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# ELECTRIC, DIELECTRIC, AND THERMOPHYSICAL PROPERTIES OF $RbNO_3$ SINGLE CRYSTAL

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In the paper the temperature dependence of electric conductivity, permittivity, dielectric loss tangent, as well as specific heat and temperature diffusivity are described. It has been found that the IV-III transition is a typically structural one and the III-II-I transition is of the order-disorder type. The III-II transition runs in two stages. Within the range of this transition the ferroelectric state may exist.

## ЭЛЕКТРИЧЕСКИЕ, ДИЭЛЕКТРИЧЕСКИЕ И ТЕРМОФИЗИЧЕСКИЕ СВОЙСТВА МОНОКРИСТАЛЛА $RbNO_3$

В работе приводится температурная зависимость электропроводимости, диэлектрической проницаемости и диэлектрических потерь, а также удельной теплоёмкости и теплопроводимости кристаллов $RbNO_3$. Было обнаружено, что переход IV-III является типичным структурным переходом, переход II-I представляет собой переход типа упорядоченный-неупорядоченный. Переход III-IIпроисходит в два этапа. В области этого перехода может существовать ферроэлектрическое состояние.

## I. INTRODUCTION

It is well known from structural measurements that $RbNO_3$ — both monocrystalline or polycrystalline — appears during heating consecutively in four stable phases [1—3]:

$$\underset{\text{trigonal}}{\text{IV}} \xrightarrow{164\,^\circ\text{C}} \underset{\text{cubic CsCl}}{\text{III}} \xrightarrow{219\,^\circ\text{C}} \underset{\text{rhombohedric}}{\text{II}} \xrightarrow{291\,^\circ\text{C}} \underset{\text{cubic NaCl}}{\text{I}}$$

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The transitions from one structure to another occur in a rather narrow temperature interval. As for the physical viewpoint, the III-II transition is the most interesting. The temperature dependence of permittivity in the transition vicinity obeys the Curie-Weiss law, which was the reason of the hypothesis [4] that phase II was antiferroelectric. Furthermore, only this phase transition is sensitive to the applied external electrical field [4].

So far all physical measurements (except the temperature dependence of permittivity [4]) have been performed on polycrystalline samples [2, 3, 5]. As for thermal measurements, the calorimetric [6] and thermal diffusivity measurements [7] in melted $RbNO_3$ are known.

In the present work we have concentrated upon electric, dielectric, and thermophysical properties of $RbNO_3$ crystals. The samples were cut approximately from the same place of the single crystal.

## II. EXPERIMENTAL

The $RbNO_3$ single crystals in the shape of a cyllinder with its long axis in the (001) direction were grown from the melt in the IKAN, Moscow. Samples cut perpendicularly to the axis were used in measurements. Perimittivity and loss tangent tg $\delta$ were measured using the General Radio 1615 A capacitance bridge at a frequency of 10 kHz. Electric conductivity was measured by the VA-J-51 (VEB Vakutronik, Dresden) electrometer. The value of electric field in the sample was $\sim 1$ V/mm. Specific heat and thermal diffusivity were measured by the pulse method with samples of $0.5 \times 0.8 \times 0.2—0.3\ cm^3$. The electric and dielectric measurements were performed with samples of $0.5 \times 0.8 \times 0.1\ cm^3$. The thermal pulses spread in the (001) direction. During thermal measurements the temperature increase rate was 0.2 deg/min. Onto the measured samples the colloid graphite Dag 570 was deposited. The samples were put between Pt electrodes. The measurements were performed in an inert atmosphere or in vacuum.

## III. RESULTS

In Fig. 1 the dc conductivity as function of temperature is plotted. The steps in the conductivity course correspond to successive structural changes. The change in the non-temperature region (70 °C) has been attributed to the influence of impurities. Using the measured course not only the temperature regions in which the structural transitions take place can be determined, but also activation energies required for the creation and migration of defects in every structural region can be calculated. In the $RbNO_3$ single crystal this has not been previously done (see Table 1).

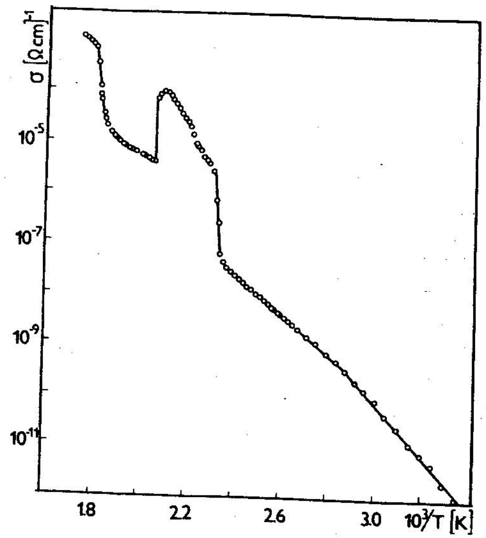


Fig. 1. Temperature dependence of the dc conductivity

Table 1

| Phase | temperature range °C | lattice type | activ energy eV |
|---|---|---|---|
| IV | 20—72 | trigonal | 1.08 |
| | 72—150 | | 0.77 |
| III | 160—198 | cubic — CsCl | 1.3 |
| II | 210—285 | rhombohedric | 0.51 |
| I | 285—310 | cubic — NaCl | 0.96 |

