INFLUENCE OF HYDROSTATIC PRESSURE ON THE ELECTRIC PROPERTIES OF $NaNbO_3$ MONOCRYSTALS

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The influence of hydrostatic pressure on the electric properties of $NaNbO_3$ monocrystals has been investigated. For temperatures $T > T_a$, the linear dependencies of electrical conductivity σ and of the reciprocal permeability $1/\varepsilon$ on pressure were obtained: $\sigma = \sigma^0 + Cp$, $1/\varepsilon = 1/\varepsilon^0 + ap$. From a comparison of the linear dependence of the activation energy E_a on pressure $E_a = E_a^0 - Bp$ and the analogous dependence obtained from the theory of the small polaron, it was shown that the small polaron was strongly scattered on the LO phonons at temperatures $T > T_a$. The rate of change of the temperature T_a of the phase transition $P \rightleftarrows R$ with pressure ($dT_a/dp = 120 \pm 12$ K/GPa) was determined from investigations of $\sigma(p)$.

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1. Introduction

Studies previously conducted on sodium niobate $NaNbO_3$ were mainly concentrated on the investigation of the dielectric and structural properties of this compound. Recent research [1, 2] has shown that $NaNbO_3$ has seven phase transitions. From our studies of the electric, thermoelectric and Hall mobility properties and tests on high pressure electric permeability ε [4], it was concluded that the most interesting of these phase transitions is that from $P \rightleftarrows R$ (see 2) in the vicinity of 360°C. The connection between electric conductivity σ and the reciprocal electric permeability $1/\varepsilon$ was either suggested or perhaps proved from of high pressure investigations [5, 6] in materials such as: $BaTiO_3$, $SrTiO_3$, $PbZrO_3$ and others. According to [5], the existence of this connection gave evidence of a strong interaction between electrons or polarons and the longitudinal optical phonons LO.

From the electric, thermoelectric and galvanomagnetic characterisics obtained, the authors of [3, 7] came to the conclusion that the mechanism of conductivity in $NaNbO_3$ had a polaron character.

The investigations of the influence of hydrostatic pressure on the electric properties of sodium niobiate were performed to confirm the polaron mechanism of conductivity in this material, especially in the neighbourhood of the $P \rightleftarrows R$ phase transition.

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2. *Experimental technique and results*

Tests were conducted on $NaNbO_3$ monocrystals obtained from an Na_2CO_3—N_6O_5—NaF (1 : 1 : 0,235 mol) solution melted at temperatures 1300–1400°C. The solution was cooled at 5 K/h to 1000°C at which temperature the solvent was poured off. The single crystals obtained were of yellow-brown colour with dimensions 3 × 2 × 0,5 mm.

The influence of hydrostatic pressure on the electric properties of $NaNbO_3$ was investigated using a high pressure chamber (Fig. 1). Pure helium was used as a working

