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The Influence of Hydrostatic Pressure
on the Phase Transition Temperature
of Ferroelectric Crystals of the KH₂PO₄-Type

By

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The shift of the transition temperature with pressure for KH_2AsO_4 ($dT_c/dp = (-3.3 \pm 0.2)$ deg/kbar) and for RbH_2PO_4 ($dT_c/dp = (-8.2 \pm 0.3)$ deg/kbar) was determined by dielectric-constant measurements under hydrostatic pressure up to 1.2 kbar. The experimental data are analysed using a formula for the shift of T_c with pressure derived from Kobayashi's theory.

Aus dielektrischen Messungen unter hydrostatischem Druck bis zu 1,2 kbar wurde die Druckverschiebung der Umwandlungstemperatur für KH_2AsO_4 ($dT_c/dp = (-3.3 \pm 0.2)$ grd/kbar) und für RbH_2PO_4 ($dT_c/dp = (-8.2 \pm 0.3)$ grd/kbar) bestimmt. Die experimentellen Daten werden auf der Grundlage einer Formel für die Druckverschiebung der Umwandlungstemperatur, diskutiert die aus der Theorie von Kobayashi abgeleitet wurde.

1. Introduction

KH_2PO_4 is the most typical substance among a group of hydrogen-bonded ferroelectrics. If hydrogen is substituted by deuterium, the transition temperature increases strongly, which has stimulated the experimental and theoretical work on KH_2PO_4 and KD_2PO_4. The influence of hydrostatic pressure on the phase transition of these substances was determined from neutron scattering by Umebayashi, Frazer, Shirane, and Daniels [1]; from dielectric-constant measurements on KD_2PO_4 by Samara [2], and on KH_2PO_4 by Hegenbarth and Ullwer [3]. Based on the tunneling model [4, 5], theoretical investigations on the influence of pressure on the phase transition have been made by Novaković [6] in the molecular-field approximation and by Blinc and Žekš [7] in the cluster approximation of Blinc and Svetina [8].

These authors explained the shift of the transition temperature with pressure in KH_2PO_4 and KD_2PO_4 thereby emphasizing the great importance of the tunneling motion of the hydrogen isotope in the $O-H \cdots O$ bonds for the understanding of the isotope effect.

It is of interest to know how the other constituents of the lattice influence the phase transition and the ferroelectic behaviour. For this reason we measured the dielectric constant as a function of temperature under hydrostatic pressure up to about 1.2 kbar for KH_2AsO_4 and RbH_2PO_4 within the region of phase transition.

From the equation for T_c in Kobayashi's theory for KH_2PO_4-type ferroelectrics [9, 10] we derived a closed expression for the shift of T_c with pressure.

With the aid of this formula, the measuring results are discussed and numerical values for the parameters of the tunnelling model are determined.

2. Experimental

Pressure was generated with the thermal-compressor method. Helium gas was used as the pressure-transmission medium. The apparatus is described in [11]. The pressure was determined by a Bourdon-type manometer to an accuracy of $\Delta p = \pm 16$ bar. For temperature measurement a platinum resistance thermometer was used. The single crystals we received from the Physics Institutes of the Czechoslovakian Academy of Sciences in Prague and the Polish Academy of Sciences in Poznań. The KH_2AsO_4 crystals had a surface of about 30 mm² and a thickness of about 1 mm, and the RbH_2PO_4 crystals were 80 mm² and 1.7 mm, respectively. Silver and gold electrodes have been evaporated under high vacuum. The capacity was measured at a frequency of 800 Hz, at an electric field strength $E < 20$ V/cm for KH_2AsO_4 and $E < 8$ V/cm for RbH_2PO_4, respectively.

3. Results

Fig. 1 and 2 show the anomalies of the dielectric constants in the phase transition region for a KH_2AsO_4 and a RbH_2PO_4 crystal. In both cases, by

