing the activation of the following new modes: at 206 cm⁻¹ (1), at 83 cm⁻¹ (2) and a very weak one at 44 cm⁻¹ (3). Besides that, a number of modes ((1) and (2) as well as the mode at 226 cm⁻¹) increases in frequency with decreasing temperature.

To analyze these results we first must identify the modes involved, taking into account that the crystal is characterized by a one dimensional displacive modulation with wavevector q along the c^* -axis (in the setting where the N-phase group is Pcmn). The symmetry adapted displacement field of such a crystal has the form:

$$\vec{u}_j^{m\ell n} = \vec{u}_j(qnc + \tau) e^{i(k_x ma + k_y \ell b + k_z nc)} \quad (1a)$$

with

$$\vec{u}_j(\tau) = \sum_{\nu} \vec{u}_j^{\nu} e^{i\nu\tau} \quad \nu \in Z \quad (1b)$$

This corresponds to a Bloch ansatz taking into account the superspace translation symmetry, which implies in particular the periodicity in the internal coordinate τ as expressed in Eq. (1b), which is based on the periodicity of the modulation wave². As has been shown by Janssen⁵ these modes can be characterized by irreducible

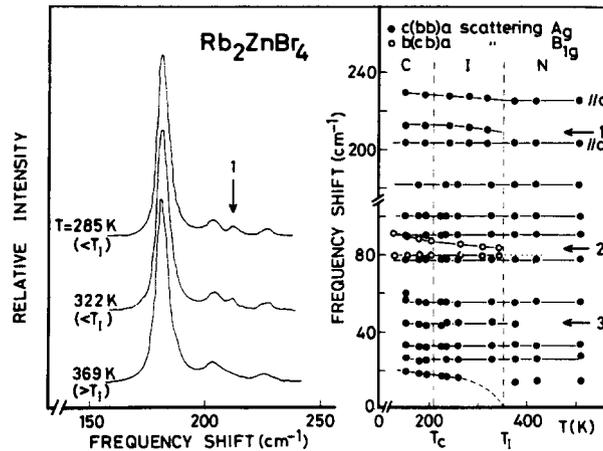


Fig. 1 : a) Part of the A_g Raman spectra of Rb_2ZnBr_4 at temperatures above (369) and below (322 and 285 K) T_I .

b) Frequency shift of observed Raman lines as a function of temperature for the $c(bb)a$ orientation and of two B_{1g} modes in the $b(cb)a$ orientation. The new activated modes in the I-phase are indicated by numbers. a and c denote the polarization of the two ν_3 modes.

representations of the superspace group. Because the latter is isomorphic with a 3-dimensional space group, all the necessary representations are known. The character of the representation is calculated with the help of formula 5.7 from ref. 5:

$$\chi(g_E, g_I) = \chi_{R_E} \cdot \sum_{b_1^*} \exp[i(\vec{k}-\vec{v}_q)\vec{u}_j - i\vec{v}_1^* \cdot \vec{v}_I] \quad (2)$$

$$R_I \vec{b}_1^* = \vec{b}_1^*$$

$$j, j' = j$$

Here (g_E, g_I) are elements of the superspace group, where g_E acts on the 3-dimensional "external" space and g_I on the 1-dimensional internal space. χ_{R_E} is the character of the point-group operation of the space group with elements g_E ; \vec{v}_I and R_I are the translation and the homogeneous part, respectively of $g_I = \{R_I | \vec{v}_I\}$, and \vec{b}_1^* is a unit vector of the internal reciprocal space.

The N-phase of Rb_2ZnBr_4 has spacegroup Pcmn (D_{2h}^{16}), $Z=4$ and the I-phase with $\vec{q} = 0.3c^*$, has presumably the superspace group $\text{Pcmn}_{ssl} 3,6$ which in the complete list of (3+1) dimensional superspace groups appears as 62.c.9.2⁷. The corresponding point groups are isomorphic with mmm and the character of the representation belonging to the modes $\vec{k} = 0, \nu \neq 0$ is $\chi(E, C_2^z, C_2^y, C_2^x, i, \sigma_z, \sigma_y, \sigma_x) = (72, 0, 0, 0, 0, 0, 24(-)^{\nu}, 0)$ for the translational and $(24, 0, 0, 0, 0, 8(-)^{\nu+1}, 0)$ for the librational modes, whereas χ for the $\vec{k} = 0, \nu = 0$ modes is the same as in the N-phase. Since to a good approximation the modulation can be assumed to be sinusoidal⁸, the main contribution will come from $\nu = 0$ and $\nu = \pm 1$. Table I gives

