

## INVESTIGATION OF THE DIELECTRIC PROPERTIES OF POTASSIUM HYDROGEN MALEATE

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The complex dielectric permittivity of potassium hydrogen maleate single crystal was measured over the frequency range from 1 kHz up to 22 GHz. The temperature varied from 123 to 333°K. Orthorhombic crystal shows a distinct dielectric anisotropy. The highest  $\epsilon'$ -value is consistent with the orientation of the hydrogen bonds O...H...O of the H-maleate anions.

A method of  $\epsilon^*$  measurements was elaborated in microwave region up to 10 GHz which made possible the estimation of the dielectric parameters for the samples oriented in nearly homogeneous electric field.

The dielectric relaxation in the microwave region was found. The absorption as well as dispersion curves correspond to a single relaxation time being equal to  $5.2 \times 10^{-12}$ s at 298°K. The enthalpy of activation equals to about 2.8 kcal/mole. The increase of  $\epsilon'$ -value with temperature indicates the nonequivalence of two minima for the charge migration responsible for the relaxation process.

Potassium hydrogen maleate (KHM) crystallizes in the orthorhombic system (space group Pbcm) with four molecules in unit cell. The dimensions of the cell are the following [1]:  $a = 4.578$ ,  $b = 7.791$ , and  $c = 15.953$  Å. The arrangements of the [OOC · CH = CH · COOH] anions as well as the positions of the potassium cations are shown in Fig. 1. According to the data so far available the free bimaleate anions are characterized by  $C_{2v}$ -symmetry [2]. In the crystal, however, they reveal some infrared optical properties which favour the  $C_s$ -symmetry. These data indicate that the hydrogen bond O...H...O in the anion is symmetric. The problem whether this bond has a single potential energy minimum or is a symmetric bond in the dynamical sense (two potential energy minima separated by a low barrier) is still not uniquely solved. Neutronographic results [3] seem to favour the completely symmetric bond, this is, however, by no means certain.

A very characteristic feature of the KHM crystal is that all hydrogen bonds are oriented along the  $c$ -axis. This fact should be somehow reflected in the anisotropic properties of this crystal. The purpose of this paper was thus the study of the dielectric properties of the KHM crystal in a wide frequency and temperature range for differently oriented samples.

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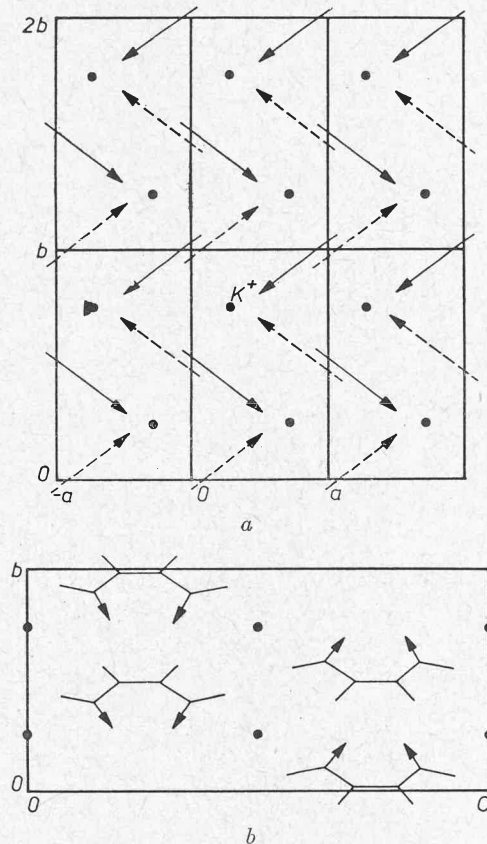


Fig. 1. Arrangement of ions in the elementary cell of KHM according to Ref. [1].

#### *Apparatus and experimental procedure*

The measurements of the permittivity in the low frequency range were made at 1 kHz and 400 kHz at temperatures ranging from that of liquid nitrogen to 60°C. A Schering bridge manufactured by General Radio was used at 1 kHz and a beat apparatus described in Ref. [4] at 400 kHz. At both frequencies the dielectric loss was very small. No phase transitions were found in the investigated temperature range.