Fig. 1. Temperature dependence of the dielectric constant under different pressure for a KH_2AsO_4 crystal in the phase-transition region (10^3 at = 0.981 kbar). Curves 1 to 4: measured with decreasing temperature; curves 1′ and 5: measured with increasing temperature
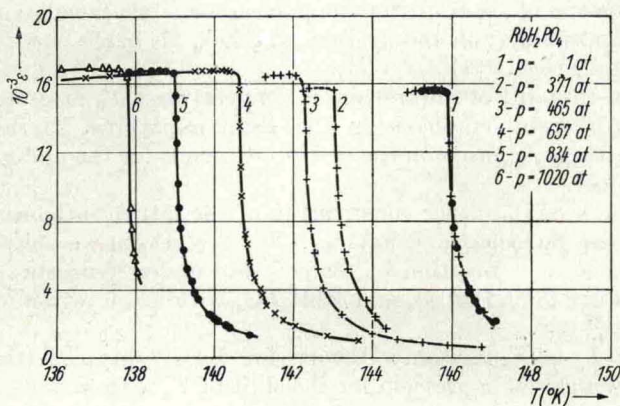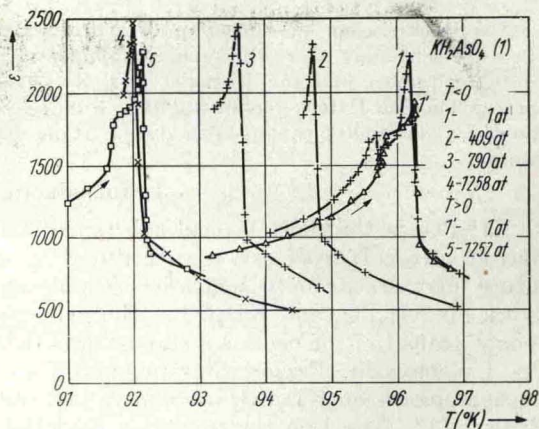

Fig. 2. Temperature dependence of the dielectric constant under different pressure for a RbH_2PO_4 crystal in the phase-transition region, measured with decreasing temperature
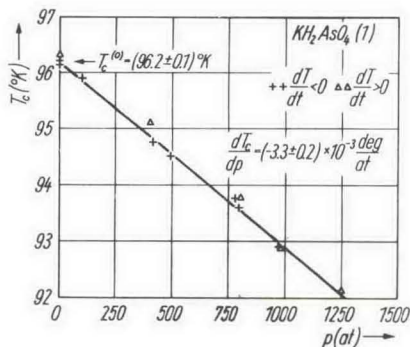
Fig. 3. Pressure dependence of the transition temperature T_c for a KH_2AsO_4 crystal (10^3 at $= 0.981$ kbar)
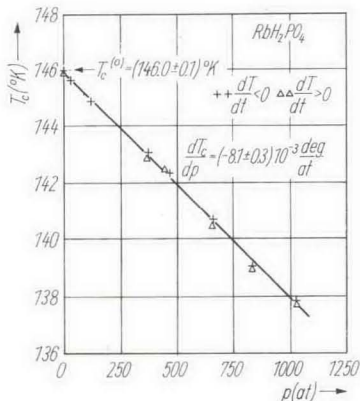
Fig. 4. Pressure dependence of the transition temperature T_c for a RbH_2PO_4 crystal

pressure the phase transition is shifted to lower temperatures with no essential change in the shape of the $\varepsilon(T)$ anomaly. The maximum values of the dielectric constant increase somewhat under pressure influence. Fig. 3 and 4 show the transition temperatures as functions of pressure. Within the measured pressure range a linear dependence was found. In the case of two KH_2AsO_4 crystals ($T_c = 96.2$ °K and 95.6 °K, respectively) the shifts of T_c with pressure, $dT_c/dp = (-3.4 \pm 0.2)$ deg/kbar and (-3.2 ± 0.2) deg/kbar, were observed. In the case of the RbH_2PO_4 crystal ($T_c = 146$ °K) we obtained $dT_c/dp = (-8.2 \pm 0.3)$ deg/kbar. These shifts and that for KH_2PO_4 [3] are listed in Table 1, and plotted in Fig. 5 against the transition temperature at atmospheric pressure. The measured points lie almost in a straight line. This may be accidental, and it should be tested experimentally with the other isomorphous ferroelectric substances, e.g. RbH_2AsO_4 ($T_c = 110$ °K).

Table 1

Experimental data of KH_2AsO_4, KH_2PO_4, and RbH_2PO_4 and derived data about the tunneling energy Ω and the interaction parameter J (cf. the text). Data of the deuterated crystals are designated by the index D

	KH_2AsO_4	KH_2PO_4	RbH_2PO_4
T_c (°K)	96	122	146
$T_{c, D}$ (°K)	162	213	218
$-\dfrac{dT_c}{dp} \left(\dfrac{\text{deg}}{\text{kbar}}\right)$	3.3	5.7 [3]	8.2
$S_1(T_c)$ (10^{-3} kbar^{-1})	1.16*)	1.13*)	1.21*)
Ω/kT_c	0.45	0.65	0.77
Ω (cm^{-1})	30	55	78
$4\,\Omega/J$	0.42	0.57	0.65
J_D/J	1.57	1.53	1.26

*) Calculated by linear extrapolation to the transition temperature from experimental data of Haussühl [16].