In Fig. 2 the temperature dependence of the dielectric loss tangent is plotted. At the phase transition temperatures some anomalies were measured. After the phase transitions IV-III and III-II had been completed there was found a remarkable scattering of the measured values in the dielectric loss tangent around 160 °C and 210 °C, respectively. This can be attributed to instabilities occurring in transitions from one structure to another. At the temperature 175 °C a maximum was observed, the origin of which we do not know how to explain. The objectivity of its existence is certified also by the fact that at this temperature a break in the dc conductivity course occured (Fig. 1) and a maximum in the permittivity course appeared (Fig. 3). On the contraty, such a maximum was not observed in the temperature course of specific heat and thermal diffusivity (Figs. 4, 5). Therefore, we predict that the relaxation maximum is due to around-the-electrodes effects. We shall not investigate them in this paper.



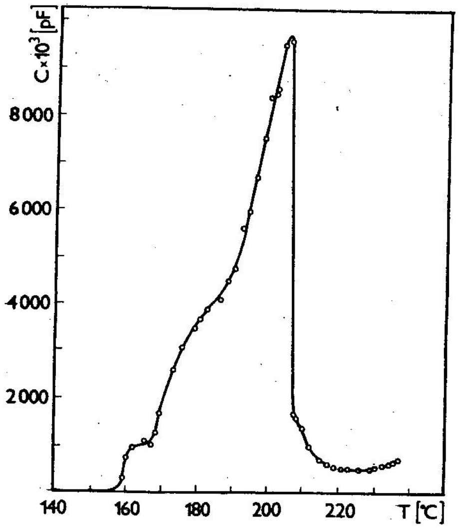


Fig. 2. Temperature dependence of the dielectric loss tangent

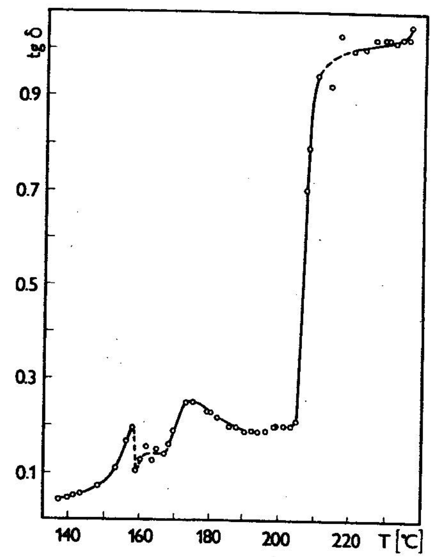


Fig. 3. Temperature dependence of the permittivity

In Fig. 3 the temperature dependence of permittivity is plotted (i. e. the value of the capacity variation). At the temperature ~200 °C a fast increase of values was observable. After the III-II transition had been finished a sudden drop occurred and permittivity decreased again to a relatively low value.

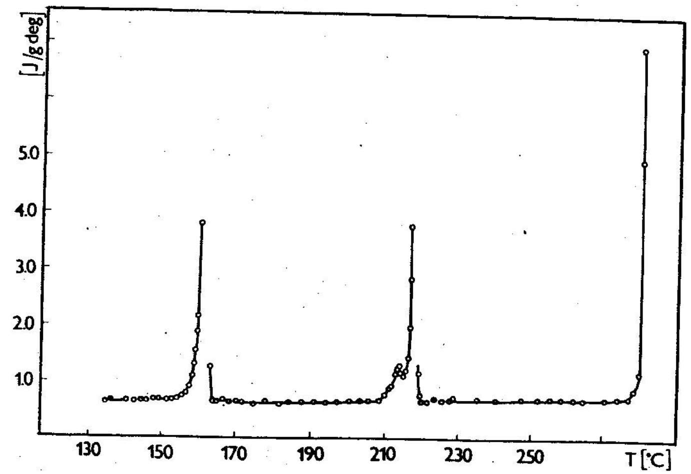


Fig. 4. Temperature dependence of the specific heat

In Fig. 4 the temperature dependence of specific heat is plotted. Its course was characterized by three maxima at 160 °C, 215 °C and 285 °C regions, respectively. The maximum at 160 °C was very sharp and also narrow. The course under and above the transition was smooth, increasing a little. On the other hand the III-II transition was characterized by two maxima, the lower being found at about 3 °C prior to the main maximum location.

