^{81}Br NQR STUDY OF PHASE TRANSITIONS IN Rb_2ZnBr_4

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ABSTRACT

^{81}Br NQR in Rb_2ZnBr_4 was measured as a function of temperature in the region from 77 K to 420 K. The spectra obtained show the existence of structural phase transitions at T$\sim$355 K, T$\sim$200 K and perhaps also at $\sim$130 K. The lattice dynamics and the structure of Rb_2ZnBr_4 strongly depend on the impurities in the sample. Different amounts of impurities could be the reason for the differences in the results obtained from three different samples.

INTRODUCTION

The crystal structure of Rb_2ZnBr_4 has been determined (1) with the neutron scattering at temperatures 373 K, 300 K and 4.2 K. Those temperatures belong to the high temperature paraelectric phase, incommensurate phase and ferroelectric commensurate phase, respectively. Measurements of the structure at 373 K showed that Rb_2ZnBr_4 belongs to $P_{cmn} - D_{2h}^{16}$ space group. Structure is pseudohexagonal. In the direction of pseudohexagonal c axis are chains of Rb ions and chains of alternating $ZnBr_4$ tetrahedra and Rb ions. Two bromines of a tetrahedron group are laying in the mirror plane and the other two are placed symmetrically to the plane. At 300 K the incommensurate modulation in the c direction was observed. The wave vector of the modulation is $q = 0.292\ c^*$. The Rb ions and the tetrahedral groups are shifted perpendicularly to the mirror plane (in the b direction). The tetrahedra are also rotated around the axes that are parallel with the crystal c and a axes. The mirror plane symmetry is destroyed. The deformation wave is polarized in the b direction.

At liquid He symmetry space group of Rb_2ZnBr_4 is P_c2_1n and the unit cell is tripled in the c direction. There are 12 formula units of Rb_2ZnBr_4 in the unit cell. The wave vector of commensurate phase is $q = c^*/3$.

EXPERIMENTAL

A superregenerative Wilks NQR - 1A spectrometer combined with the PAR Model 128 lock-in amplifier was used for the measurements of the temperature dependence of ^{81}Br NQR in Rb_2ZnBr_4. Few different samples were tested (powder, polycrystalline and monocrystal Rb_2ZnBr_4 were prepared at J. Stefan institute, Ljubljana). Weak signals and very low signal-to-noise rations forced us to improve the thermal stabilization of the sample. The thermal stability during the measuring time and the temeprature gradient over the sample never exeeded 0.2 K. The sample size was approximately 1 cm^3.

RESULTS AND DISCUSSION

We started our measurements in the high temperature paraelectric phase where we found three NQR signals belonging to ^{81}Br. The corresponding ^{79}Br NQR lines were also observed to confirm the results. Two of the four Br atoms in $ZnBr_4$ tetrahedron that are laying symmetrically regarding the mirror plane are chemically equivalent and only one NQR line is expected from them. The intensity of the lowest frequency line is approximately twice as large as the intensity of the other two ^{81}Br lines and it belongs therefore to the bromine atoms laying symmetrically regarding the mirror plane. The fourth line was found at 62 MHz and the existence of it is not yet completely understood. It probably belongs to some impurities in Rb_2ZnBr_4. To identify this line we tested the pure $ZnBr_2$ sample and the corresponding ^{81}Br line was found close to that frequency but the temperature dependences of both lines were not the same. Iz is also possible that this line belongs to Rb_3ZnBr_5 impurities (2).

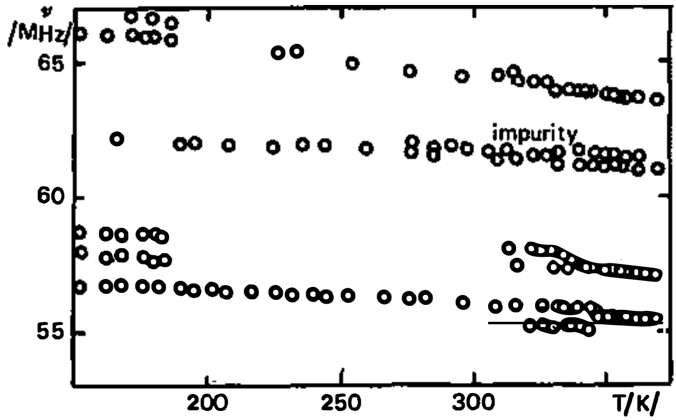

Fig. 1: Temperature dependence of the ^{81}Br NQR spectra in Rb_2ZnBr_4

Lowering the temperature, the NQR lines start to split at around 355 K what corresponds to the para - incommensurate phase transition temperature. With the simple point charge model and the use of the structure measurements we explained the splitting of the NQR lines (3). Relative intensities of the split lines were very different and at lower temperatures some of them were lost in the noise background. Below 200 K another anomaly was observed in the behavior of ^{81}Br NQR. The intensities of all NQR lines were very weak and the signals did not recover down to 77 K. Probably we have not detected all ^{81}Br NQR signals in this low temperature region but it is evident that there is another phase transition around 200 K. That is the transition to commensurate phase according to some authors (4,5,6). If that is true one would expect the NQR lines to become more intense below the transition temperature as it was observed in the case of Rb_2ZnCl_4(7). On the other side, it might be also true that at about 200 K the transition to another incommensurate phase takes place.

To answer this one should follow the temperature dependence of ^{81}Br NQR lines down to liquid He, what we could not do at present with our experimental equipment.

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REFERENCES

1) J. C. de Pater, Acta Cryst. B 35, 299 (1979)
2) W. J. Asker et al. Aust. J. Chem. 25, 2301 (1972)
3) J. Pirnat et al., Bulletin of Magn. Res. (in print)
4) C. J. de Pater, thesis (1978) Technische Hogeschool Delft
5) Th. Rasing et al., Ferroel. 26, 707 (1980)
6) V. Rutar et al., Bulletin of Magn. Res. (in print)
7) A. K. Moskalev, I. A. Belobrova, I. P. Aleksandrova, Fiz. tv. tela 20, 3288 (1978)