In the frequency range from 80 MHz to 4 GHz the measurements were made by means of coaxial measuring lines (Rohde-Schwarz LMM BN 3916/50 for 80–300 MHz) and ORION type E2M-1 for 500 MHz to 4 GHz supplied by generators G4-44, G4-37A; G4-8 (Soviet production) and ORION type 1271. The standing wave ratio was measured by means of a selective amplifier ORION type TZA 201 or UNIPAN 203. In all cases frequency modulation of 1 kHz was used.

A thermostatic coaxial line terminator has been designed and constructed which permitted the measurements of the complex permittivity to be made with crystal samples of various size. The terminator is in principle a capacitor whose one plate is the short-circuited

external cylinder of the line and the other is the conical transition of the internal conductor. A schematic drawing of the measuring terminator is shown in Fig. 2. The temperature was kept constant by means of a suitable jacket. In the low temperature range the temperature was controlled automatically by nitrogen vapour flow. For higher temperatures an ultra thermostat was used.

For frequencies in the 4.5 cm band (waveguide line manufactured by PIT) the waveguide-coaxial line transition was slightly changed with respect to that used below 4 GHz; the dimen-

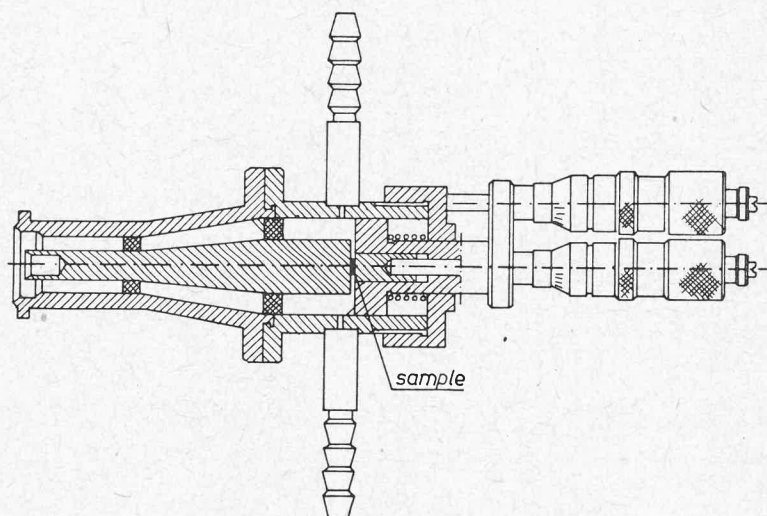


Fig. 2. Schematic drawing of the microwave capacitor

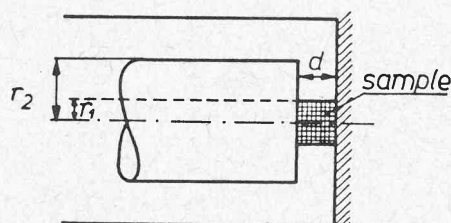


Fig. 3. Parametrization of the capacitor

sions of the external cylinder and the internal conductor were suitably decreased and a diaphragm contact (platinum foil) was used to improve the short-circuiting contact.

The distribution of the field in the cylindrical system shown in Fig. 3 is described by the wave equation

$$\frac{\partial^2 U}{\partial r^2} + \frac{1}{r} \frac{\partial U}{\partial r} + \frac{1}{r^2} \frac{\partial^2 U}{\partial \varphi^2} + \frac{\partial^2 U}{\partial z^2} + K^2 U = 0 \quad (1)$$

where  $K = k \sqrt{\epsilon \mu}$ , and  $k = \frac{\omega}{c}$ .

