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 $\alpha\, S_1 = 9.4\times10^{-3}\,\mathrm{kbar}^{-1}$. 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 $\Omega = 1.09\times10^{-14}$ erg. This

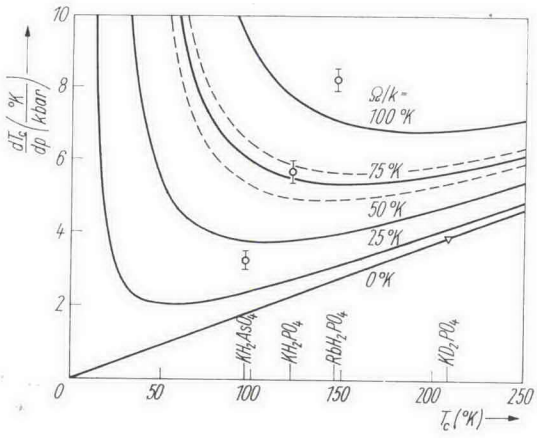

Fig. 5. Pressure shift $-\mathrm{d}T_c/\mathrm{d}p$ as a function of the phase-transition temperature T_c according to (9) for various values of Ω. The curves were fitted to the measured value [2] for KD_2PO_4 (cf. the text). For the parameter value $\Omega/k = 75$ °K also curves with $\zeta = 0.15$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