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 $J = \Sigma_{l'} J_{ll'} + J_L$ 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

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

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,