the factorgroup analysis of the normal modes in the N- and I-phase showing that the extra activated Raman lines are classified as $16 A_g + 26 B_{1g} + 16 B_{2g} + 26 B_{3g}$. The two modes at respectively 203 and 226 cm^{-1} in the N-phase originate from the internal ν_3 tetrahedron mode⁹, which in the crystal gives rise to two A_g modes, with eigenvectors along the a- and c-axis respectively. From Table I we see that in principle one may expect 2 extra ν_3 modes in the I-phase, of which one is observed at 206 cm^{-1} (1). The B_{1g} mode at 80 cm^{-1} probably originates from the internal ν_2 mode⁹ so that the new one at 83 cm^{-1} will be a $\nu_2(\nu = \pm 1)$ mode.

The effect of the modulation on the vibration spectrum and the temperature dependence of the latter can also be understood with the help of a simple harmonic oscillator model, with modulated spring constants. Here we will concentrate on the internal modes. The basic results, however, are more general and also confirmed experimentally as will be shown in a following paper¹⁰. 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 ($\cong 4 m_{\text{BR}}$), containing a particle of mass m_0 ($\cong m_{\text{Zn}}$), connected by a spring constant α . In the chain we consider two kinds of nearest neighbour interactions: one between inside- and outside- and one between outside-particles of different spheres, represented by the spring constants β and γ respectively. The coupling between neighbouring chains is represented by a spring constant ξ_{ij} where i denotes the direction of the chain and j that of the coupling (see Fig. 2). Further, we take modulated spring constants for the nearest neighbour interactions along the c-axis, which is a necessary and sufficient assumption to simulate the modulation (see ref. 11 and 12):

Table I: Factorgroup analysis of Rb_2ZnBr_4 in the N- ($Pcmm$, $\nu = 0$) and I-phase (P_{ssl}^{Pcmm} , $\nu = 1$). N,A,T,R and I are numbers of normal modes, acoustical, translational optical, librational optical and internal modes. The notation of the representations are as in ref. 16.

D_{2h}	N	A	T	R	I	Raman	FIR
Ag	13+16V		6+6V	1+4V	6+6V	$\alpha_{xx}, \alpha_{yy}, \alpha_{zz}$	
B _{1g}	8+26V		3+12V	2+2V	3+12V	α_{yz}	
B _{2g}	13+16V		6+6V	1+4V	6+6V	α_{xz}	
B _{3g}	8+26V		3+12V	2+2V	3+12V	α_{xy}	
Au	8+26V		3+12V	2+2V	3+12V		
B _{1u}	13+16V	1+V	5+5V	1+4V	6+6V		x
B _{2u}	8+26V	1+V	2+11V	2+2V	3+12V		y
B _{3u}	13+16V	1+V	5+5V	1+4V	6+6V		z

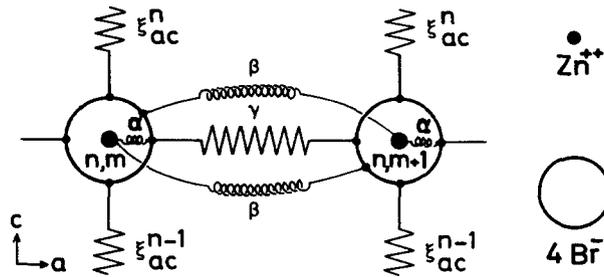


Fig. 2 : Schematic picture of our tetrahedron model for a chain along the a-axis; the different spring constants are as explained in the text.

$$\beta_c^n = \beta_c + \delta \cos(nqc + \tau) \quad (3a)$$

$$\gamma_c^n = \gamma_c + \epsilon \cos(nqc + \tau) \quad (3b)$$

$$\xi_{ac}^n = \xi_{ac} + \rho \cos(nqc + \tau) \quad (3c)$$

internal mode frequencies squared:

$$\omega_a^2 = \omega_o^2 + \frac{4\xi_{ac}}{m_1} \sin^2\left(\frac{\nu qc}{2}\right) + \text{(h.o. terms in } \xi_{ac}/\omega_o^2) \quad (5a)$$

where δ , ϵ and ρ may depend on the modulation amplitude and where τ is the internal coordinate. For the corresponding displacement field \vec{u}_j ($j = 0$ or 1) we look for "normal mode" solutions of the form of Eq. (1). Putting these in the equations of motion and taking terms with the same factor $e^{i\nu\tau}$ we get an infinite set of coupled equations

