Ferroelectrics, 1980, Vol. 26, pp. 707—710
0015—0193/80/2603—0707$04.50/0

TEMPERATURE DEPENDENCE OF THE FAR INFRARED TRANSMISSION OF THE MODULATED STRUCTURE Rb_2ZnBr_4

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Abstract---The far infrared transmission between 5 and 140 cm^{-1} of Rb_2ZnBr_4 has been measured as a function of temperature from 4 to 400 K. We have observed a temperature dependent mode, which broadens strongly with increasing temperature. Moreover, we have found strong indications of a new phase transition at 50 K.

From structural investigations, Rb_2ZnBr_4 is known to have an incommensurate structure between 200 K (= T_c) and 353 K (= T_i) with a modulation wave vector of $0.3\,\vec{c}^*$, while below T_c the modulation is commensurate with a wave vector of $1/3\,\vec{c}^*$ [1]. The space group in the normal phase (> T_i) is P_{cmn} (same setting as in ref. 1), with a pseudo hexagonal c-axis. In the modulated phase, the three dimensional periodicity is lost, which means that the crystal cannot be described by one of the known crystallographic space groups. As has been shown by de Wolff[2] and Janner and Janssen[3] the proper symmetry group is a space group in more than three dimensions, the so-called superspace group. The detailed structure of the incommensurate phase of Rb_2ZnBr_4 is not yet known. On the basis of the data available so far[4] the superspace group assigned to it is $P^{P_{cmm}}_{ss\bar{1}}$. The meaning of the symbols used to label this four dimensional space group is explained in ref. 5.

The superspace group approach has already been successful in explaining X-ray diffraction results. Work is in progress showing that it also can be used for deriving the selection rules for I.R. and Raman active modes in Rb_2ZnBr_4. In order to have a first understanding of the low temperature transition (at $\pm$ 50 K) in addition to the already observed phase transition at 200 K, a model is proposed for incommensurate crystals undergoing a lock-in transition. More details hereon can be found elsewhere in these proceedings[6].

The order parameter of a modulated crystal can be written as $u(x) = ve^{i\varphi(x)}$, with $\varphi(x) = qx + h(x)$, $q = 2\pi/p$, for Rb_2ZnBr_4 $p = 3$. If $h(x) = h_o x$ (h_o = constant $\neq 0$) then $\varphi = (q + h_o)x$ and the structure will in general be incommensurate and can be described by a superspace group. If $h(x)$ is constant over a length L and then has a jump of $2\pi/n$, one gets a domain-like structure of commensurate pieces. As a result, part of the translation symmetry of the superspace group is then lost, leading to a subgroup of index p (the supercell is p-times larger). With decreasing temperature, the number of domains decreases until finally the whole crystal becomes commensurate. According to this picture, we may expect the following phases going from high to low temperatures: first (at T_c) the crystal becomes incommensurate modulated, at T_c there is a transition to a domain structure while at $T_{c'}$

the whole crystal becomes commensurate. At T_i and T_c, we have transitions between a normal and a superspace group while at T_c there is a transition between two superspace groups.

We have measured the far infrared transmission on single crystals of Rb_2ZnBr_4 using a Michelson interferometer and a He-cooled bolometer. In figure 1 the transmission along the a- and c-axis is presented between 20 and 140 cm^{-1} for three temperatures. There is only a substantial transmission around 140 cm^{-1} and at very low frequencies, where some additional structure is present. For both directions, the spectrum resembles that of a strong optical mode with $\omega_{to} \approx 45$ and 30 cm^{-1} respectively for the a- and c-direction, and some less stronger modes at lower frequencies. From neutron data, only one optical branch is known, with $\omega(k=o) \approx 31$ cm^{-1}.

By looking at the structure of Rb_2ZnBr_4, we can qualitatively understand the origin of these rather low frequencies. In the c-direction there are chains of alternating $ZnBr_4$ tetrahedra and Rb atoms, and chains of only Rb atoms, so that the latter have a relative large freedom of motion resulting in a low frequency mode. Perpendicular to the c-axis the structure of Rb_2ZnBr_4 is approximately hexagonal except for the two planes at $c \approx 0$ and $c \approx \frac{1}{2}$. Here only half of the atoms, necessary for a hexagonal cell are present which allows a large freedom of motion in the a-direction (see figure 2).

With respect to the spectra, the first mode will be active in the spectrum measured along the a-axis and the second in the spectrum along the c-axis. Without approximation we would expect 39 I.R. active modes in the orthorhombic cell, while in the hexagonal approximation and taking the tetrahedra as rigid, only 2 active A_{1u} and 2x2 (degenerate) E_{1u} modes are expected. For a clear identification of the modes a more detailed analysis will be necessary.

