Fig. 3. Pressure dependence of the transition temperature T_c for a KH_2AsO_4 crystal (10^3 at = 0.981 kbar)
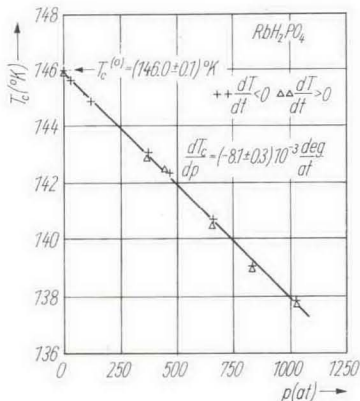

Fig. 4. Pressure dependence of the transition temperature T_c for a RbH_2PO_4 crystal

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
$-\dfrac{dT_c}{dp}\left(\dfrac{deg}{kbar}\right)$	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$\cdots$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

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

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 $dJ/d\zeta = 2\,J/\zeta$. For the simple double minimum potential composed of the potentials of two harmonic oscillators (mass m,