The solutions of this equation are the functions:

$$R_m \cos m\varphi, \quad \text{or} \quad R_m \sin m\varphi,$$

where  $R_m$  is a function fulfilling the Bessel equation

$$\frac{\partial^2 R_m}{\partial x^2} + \frac{1}{x} \frac{\partial R_m}{\partial x} + \left(1 - \frac{m^2}{x^2}\right) R_m = 0 \quad (2)$$

and  $m$  is an arbitrary real number and  $x = Kr$ . The solution of the latter equation is a Bessel function of the type  $J_m(x)$ . Assuming that only the  $z$ -component of the electric field exists in the sample one obtains [5]

$$\frac{\partial^2 E_z}{\partial r_1^2} + \frac{1}{r_1} \frac{\partial E_z}{\partial r_1} + K^2 E_z = 0.$$

In case of a dielectric without magnetic losses ( $\mu = 1$ ) the solutions becomes a zero-order Bessel function

$$E_z = AJ_0(k\sqrt{\varepsilon}r_1) \quad (3)$$

where  $A$  is a normalization constant which can be determined experimentally.

The equation for the azimuthal component of the magnetic field in the conditions described is (according to Ref. [6])

$$H_\varphi = \frac{1}{i\omega} \frac{\partial E_z}{\partial r_1} = -\frac{k\sqrt{\varepsilon}}{i\omega} AJ_1(k\sqrt{\varepsilon}r_1) \quad (4)$$

where  $J_1$  is a first-order Bessel function.

The solution obtained above describes the distribution of the field in the part of the capacitor filled with the dielectric. The distribution of the field in the unfilled part of the capacitor is given by the equation (Ref. [7]):

$$E_z = \varrho_1 J_0(kr_2) + \varrho_2 N_0(kr_2) \quad (5)$$

where  $\varrho_1$  and  $\varrho_2$  are normalization factors.

The corresponding expression for  $H_\varphi$  is

$$H_\varphi = -\frac{k}{i\omega} [\varrho_1 J_1(kr_2) + \varrho_2 N_1(kr_2)] \quad (6)$$

where  $N_0(kr_2)$  and  $N_1(kr_2)$  are Neumann functions of zero- and first-order, respectively.

By assuming that both  $E_z$  and  $H_\varphi$  are continuous at the boundary of the sample [7] one obtains the equations

$$\begin{aligned} AJ_0(k\sqrt{\varepsilon}r_1) &= \varrho_1 J_0(kr_2) + \varrho_2 N_0(kr_2) \\ AJ_1(k\sqrt{\varepsilon}r_1) &= \varrho_1 J_1(kr_2) + \varrho_2 N_1(kr_2) \end{aligned} \quad (7)$$

which permit  $\varrho_1$  and  $\varrho_2$  to be eliminated. As a result we obtain

$$E_z = A \frac{[J_0(x_1\sqrt{\varepsilon})N_1(x_1) - \sqrt{\varepsilon}J_1(x_1\sqrt{\varepsilon})N_0(x_1)]J_0(x_2) + [\sqrt{\varepsilon}J_1(x_1\sqrt{\varepsilon})J_0(x_1) - J_0(x_1\sqrt{\varepsilon})J_1(x_1)]N_0(x_2)}{J_0(x_1)N_1(x_1) - J_1(x_1)N_0(x_1)} \quad (8)$$

$$H_\varphi = A \frac{[J_0(x_1\sqrt{\varepsilon})N_1(x_1) - \sqrt{\varepsilon}J_1(x_1\sqrt{\varepsilon})N_0(x_1)]J_1(x_2) + [\sqrt{\varepsilon}J_1(x_1\sqrt{\varepsilon})J_0(x_1) - J_0(x_1\sqrt{\varepsilon})J_1(x_1)]N_0(x_2)}{J_0(x_1)N_1(x_1) - J_1(x_1)N_0(x_1)} \quad (9)$$

where  $x_1 = kr_1$ , and  $x_2 = kr_2$ .