4. Discussion

In the theoretical explanation of the pressure dependence of T_c our approach is similar to those of Novaković [6] and Blinc and Žekš [7], but our derivation is based on Kobayashi's dynamic theory [9, 10] which at present seems to be the most satisfactory theory for KH_2PO_4-type ferroelectrics. In this theory the total Hamiltonian is of the form $H = H_P + H_L + H_{PL}$, H_P describing the proton tunneling motion in the double minimum potentials along the O–H···O bonds, H_L the lattice vibrations, and H_{PL} the coupling between tunneling motion and lattice vibrations. The tunneling term is generally expressed as [5]

$$H_P = -2\,\Omega\,\sum_l X_l - \frac{1}{2}\,\sum_{ll'} J_{ll'}\,Z_l\,Z_{l'}\,, \tag{1}$$

X_l and Z_l being components of the pseudo-spin, Ω the tunneling energy, and $J_{ll'}$ the parameters of the proton–proton coupling which favours the formation of the ferroelectric state.

The transition temperature T_c is defined as the temperature at which the frequency of the ferroelectric mode, which is a coupled proton tunneling and optical lattice vibration mode, tends to zero. T_c is determined by the equation [9, 10]

$$4\,\Omega - J \tanh \frac{\Omega}{kT_c} = 0\,, \tag{2}$$

where $J = \sum_{l'} J_{ll'} + J_L$ and k is Boltzmann's constant. The part J_L which results from the proton–lattice coupling has been explicitly given by Kobayashi [9] and Cochran [10]. For $J_L = 0$ equation (2) reduces to the equation for T_c in the molecular-field approximation of the tunneling model [12]. This approximation has been used by Novaković [6] for his investigation assuming J to be pressure-independent.

In the case of pressure application, the distance $2\,\zeta$ between the two equilibrium sites in the double minimum potential is reduced, the values Ω and J are varying, resulting in a variation of T_c. Hence we have

$$\frac{\mathrm{d}T_c}{\mathrm{d}p} = \left(\frac{\partial T_c}{\partial J}\,\frac{\partial J}{\partial \zeta} + \frac{\partial T_c}{\partial \Omega}\,\frac{\partial \Omega}{\partial \zeta}\right)\frac{\partial \zeta}{\partial p}\,. \tag{3}$$

From equation (2) we derive

$$\frac{\partial T_c}{\partial J} = \frac{k}{4}\left(\frac{T_c}{\Omega}\sinh\frac{\Omega}{kT_c}\right)^2 \tag{4}$$

and

$$\frac{\partial T_c}{\partial \Omega} = -\frac{T_c}{\Omega}\left(\frac{kT_c}{2\,\Omega}\sinh\frac{2\,\Omega}{kT_c} - 1\right) \leqq 0\,. \tag{5}$$

The dependence of J on ζ is known from the papers of Blinc et al. [7, 8] and Kobayashi [9]: $J \sim \zeta^2$, thus $\mathrm{d}J/\mathrm{d}\zeta = 2\,J/\zeta$. For the simple double minimum potential composed of the potentials of two harmonic oscillators (mass m,

ground state energy E_0, distance $2\,\zeta$) in case of $q^2 \gg 1$, the tunneling energy is given by [6, 7]

$$\Omega = \frac{\hbar^2}{\sqrt{\pi}\,m\,\zeta^2}\,q^3 \exp\left(-q^2\right)\,; \qquad q^2 \equiv \frac{2\,m\,E_0\,\zeta^2}{\hbar^2}. \tag{6}$$

Thus,

$$\frac{\mathrm{d}\Omega}{\mathrm{d}\zeta} = -\left(2\,q^2 - 1\right)\frac{\Omega}{\zeta}. \tag{7}$$

By substituting (4), (5), (6), and (7) in (3) we find

$$\frac{\mathrm{d}T_c}{\mathrm{d}p} = \frac{T_c}{\zeta}\frac{\mathrm{d}\zeta}{\mathrm{d}p}\left[\frac{kT_c\,J}{2\,\Omega^2}\left(\sinh\frac{\Omega}{kT_c}\right)^2 + \left(2\,q^2 - 1\right)\left(\frac{kT_c}{2\,\Omega}\sinh\frac{2\,\Omega}{kT_c} - 1\right)\right]. \tag{8}$$