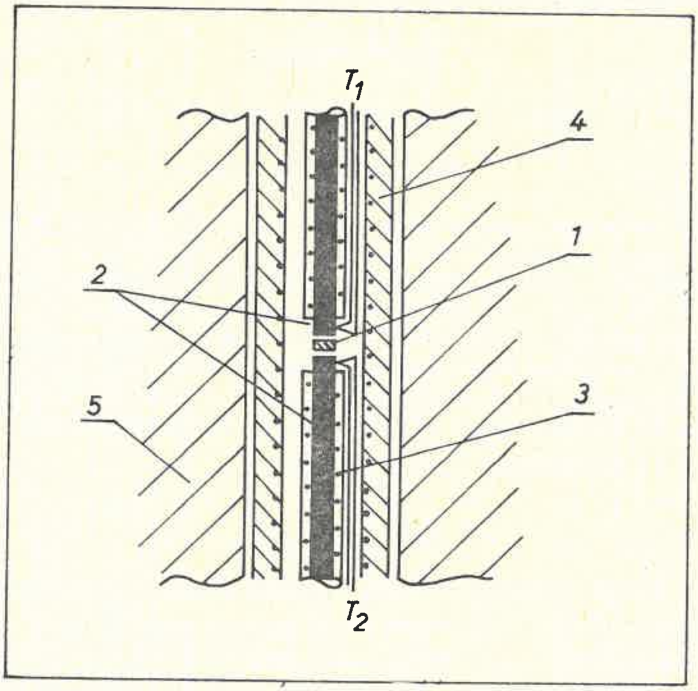

Fig. 1. Diagram of the main part of the high-pressure chamber; 1 — sample, 2 — silver blocks, 3 — heaters producing temperature gradient, 4 — main heater, 5 — chamber wall

medium. The investigated sodium niobiate monocrystal, with platinum electrodes, was placed between two silver blocks (Fig. 1, number 2) providing good heat abstraction. Thermocouples placed inside the blocks close to the sample made it possible to control the temperature with an accuracy of 0.1 K.

Temperature was regulated by means of heaters (3 and 4 on, Fig. 1). All electric conductors needed for the experiment were led out from the chamber through high pressure bushing sealed by means of pyrophyllite. The resistance between the measuring wires (and pyrophyllite) and the casing of the bushing was greater than 50 GΩ.

Electric conductivity $\sigma(T)$ was measured in a stabilized constant field of 20 V/cm by a sensitive current meter (order of 10^{-13} A) coupled at the output to a recorder.

The relations of $\sigma(T)$ were measured during heating and cooling with a temperature change rate of approximately 100 K/h at the determined pressure value which was constant for each temperature plot. Hydrostatic pressure was measured with a manganite coil with an accuracy $<1\%$.

Fig. 2 shows the dependence $\ln \sigma = f(10^3/T)$ for a wide temperature range, obtained for the selected values of pressure. This curve may be divided into 4 basic zones:

(*i*) Zone with a positive coefficient of resistance ($20° \leqslant T \leqslant 150°C$).

(*ii*) The antiferroelectric zone of the phase P, in the temperature range $150°C \leqslant T \leqslant 360°C$ and pressure range $0 \leqslant p \leqslant 0.4$ GPa. The dependence $\ln \sigma = f(10^3/T)$ is linear

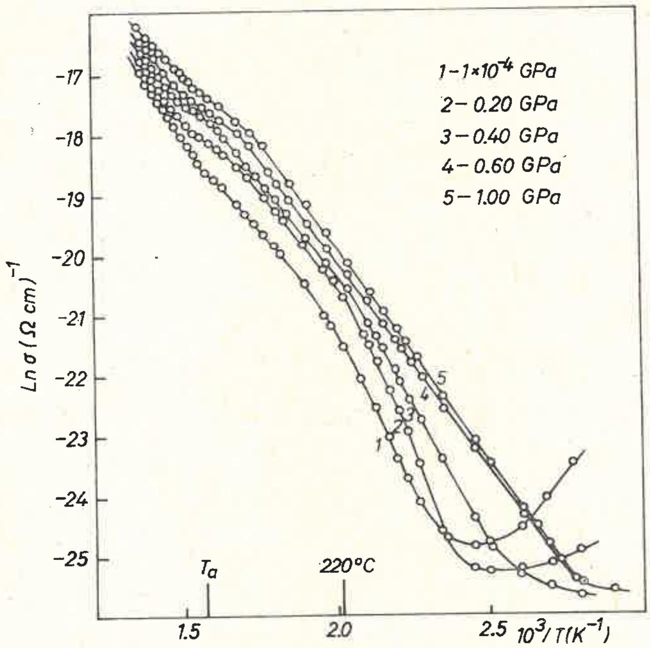

Fig. 2. Isobaric variations of electric conductivity σ of $NaNbO_3$ versus temperature for selected hydrostatic pressure values

within the particular temperature limits. The determined activation energy changes from 0.5 eV to 1 eV at a temperature of about 220°C. Such anomalies are not observed for pressures $p > 0.4$ GPa and the activation energy in this case is about 0.6 eV.