The complex input impedance of the capacitor as a function of  $r$  has the form

$$Z(r) = \frac{d}{2\pi} \frac{E_z(r)}{H_\varphi(r)}. \quad (10)$$

For the part of the capacitor filled with the substance (neglecting the dielectric loss)

$$Z(r_1) = \frac{d}{i2\pi} \frac{J_0(k\sqrt{\varepsilon'}r_1)}{k\sqrt{\varepsilon'}r_1 J_1(k\sqrt{\varepsilon'}r_1)} = \frac{1}{i\omega C'_1} \quad (11)$$

where

$$C'_1 = \frac{\sqrt{\varepsilon'}J_1(k\sqrt{\varepsilon'}r_1)}{1.8kdJ_0(k\sqrt{\varepsilon'}r_1)} \text{ (pF)}.$$

The impedance of the whole capacitor is given by the equation

$$Z(r_2) = \frac{d\omega}{i2\pi x_2} \times \frac{N_1(x_2)J_0(x_2^2) - C'_1 \frac{d\omega^2}{2\pi x_1} [N_0(x_1)J_0(x_2) - J_0(x_1)N^2(x_2)] - N_0(x_2) - N_0(x_2)J_1(x_1)}{C'_1 \frac{d\omega^2}{2\pi x_1} [J_0(x_1)N_1(x_2) - N_0(x_1)J_1(x_2)] + N_1(x_1)J_1(x_2) - J_1(x_1)N_1(x_2)} = \frac{1}{i\omega C'}. \quad (12)$$

Denoting by  $C_0$  the capacitance for the unfilled part of the capacitor one can obtain a general relationship between the capacitance  $C'$  and the dimensions and permittivity of the sample:

$$C' = (\beta C'_1 + C_0)/(1 - \alpha C'_1) \quad (13)$$

where

$$\alpha = \frac{1.8k^2d}{x_2N_1(x_1)} \left[ N_0(x_1) - \frac{J_0(x_1)}{J_0(x_2)} N_0(x_2) \right]$$

$$\beta = \frac{x^2}{x_1J_0(x_2)N_1(x_1)} [J_0(x_1)N_1(x_2) - N_0(x_1)J_1(x_2)]$$

$$C_0 = \frac{x^2}{1.8k^2d} \left[ \frac{J_1(x_2)}{J_0(x_2)} - \frac{N_1(x_1)J_1(x_1)}{N_1(x_2)J_0(x_2)} \right].$$

After suitable rearrangement of Eq. (12) one obtains the expression for  $C'_1$ :

$$C'_1 = \frac{C' - C_0}{\alpha C' + \beta} = \frac{k \sqrt{\varepsilon'} J_1(k \sqrt{\varepsilon'} r_1)}{1.8 k^2 d J_0(k \sqrt{\varepsilon'} r_1)}. \quad (14)$$

Finally one can obtain the formula which permits the calculation of  $\varepsilon'$

$$\begin{aligned} & \frac{\sqrt{\varepsilon'} J_1(k \sqrt{\varepsilon'} r_1)}{J_0(k \sqrt{\varepsilon'} r_1)} = \\ & = \frac{1.8 k^2 d C' - x^2 \left[ \frac{J_1(x_1)}{J_0(x_2)} - \frac{N_1(x_2) J_1(x_1)}{N_1(x_1) J_0(x_2)} \right]}{\frac{1.8 k^2 d C'}{N_1(x_1)} \left[ N_0(x_1) - \frac{J_0(x_1)}{J_0(x_2)} N_0(x_2) \right] + \frac{x^2}{J_0(x_2) N_1(x_1)} [J_0(x_1) N_1(x_2) + N_0(x_1) J_1(x_2)]}. \end{aligned} \quad (15)$$

The quantity  $C'$  can be directly determined from the measurement of the standing wave ratio  $S$  and the phase shift  $x_0$  [8]:

$$C' = \frac{(S^2 - 1) \tan \frac{2\pi x_0}{\lambda}}{Z_0 \omega \left( 1 + S^2 \tan^2 \frac{2\pi x_0}{\lambda} \right)} \quad (16)$$

where  $Z_0$  is the impedance of the line.