We introduce $\zeta^{-1}\,\mathrm{d}\zeta/\mathrm{d}p = -\alpha\,S_1$ with $S_1 = a^{-1}\,\mathrm{d}a/\mathrm{d}p = s_{11} + s_{12} + s_{13}$, and $\alpha = (a/\zeta)\,\mathrm{d}\zeta/\mathrm{d}a$, a being the lattice constant, and s_{ij} the elastic compliances. Finally, after eliminating J by means of equation (2) we obtain

$$\frac{\mathrm{d}T_c}{\mathrm{d}p} = -\alpha\,S_1\,T_c\left[2 + \left(2\,q^2 + 1\right)\left(\frac{kT_c}{2\,\Omega}\sinh\frac{2\,\Omega}{kT_c} - 1\right)\right]. \tag{9}$$

The second term in the square bracket of equation (9) describes the effect of proton tunneling on the shift of T_c with pressure. It is a positive quantity and may be neglected under the condition $\Omega/kT_c \ll 1$ which can be considered to be fulfilled for the deuterated crystals.

Since α is a positive quantity ($\mathrm{d}\zeta/\mathrm{d}a > 0$), the transition temperature T_c, according to equation (9), is always shifted towards lower temperatures with pressure. At given T_c the shift increases with increasing Ω. In Fig. 5, the pressure shift $-\mathrm{d}T_c/\mathrm{d}p$ is represented as a function of T_c according to equation (9), with $\alpha\,S_1 = 9.4 \times 10^{-3}\,\mathrm{kbar^{-1}}$. This value has been chosen so that for KD_2PO_4 ($\Omega/kT_c \ll 1$) equation (9) gives $\mathrm{d}T_c/\mathrm{d}p = -3.9\,\mathrm{deg/kbar}$ ($T_c = 208\,°K$) which was measured by Samara [2]. The value of $\alpha\,S_1$ found for KD_2PO_4 can also be taken in good approximation for KH_2PO_4. Then equation (9) can be used to determine Ω from the measured value of $\mathrm{d}T_c/\mathrm{d}p$. The necessary relation between q and Ω is given by equation (6). For KH_2PO_4 we use $\zeta = 0.19\,Å$ [13] and obtain $\Omega/k = 79\,°K$ or $\Omega = 1.09 \times 10^{-14}\,\mathrm{erg}$. This
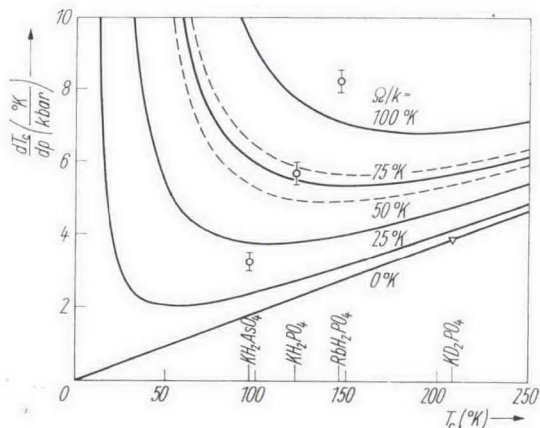

Fig. 5. Pressure shift $-\mathrm{d}T_c/\mathrm{d}p$ as a function of the phase-transition temperature T_c according to (9) for various values of Ω. The curves were fitted to the measured value [2] for KD_2PO_4 (cf. the text). For the parameter value $\Omega/k = 75\,°K$ also curves with $\zeta = 0.15\,Å$ and $\zeta = 0.25\,Å$ in dashed lines are given in addition to the curve with $\zeta = 0.19\,Å$

value is smaller by a factor of about 3 to 4 than those values given by Blinc et al. [7, 8] and Novaković [6]. It is, however, almost the value $\Omega = 1.0 \times 10^{-14}$ erg which has recently been determined by Cochran [10] from Raman-scattering data of Kaminow and Damen [14].