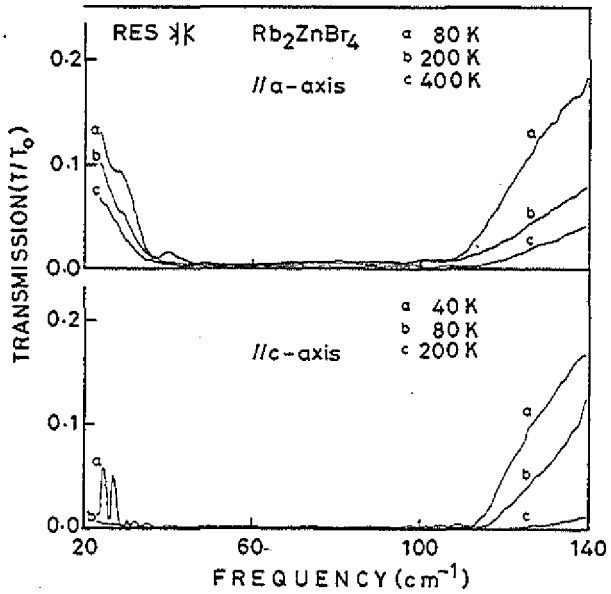

FIGURE 1 Transmission of Rb_2ZnBr_4 along two different crystal axes between 20 and 140 cm^{-1} for three temperatures.

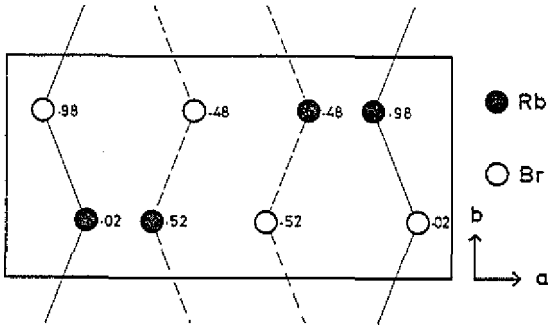

FIGURE 2 Part of the structure of Rb_2ZnBr_4, showing the atomic positions in two planes perpendicular to the c-axis. The numbers give the fractional c-coordinates. At both these levels the atoms form two chains with a rather large freedom of motion in the a-direction.

The most interesting part of the spectra is shown in figure 3 for the c-direction. The two most striking features are the following: the mode at 22 cm^{-1} broadens very strongly with increasing temperature while the mode at 14 cm^{-1}, present at 40 K, disappears in the 60 K spectrum, leading to an increase in transmission at that frequency. From the complete transmission data, measured in steps of 5 K, we found that the actual transition takes place at $\sim$ 50 K.

This sudden change in the spectrum must be the consequence of a phase transition where the selection rules for the I.R. active modes change. According to the ideas mentioned in the first part of this paper, this transition might be the real lock-in, below which the structure is commensurate. Between 50 K and 200 K, the crystal then would have a domain structure. This would mean that at 50 K there is a transition between a normal and a superspace group, while at 200 K there would be a transition between two superspace groups.

In figure 3, the 200 K transition is much less pronounced. A more careful analysis of the spectra showed that the strong broadening of the 22 cm^{-1} mode, slowly relaxates towards 200 K, indicating more a second than a first order phase transition, in agreement with the group-subgroup relation of these two phases (see above). The observed strong broadening also may explain the overdamped nature of the neutron results of ref. 1.

In conclusion, we would like to state that we have found from our far infrared transmission data of Rb_2ZnBr_4, in addition to the known phase transitions, evidence

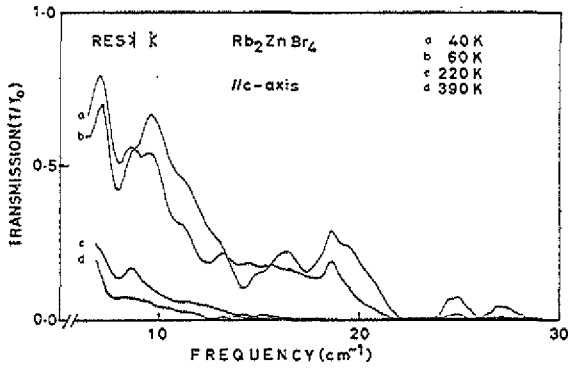

FIGURE 3 Low frequency part of the transmission spectrum along the c-axis at temperatures in all the different phases of Rb_2ZnBr_4. From 60 K to 40 K an extra mode appears at 14 cm^{-1}. At high temperatures the mode at 22 cm^{-1} is strongly broadened.

for a new transition at 50 K. Tentatively the latter is ascribed to the lock-in transition while the higher transition at 200 K can then be understood as a transition between two incommensurate crystal structures, the one with essentially a sinussoidal modulation, the other with a periodic succession of commensurate microdomains separated by rapidly varying modulation phases. The spectra at all temperatures above $\pm$ 100 K are very smooth and relaxation like, due to the strong broadening of a mode at 22 cm^{-1}. A more quantitative analysis will be presented shortly.

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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