Taking into account that  $C^* = C' - iC''$  and  $C'' = C' \operatorname{tg} \delta$  one can express the loss tangent  $\tan \delta$  of the sample by means of the formula

$$\tan \delta = \frac{C'' \cdot C_x \left\{ 1 - \frac{1.8 k^2 d}{x_1 N_1(x_1)} \left[ N_0(x_1) - \frac{J_0(x_1)}{J_0(x_2)} N_0(x_2) \right] C'_1 \right\}}{C'_1 (C' - C_0)} \quad (17)$$

where  $C_x = \varepsilon' r_1^2 / 3.6d$  is the capacitance of the sample.  $C''$  is connected with the measured quantities  $S$  and  $x_0$  by the following relationship:

$$C'' = \frac{S \left( 1 + \tan^2 \frac{2\pi x_0}{\lambda} \right)}{Z_0 \left( 1 + S^2 \tan^2 \frac{2\pi x_0}{\lambda} \right)}. \quad (18)$$

An analysis of the distribution of the field in the microwave capacitor has shown that Eqs (15) and (17) can be applied in case of systems which satisfy the following conditions:

$$k \sqrt{\varepsilon'} r_1 < 1.5 \quad \text{and} \quad \tan \delta < 0.6.$$

The standing wave ratio was determined by means of the double-minimum method taking into account the corrections of Westphal. The calculations have been carried out using the Elliott 803 computer.

The measurements in the  $K$  band were made by means of the method of Le Bot — Le Montagner [9] with a waveguide line manufactured by UNIPAN (type  $K$ ).

KHM crystals with dimensions greater than  $1 \text{ cm}^3$  were grown by two methods: either by slow temperature decrease or by isothermal evaporation of the solution (for several

weeks). The optimum pH-value is 5.0. The crystals grown had always regular shape and there were no difficulties in cutting out samples with walls perpendicular to the particular axes. In addition the samples were also cut out parallel to the  $b$  and  $c$  axes. The orientation of the samples was determined by means of X-ray diffraction methods.

The method of very slow isothermal evaporation permitted optically uniform crystals to be grown.

### *Results and their discussion*

#### A. Static permittivity of KHM

The results of measurements of the permittivity of variously oriented samples are listed in Table I.

It follows from Table I the principal component of the permittivity tensor which corresponds to the  $c$ -axis has a greater value. There are so far only a few data available about the anisotropy of the permittivity of crystals of no-ferroelectrics with no water contents [10]. In case

TABLE I  
Anisotropy of static permittivity of KHM ( $\nu = 400$  kHz,  $T = 298^\circ\text{K}$ )  $\varphi_1, \varphi_2, \varphi_3$ , are the angles of the normal to the surface of the sample with respect to the crystallographic axes  $c, b, a$ , respectively

$\varphi_1$	$\varphi_2$	$\varphi_3$	$\varepsilon'_{\text{exp}}$	$\varepsilon'_{\text{calc}}$
$0^\circ$	$90^\circ$	$90^\circ$	10.17	
90	0	90	6.34	
90	90	0	4.60	
30	60	90	9.10	9.18
75	15	90	6.50	6.59
90	36	54	5.56	5.74
90	67	23	4.90	4.87

of hydrates large values of permittivity in certain directions are often observed, the dispersion range lying at low frequencies. Some ionic crystals are characterized by high permittivity values which sometimes considerably exceed the square of the refraction index  $n^2$ . For irregular crystals a certain anisotropy is then observed. Such facts are interpreted by high ionic polarizability which should result from an anisotropic distribution of the inter-ionic potential. Such crystals should have a constant value of the permittivity up to the infrared where absorption of the electromagnetic field energy becomes resonant. An analysis of the distribution of ions in the KHM lattice shows that also in this case there exists a considerable anisotropy of the potential which could explain the anisotropy of the permittivity. It seems impossible, however, that the big difference between  $\varepsilon'$  and  $n^2$  would in all cases be produced by anomalously high ionic polarizability. It follows from the studies on ferroelectrics that the value of  $\varepsilon'_\infty$  extrapolated by means of the Cole-Cole arc from measurements in the microwave range is only slightly different from  $n^2$  and is of the order of  $4 \div 5$  [11]. Such small difference between  $\varepsilon'$  and  $n^2$  seems to be reasonable.