Since the values of S_1 for KH_2AsO_4, KH_2PO_4, and RbH_2PO_4 differ only slightly (cf. Table 1), we used for KH_2AsO_4 and RbH_2PO_4, too, the value $\alpha S_1 = 9.4 \times \times 10^{-3}$ kbar^{-1} determined for KD_2PO_4. In this way, we found $\Omega/k = 43$ °K for KH_2AsO_4, and $\Omega/k = 112$ °K for RbH_2PO_4. In this estimate we assumed the same value for ζ as for KH_2PO_4, because no experimental data for ζ are available for KH_2AsO_4 and RbH_2PO_4. However, this assumption is not so important because there is only a weak dependence of the estimated values of Ω on ζ. This is shown in Fig. 5 where for the parameter value $\Omega/k = 75$ °K also curves with $\zeta = 0.15$ and 0.25 Å are given as dashed lines.

If instead of the dielectric data for the shift of T_c with pressure of KH_2PO_4 and KD_2PO_4 the neutron diffraction data of Umebayashi et al. [1], $dT_c/dp = = -4.5$ deg/kbar and $dT_{c, D}/dp = -2.6 \times 10^{-3}$ deg/kbar, are used, the same method results in $\alpha S_1 = 6.1 \times 10^{-3}$ kbar^{-1} and $\Omega/k = 93$ °K. The Ω-value does not differ essentially from that obtained from dielectric data. For reasons of comparison, data from dielectric-constant measurements have only been taken in Fig. 5.

From (6), with $q^2 \sim m^{1/2} \zeta^2$, the ratio of the tunneling energies follows: $\Omega_D/\Omega = 2^{-1/4} (\zeta_D/\zeta) \exp \{- q^2 [\sqrt{2} (\zeta_D/\zeta)^2 - 1]\}$, the quantities of the deuterated crystal having the index D. Assuming $\zeta_D/\zeta = 1.0$ to 1.1, for all three substances $\Omega_D/\Omega < 0.2$ and $\Omega_D/kT_{c, D} < 0.1$ result. This justifies our neglect of the influence of tunneling on the shift of T_c for the deuterated crystals as assumed above. For these crystals, therefore, the linear relation $dT_{c, D}/dp \approx \approx -0.02 \, T_{c, D}$ kbar^{-1} is expected to hold.

Contrary to our determination of the value of α from experimental data Novaković [6], and Blinc and Žekš [7] determined α by a-priori assumptions which, however, resulted in very different values for α. Novaković puts $d\zeta/da = \zeta/a$, i.e. $\alpha = 1$. Blinc and Žekš assume that with compression the O–H···O bonds (two per lattice constant) are shortened only and that within these bonds the distance 2ζ between the potential minima is reduced only, i.e. $d\zeta = da/4$ or $\alpha = 9.5$. This value is approximately the same we used ($\alpha = 7.8$ to 8.3). According to the semi-empirical model for the O–H···O bonds of Lippincott and Schroeder [15] one might expect $d\zeta/da \approx 0.29$ or $\alpha \approx 11$. A direct experimental determination of α (by neutron-diffraction measurements under pressure) would be of interest because the a-priori choice of α is affected with a considerable uncertainty.

Having determined Ω/kT_c, Ω/J is directly obtained from (2). For the deuterated crystals, (2) simplifies to $J_D \approx 4 \, kT_{c, D}$. In Table 1, values of $4 \, \Omega/J$ and J_D/J are also listed. Obviously, the ferroelectric interaction in the deuterated crystals is stronger; this fact corresponds qualitatively to the theoretical expectations

Within the range of the applied pressures up to 1.2 kbar, no deviation from the linear dependence between T_c and p was observed. From the above mentioned dependence of the values Ω and J on ζ, according to (2), we have to expect, however, that due to tunneling, at higher pressures the transition temperature T_c decreases more rapidly, and ferroelectricity disappears com-

Fig. 6. Qualitative dependence of the transition temperature T_c on the pressure p according to (2). The deviation from the linear dependence (dashed line) at high pressures is caused by the proton tunneling motion
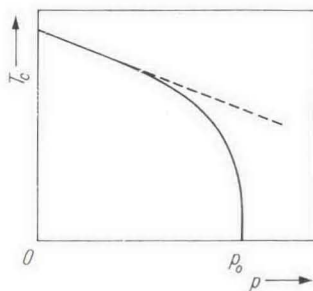
pletely at a certain pressure p_0 at which $-\mathrm{d}T_c/\mathrm{d}p$ tends to infinity. This is qualitatively shown in Fig. 6. Deviations from the linear dependence between T_c and p for the three ferroelectrics of Table 1 may be expected above 3 kbar according to our estimated Ω- and J-data, and the p_0-values are to be expected in the range from 5 to 10 kbar. Experiments for investigating these predictions are under preparation.

Acknowledgement

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