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

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

Thus,

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

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

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

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

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

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 $\mathrm{d}T_c/\mathrm{d}p = -3.9$ 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 $\Omega = 1.09 \times 10^{-14}$ erg. This

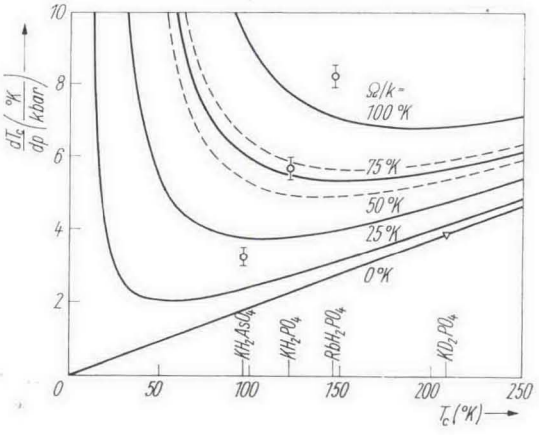

Fig. 5. Pressure shift $-\mathrm{d}T_c/\mathrm{d}p$ as a function of the phase-transition temperature T_c according to (9) for various values of Ω. The curves were fitted to the measured value [2] for KD_2PO_4 (cf. the text). For the parameter value $\Omega/k = 75$ °K also curves with $\zeta = 0.15$ 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 $\alpha\, S_1 = 9.4 \times \times 10^{-3}\,\mathrm{kbar}^{-1}$ 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], $\mathrm{d}T_c/\mathrm{d}p = = -4.5$ deg/kbar and $\mathrm{d}T_{c,D}/\mathrm{d}p = -2.6 \times 10^{-3}$ deg/kbar, are used, the same method results in $\alpha\, S_1 = 6.1 \times 10^{-3}\,\mathrm{kbar}^{-1}$ 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 $\mathrm{d}T_{c,D}/\mathrm{d}p \approx \approx -0.02\, T_{c,D}\,\mathrm{kbar}^{-1}$ 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 $\mathrm{d}\zeta/\mathrm{d}a = \zeta/a$, 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. $\mathrm{d}\zeta = \mathrm{d}a/4$ 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 $\mathrm{d}\zeta/\mathrm{d}a \approx 0.29$ 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-