### B. Values of $\epsilon^*$ in the high frequency range

Owing to the above-mentioned considerations it seemed interesting to investigate the properties of KHM in the microwave range. Such measurements also seemed to be of interest because of the fact that the highest value of  $\epsilon'$  is consistent with the direction of orientation of the hydrogen bonds and it cannot be ruled out that the high  $\epsilon'_c$ -value is connected with the motion of the proton. The observation of dielectric absorption of Debye type in the microwave range would indicate the existence of approximately equivalent energy minima for various positions of the ions in the lattice.

The results of measurements at frequencies from 1 GHz to 22 GHz for samples cut out perpendicularly to the  $c$ -axis are listed in Table II. Fig. 4 shows the comparison of the

TABLE II

Values of  $\epsilon'$  and  $\epsilon''$  for KHM in the high frequency range at different temperatures

Temperature °K	Frequency (GHz)	$\epsilon'$	$\epsilon''$	$\tau \cdot 10^{12}s$
298	1.0	10.10	0.17	$5.2 \pm 0.8$
	2.0	9.90	0.41	
	3.0	9.95	0.62	
	4.0	9.90	0.76	
	7.7	9.72	1.40	
	8.6	9.70	1.56	
	22.0	8.00	3.05	
273	1.0	10.00	0.23	$6.1 \pm 0.9$
	2.0	9.98	0.43	
	3.0	9.90	0.69	
	4.0	9.86	0.94	
	7.7	9.50	1.70	
	8.6	9.40	1.95	
	22.0	7.25	2.93	
233	1.0	9.58	0.28	$8.0 \pm 1.4$
	2.0	9.56	0.57	
	3.0	9.44	0.83	
	4.0	9.30	1.00	
	7.7	8.82	1.86	
	8.6	8.74	2.08	
	22.0	6.26	2.72	
123	1.0	8.90	0.58	$18 \pm 2.8$
	2.0	8.79	1.06	
	3.0	8.35	1.52	
	4.0	8.15	1.90	
	7.7	6.80	2.45	
	8.6	6.60	2.50	
	22.0	4.70	1.80	



experimental results at  $T = 298^\circ\text{K}$  obtained with two different samples with the theoretical absorption and dispersion curves calculated under the assumption of monodispersive character of relaxation. Using the best fit method for the parameters of the curves the values of  $\epsilon'_\infty$  and  $\tau$  have been found to be 4.02 and  $5.2 \times 10^{-12}\text{s}$ , respectively (calculations were made using the Elliott 803 computer).

Measurements of the index of refraction of light by means of the immersion liquid method have shown that the value of  $n_D$  is only weakly dependent on orientation and amounts to

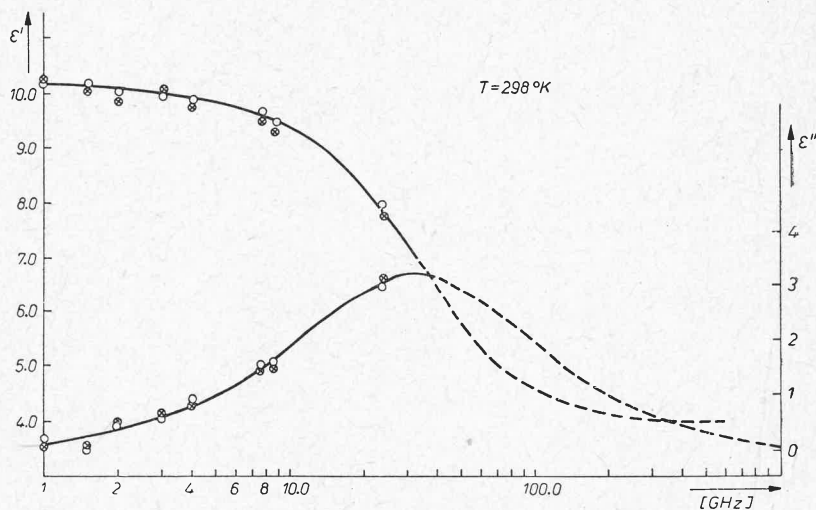


Fig. 4. Absorption and dispersion curves of the KHM crystal at  $298^\circ\text{K}$  in the high frequency range (sample cut out perpendicularly to the  $c$ -axis)

about 1.8. The value of  $\epsilon'_\infty$  is thus only slightly greater than  $n^2$  which can be understood on the basis of the atomic and ionic polarization.