(*iii*) Zone in the vicinity of T_a — the temperature of the phase transition $P \rightleftarrows R$. Temperature T_a shifts to higher values with inceasing hydrostatic pressure (Fig. 3, curve *1*). The rate of temperature change, determined from the slope of the straight line, is $dT_a/dp = 120 \pm 12$ K/GPa. This result is comparable with the analogous result obtained from the measurements of electric permeability vs pressure [4].

(*iv*) Zone of temperatures $T > T_a$ characterized by a linear dependence $\ln \sigma = f(1/T)$, which changes its slope with pressure. Activation energy, determined in this temperature region, as a function of pressure is presented in Fig. 3 (curve *2*). The presented dependence is linear and is a decreasing function of pressure

$$E_a = E_a^0 + Bp, \tag{1}$$

where E_a — activation energy under normal pressure, $B = -0.22$ eV/GPa is the pressure coefficient of activation energy.

The linear dependences; $\sigma/\sigma^0 = f(p)$, and $\varepsilon^0/\varepsilon = f(p)$, presented in Fig. 4 for selected temperatures $T > T_a$ (σ^0 and ε^0 are electric conductivity and electric permeability under

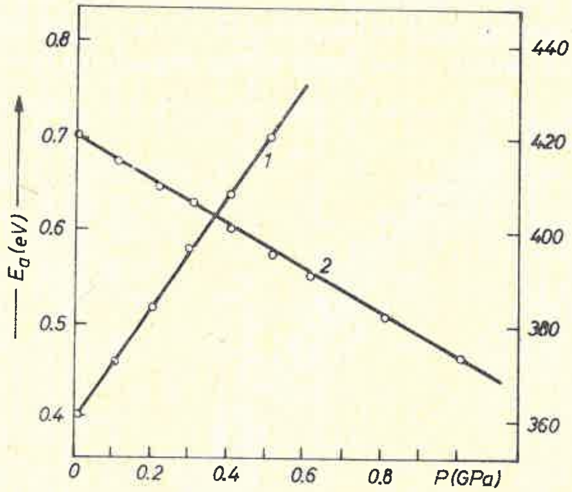

Fig. 3. $P \rightleftarrows R$ phase transition temperature T_a variations (curve *1*) and activation energy E_a variations (curve *2*) versus hydrostatic pressure

a normal pressure, respectively) were obtained from the investigation of the influence of pressure on electric conductivity σ and electric permeability ε [4]. These dependences provide evidence suggesting a strong scattering of polarons on LO phonons, which will be discussed in the next part of this paper.

3. *Discussion*

Probably, in zone (*ii*), at a temperature of about 220°C and under pressures $0 < p < 0.4$ GPa, the change of activation energy from the value of 0.5 eV to 1 eV can be interpreted as a pressure-induced new phase transition from the ferroelectric phase Q to the antiferroelectric phase P. The occurrence of this phase transition was previously observed by Lefkovitz et al. [8]. They reported, on the basis of X-ray investigations, the existence of the ferroelectric phase Q in the temperature range $20° \leqslant T \leqslant 260°$C. According to [8] this temperature range can vary, depending on the internal stresses inside the crystal. Distinct anomalies in the dependences: $\varepsilon(T)$, at temperature $T < T_a$, under pressures $0 < p \leqslant 0.3$ GPa, were observed [4]. These anomalies are connected with the existence of the phase Q inside the phase P. The observed changes in the slope of curves $\ln \sigma(1/T)$ in the neighbourhood of 220°C for analogous pressures appear to confirm the occurrence of such a phase transition.