$$A_\nu u^{\nu-1} + D_\nu u^\nu + B_\nu u^{\nu+1} = 0 \quad \nu \in Z, \quad (4)$$

where u^ν stands for (\vec{u}_0^ν) . In zeroth order we

consider only one Fourier component labeled by ν and neglect coupling with the other components $\nu' \neq \nu$ i.e. we take $A_{\nu'} = B_{\nu'} = 0$. The eigenfrequencies can then be calculated from $\|D_\nu\| = 0$ yielding for the a and c direction the following

$$\omega_c^2 = \omega_o^2 + \frac{4\gamma_c}{m_1} \sin^2\left(\frac{\nu qc}{2}\right) + \text{(h.o. terms in } \gamma_c/\omega_o^2) \quad (5b)$$

with $\omega_o = (\alpha + 2\beta_c)/\mu$ and $\mu = m_1 m_o / (m_1 + m_o)$. In the N-phase only the term $\nu = 0$ can occur (no modulation) and we have two optical modes with different frequencies depending on β_c and β_a ; 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. Regarding the mutual distances of the tetrahedra along both directions and the elastic constants⁶ it follows that $\beta_c > \beta_a$; therefore the observed modes can be assigned as $\omega_c(\nu=0) = 226 \text{ cm}^{-1}$,

$\omega_a(\nu=0) = 203 \text{ cm}^{-1}$ and $\omega_a(\nu=\pm 1) = 206 \text{ cm}^{-1}$ (= 1 in Fig. 1). By neglecting the coupling between the modes, the temperature dependent coupling constants δ , ϵ and ρ have been dropped out. In the next approximation the set of 3 modes ν and $\nu \pm 1$ are considered to be decoupled from the remaining ones. As discussed above, in the present case $\nu = 0$ and $\nu = \pm 1$ are the relevant ones. The determinantal equations yielding the eigenfrequencies now gets the form¹⁰

$$\| D_0^a \| \cdot \| D_1^a D_2^a + \rho^2 X \| = 0 \quad (6a)$$

$$\| D_1^c \| \cdot \| D_0^c D_1^c + \epsilon^2 Y \| = 0 \quad (6b)$$

where X and Y depend on m_0 , m_1 and on the spring constants. This gives the interesting result that to this order: for the a -direction the original $\nu = 0$ mode remains unaffected and the new $\nu = \pm 1$ mode is perturbed via ρ^2 ; the opposite happens for the c -direction, where the $\nu = 0$ mode is perturbed and the new one not. We see from Fig. 1 that in the I-phase the modes $\omega_a(\nu=0)$ and $\omega_a(\nu=\pm 1)$ (denoted by 1) both shift as a function of temperature, in agreement with the conclusions from Eq. (6). Again in qualitative agreement with Eq. (6) the ν_2 ($\nu=\pm 1$) mode at 83 cm^{-1} (2 in Fig. 1) increases also in frequency. Finally there is a temperature dependent mode around 15 cm^{-1} in the I-phase. From its symmetry and temperature dependence, this might be assigned as the soft amplitude mode¹³.

Summarizing we have observed new activated Raman lines in the I-phase of Rb_2ZnBr_4 in accordance with the predicted change in selection rules as derived from superspace symmetry. The measurements can be interpreted by means of a simple harmonic model of chains of spheres connected by modulated spring constants and a Bloch ansatz for the vibrational modes reflecting the superspace translational symmetry. The observed temperature dependent shifts can be related in the model to the amplitude of the modulated spring constants which in the crystal will be the result of the temperature dependence of the amplitude of the displacive modulation. It appears that the effect of the modulation becomes most clear for the internal ZnBr_4 modes supporting the idea that the modulation wave mainly consists of large rotations of these tetrahedra¹⁴. A similar effect is very recently observed in Na_2CO_3 ¹⁵, which can also be interpreted with our phenomenological model.

Acknowledgement - We would like to thank W. v.d. Linden for growing the single crystals and R. van Kleef for his skilful assistance in setting up the Raman experiment and A. Maciel and J.F. Ryan for sending us a preprint of their work prior to publication. Part of this work has been supported by the "Stichting voor fundamenteel Onderzoek der Materie" (FOM) with financial support of the "Nederlandse Organisatie voor Zuiver Wetenschappelijk Onderzoek" (ZWO).

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