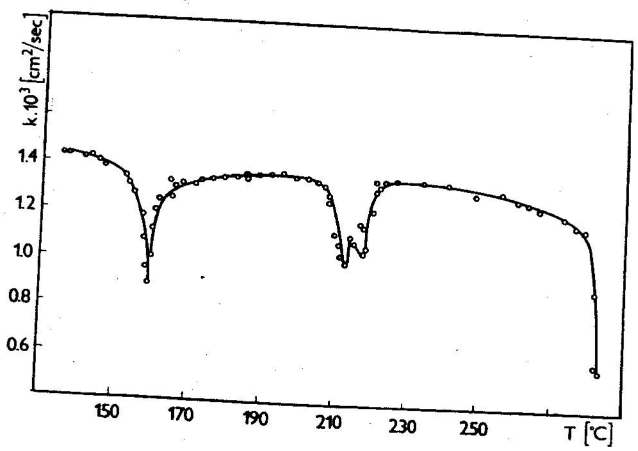


Fig. 5. Temperature dependence of the thermal diffusivity

The thermal diffusivity at temperatures from 20 to 280 °C can be seen in Fig. 5. The curves in the vicinity of the phase transitions were characterized by minima, moreover the III-II transition was not simple but had two extremes at about 3 °C from each other. A similar anomaly as in the curves in Figs. 4 and 5 at the III-II transition was also observed in the conductivity course (Fig. 1).

## IV. DISCUSSION

It follows from the temperature dependences of specific heat and dc conductivity hat the IV-III transition is very similar to that observed in $CsNO_3$ crystals [10]. he transition mechanism takes place in a very narrow temperature interval. This is aused by the same structure of $RbNO_3$ and $CsNO_3$ crystals in the given emperature interval. It is a typical structural transition. The II-I transition is of the rder-disorder type, which is confirmed not only by the temperature dependence of e dc conductivity, but also by structural measurements [11]. As it follows from e dc measurements, this transition appears gradually in a rather broad tempera-re interval, similarly as in $NaNO_3$ crystals [12].



The temperature dependences of specific heat and thermal diffusivity in the vicinity of the III-II trasition show that this transition runs in two stages. In the curves a small maximum and minimum occur, respectively. They cannot be attributed to impurities since their presence in such a concentration which causes the formation of maxima should necessarily result in the splitting of the phase transition, thus lowering the main extreme.

Realizing that thermal diffusivity can be expressed as

$$k = \frac{1}{3} v l$$

where $v$ is the mean velocity of phonons and $l$ is the mean free path of phonons, we see that with the exception of the phase transition vicinities both the velocity and the mean free path of phonons vary little. In the vicinity of the IV-III and II-I transitions the free mean path of phonons decreases because of the rearrangement of the lattice during transition. After the phase transition is finished $l$ reaches its original value. In the case of the III-II transition expressive minima apparently confirm the two-stages mechanism of the transition. In this connection we must note that a similar situation occurs in $KNO_3$ crystals, supposing that specific heat and dc conductivity are measured with decreasing temperature. Then a metastable ferroelectric phase [13] is formed (in $KNO_3$) in a narrow temperature.

It is quite possible that a similar situation occurs also in a $RbNO_3$ crystal. This asumption is supported by the facts that in the III-II phase transition permittivity quickly increases with temperature (by three ordes), the external field remarkably influences the maximum temperature, and the Curie-Weiss law becomes valid. The existence of the metastable state was also confirmed by structural measurements of Kennedy [11].

The temperature dependence of dc conductivity indicates the presence of thermally activated defects which cause ionic conductivity. The activation energies of formation and migration of these defects in individual structures correspond to the degree of the tight-binding of lattices. The tightest lattice (III-CsCl type) gives the highest activation energy (1.3 eV) whilst the rhombohedric lattice 0.51 eV only. The presence of a small amount of impurities is supported by the break in $\ln \sigma = f(1/T)$ in phase IV around 72 °C. The character of the break can be explained similarly as in $NaNO_3$ [14]. Thermally activated impurities — originally precipitated — are substitued into the lattice, thus causing a conductivity increase in the impurity region due to the rise of concentration of the carriers.

## V. CONCLUSION

The physical properties of $RbNO_3$ single crystals were measured and compared, namely, the temperature dependences of conductivity, permittivity, dielectric loss tangent, specific heat, and thermal conductivity.

From the measured dependences it follows that the IV-III transition is a typically structural one, while the II-I transition is of the order-disorder type. The phase transition III-II runs in two stages. An anomalously large value of permittivity, validity of the Curie-Weiss law, and a similarity with the ferroelectric phase in $KNO_3$ have led us to the conclusion that in this narrow temperature region the ferroelectric state can exist.

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