The results obtained for zone (*iv*) (temperatures $T > 360$°C) are of particular interest. The linear dependences σ/σ^0 and $\varepsilon^0/\varepsilon$ v.s hydrostatic pressure (Fig. 4), for sodium niobate, correspond to the dependences obtained, in the paraelectric phase only, for $BaTiO_3$, $SrTiO_3$, $KTaO_3$ and $KTa_{1-x}Nb_xO_3$ ($x = 0.02, 0.1, 0.25$) [5]. This similarity of the dependence obtained suggests that in $NaNbO_3$, the paraelectric phase occurs already above 360°C, since at a temperature of 480°C (the transition temperature from the antiferroelectric to paraelectric phase [9]), no or virtually no anomalies of σ and ε are observed.

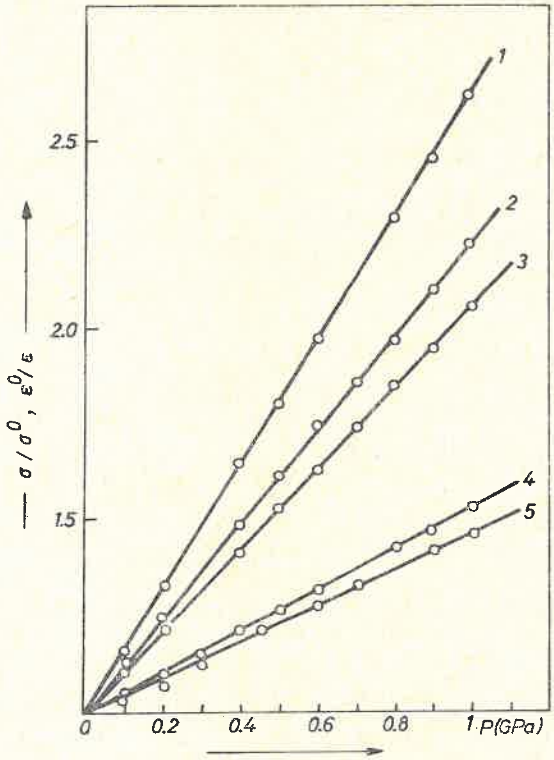

Fig. 4. Dependence of normalized conductivity σ/σ^0 (curve *1*–*3*) and reciprocal permeability $\varepsilon^0/\varepsilon$ (curve *4*, *5*) on hydrostatic pressure for temperature $T = 420$°C (curve *1*, *4*), $T = 440$°C (curve *2*) and $T = 460$°C (curve *3*, *5*)

The linear dependence $\sigma/\sigma^0(p)$ and $\varepsilon^0/\varepsilon(p)$, obtained experimentally, suggests the occurrence of a relation between σ and $1/\varepsilon$, which can be written most simply as follows:

$$\sigma \sim (1/\varepsilon + \text{const}). \tag{2}$$

The authors of [5] worked out an analytical relation based on the empirical rule [2] and the Curie–Weiss law. At the same time, they showed the equality of the coefficients $\frac{\partial}{\partial T}[(d(\sigma/\sigma^0)/dp)^{-1}]$ and $\frac{\partial}{\partial T}[(d(\varepsilon^0/\varepsilon)/dp)^{-1}]$ in a wide temperature range. In this way they showed the strong scattering of polarons on longitudinal optical phonons LO. From experimental data obtained for $NaNbO_3$, partly presented in Fig. 4, the coefficients

$[d(\sigma/\sigma^0)/dp]^{-1}$ and $[d(\varepsilon^0/\varepsilon)/dp]^{-1}$ were calculated. The temperature dependences of these coefficients are presented in Fig. 5. The parallelism of the obtained straight lines gives evidence of the equality of their slopes inside a wide temperature range. Thus, the strong scattering of polarons on LO phonons is proved in $NaBbO_3$, at temperatures $400^0 < T < 480°C$.