The temperature dependence of  $\gamma_m = \frac{1}{2\pi\tau}$  which is shown in the figure permitted the estimation of the activation enthalpy. The latter amounts to  $2.8 \pm 0.7$  kcal/mole. The charge shift barrier is thus very low.

The increase in  $\epsilon'$  with increasing temperature indicates that the positions of the two minima are not equivalent. Table III gives the comparison of the static permittivity for several temperatures. Using the expression from Ref. [12]

$$\epsilon'_0 - \epsilon'_\infty = \frac{C}{T} \left( 1 + \cosh \frac{\Delta U_0}{kT} \right)^{-1}$$

where  $C$  is a constant it was possible to estimate the energy difference  $\Delta U_0$  between the two minima. It amounts to 0.8 kcal/mole.

It is as yet not possible to explain the mechanism of the observed dielectric relaxation in KHM. It seems, however, that one should take into account two effects:

- a) a shift of either potassium or maleate ions,
- b) change in the position of the atoms in the hydrogen bond.

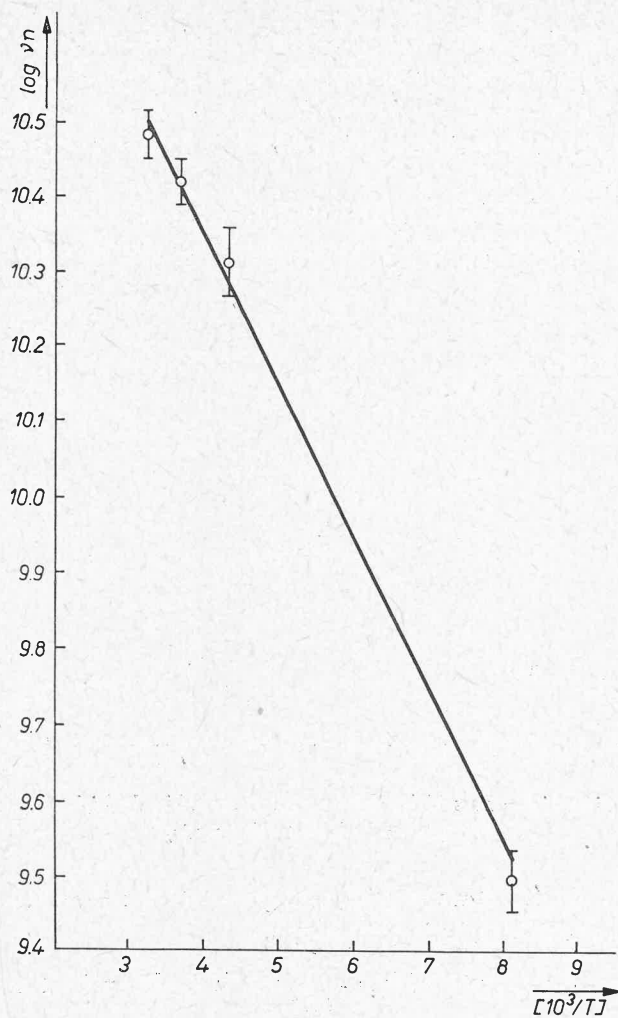
Fig. 5. Dependence of  $\log \nu_m$  on  $1/T$ 

TABLE III

Dependence of  $\epsilon'_0$  on temperature for a sample oriented perpendicularly to the  $c$ -axis

T °K	$\epsilon'_0$
298	10.14
273	10.00
233	9.62
123	9.02

The very low transition barrier could suggest the proton mechanism of dielectric relaxation. On the other hand it is not quite clear why the positions of the minima should not be equivalent.

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