The dominating role of polarons in the transport processes in $NaNbO_3$ prompts the search for a more precise determination of the polaron type and the influence of hydro-

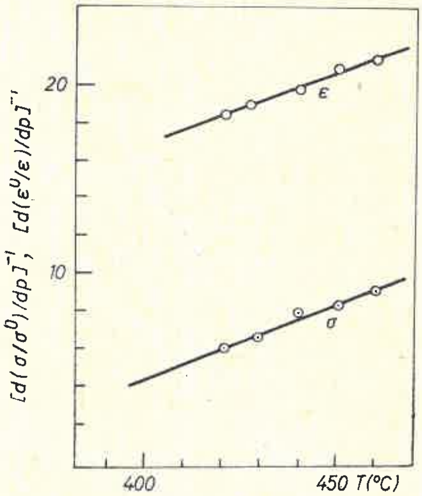

Fig. 5. Temperature dependence of the reciprocal pressure derivatives (reciprocal slopes in Fig. 2) in $NaNbO_3$

static pressure on the parameters of the polaron. On of these parameters is the polaron-LO phonon binding energy.

From the small polaron theory the activation energy or the polaron-phonon binding energy depending on $1/\varepsilon$ may be written as follows [10, 11]:

$$E_a = \tfrac{1}{2} N \sum_q \hbar\omega_q |\gamma_q|^2, \tag{3}$$

where

$$|\gamma_q|^2 = (4\pi e^2/\hbar\omega_q a^3 q^2)\,(1/\varepsilon_\infty - 1/\varepsilon) \tag{4}$$

is the constant of the polaron-phonon coupling, a — an average lattice constant.

In order to obtain an analytical dependence of E_a on pressure and to compare it with the experimental results (formula 1), the change of $1/\varepsilon(p)$ must be taken into consideration. This change has the form

$$1/\varepsilon = 1/\varepsilon^0 + Cp, \tag{5}$$

where $1/\varepsilon^0$ is the reciprocal electric permeability under normal pressure.

Substituting (5) into (4), one can obtain the dependence of the coupling constant $|\gamma_q|^2$ on pressure

$$|\gamma_q|^2 = |\gamma_q^0|^2 - Ap, \tag{6}$$

where

$$|\gamma_q^0|^2 = (4\pi e^2/\hbar\omega_q a^3 q^2)(1/\varepsilon_\infty - 1/\varepsilon^0) \tag{7}$$

is the small polaron-phonon coupling constant under normal pressure. A is a constant.

Substituting (6) into (3), one can obtain the dependence of the polaron binding energy on pressure

$$E_a = E_a^0 - B_t p, \tag{8}$$

where

$$E_a^0 = \frac{1}{2} N \sum_q \hbar\omega_q |\gamma_q^0|^2$$

is the activation energy under normal pressure. B_t is the pressure coefficient of the activation energy.

Substituting equation (8) in the formula describing $\sigma(T, 0)$ under normal pressure

$$\sigma(T, 0) = \sigma_0 \exp(-\beta E_a), \tag{9}$$

where $\beta = (kT)^{-1}$ one obtains

$$\sigma(T, 0) = \sigma_0 \exp[-\beta(E_a^0 - Bp)]. \tag{10}$$

Making simple transformations in (10) and taking into consideration that $\exp(\beta Bp) \simeq 1 + \beta Bp$, the linear dependence of conductivity σ as a function of pressure is obtained

$$\sigma(T, 0) = \sigma^0 + Gp, \tag{11}$$

where $\sigma^0 = \sigma_0 \exp(-\beta E_a^0)$ — electric conductivity under normal pressure, G — pressure coefficient of electric conductivity.

The derived formula (11) satisfactorly describes the dependences $\sigma(p)$, presented in Fig. 4. The agreement between formulae (8) and (11) and the experimental determinations confirm the interpretation of transport phenomena in $NaNbO_3$. It also indicates, on the basis of the small polaron theory, the strong scattering of small polarons on optical phonons LO, at temperatures $400° < T < 480°C$. The linear dependence $\ln \sigma(1/T)|_{p=\mathrm{const.}}$ at temperatures $T > T_a$ can indicate (according to [10, 11, 3]) the hopping model of a small polaron. Thus the results presented may be taken as a full explanation of the mechanism of current conduction in $NaNbO_3$.

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