Above 2 GPa, the phase diagram of ice is characterized by the VII-VIII order-disorder transition. The observed pressure dependence of the Curie temperature is discussed in connection with the physical nature of the proton disorder in ice VII.

The phase diagram of ice above 2 GPa exhibits only two phases: ice VII, which is a proton-disordered solid, and ice VIII, obtained on lowering temperature, which is a proton-ordered solid. These solids are respectively cubic (paraelectric) and tetragonal (antiferroelectric). The transition line between these two forms was determined by Raman scattering. The result for H_2O is plotted in Fig. 1. Three regimes are observed for the pressure dependence of the transition temperature, or Curie temperature T_c. Up to 15 GPa T_c is to a first approximation not pressure dependent. From 20 to 50 GPa T_c decreases linearly with pressure, and around 60 GPa it drops to 0 K.

Under very high pressure the proton potential is expected to be strongly modified. Accordingly and depending on the pressure range, different types of disorder dominate in ice VII. Each type of disorder involves a specific fluctuation for the molecular dipoles which conditions the transition: specifically the balance between the disorder term and the dipolar interaction, which tends to order the system, determines the transition temperature T_c. This viewpoint is discussed qualitatively further on.

Around 2.4 GPa ice VII, as shown from neutron diffraction, is orientationally disordered. In the first regime (2 to \( \sim \) 15 GPa), the transition appears to be driven by a pure thermal effect: T_c is pressure-independent. This suggests that in this pressure range, thermal activation dominates with a resulting constant potential barrier for rotational disorder. As pressure increases the potential barrier for rotational disorder must increase and a change of regime is expected. Actually this change occurs over a narrow pressure range and above 20 GPa, T_c, as mentioned above, decreases linearly. This regime and the one observed at 60 GPa are assigned to classical and quantum mechanisms, respectively. This assignment is supported by the following arguments:

i) The behaviour of T_c in ice above 20 GPa shows strong analogies with that observed in a variety of ferroelectrics, for instance KH_2PO_4. The assignment given above fits within the framework of theoretical works developed for ferroelectrics. On decreasing the dipolar interaction, using an external parameter e.g. pressure (see point ii), the temperature of the ferro-paraelectric transition decreases. At high temperature the slope is linear, on lowering temperature, and in the region where zero-point motions play a role (quantum regime), T_c decreases rapidly.

ii) A more quantitative support is given by our analysis of the VII-VIII transition using the pseudo-spin formalism. First, it is shown that in the linear regime the transition is described by an Ising model i.e. the system orders below T_c given by

\[
T_c \sim J/k_B
\]  

(1)
where \( J \) is the dipolar interaction. This quantity which represents the long-range interaction is expected to decrease with pressure due to the contraction of the O-H–O bonds. From the fit of our transition data points it is found that \( J \) is to a first approximation linear with pressure, which accounts (Eq. 1) for the linear pressure dependence of \( T_c \); however a better representation is given by a quadratic function. It is also found that the O-H covalent bond length has a negligible pressure dependence up to \(~45\) GPa. This unexpected feature was also found with \textit{ab initio} computations\(^8\) and confirmed by neutron diffraction\(^9\) up to \( 20\) GPa the upper limit of the pressure range investigated. Secondly, in this formalism, the drop of \( T_c \) at \( 60\) GPa is accounted for by a rapid increase of the tunnelling effect which prevents the formation of the proton-ordered solid VIII even at \( 0\) K. It is likely that in this region the proton zero-point motion may also cause the transition to the quantum regime.\(^7\)

In the classical regime the vanishing of the long-range order at \( T_c \) is due to the thermal energy which becomes larger than \(~ J \) (Eq. 1). At this point it must be recalled that due to the ice rule, there exists a short-range order in ice VII. The dipole moments of the short-range order domains are disordered and compared to ice VIII, ice VII adopts a dipolar glass behaviour. In this range the tunnelling energy, which may be estimated \textit{e.g.} with the pseudo-spin formalism, is small compared to the dipolar interaction but may play a role in the reordering of the nanodomains. This feature is very likely to be one of the keys of the microscopic mechanism of the VII-VIII transition in this range.

On approaching \( 60\) GPa, the tunnelling effect is enhanced due to the decrease of the proton double-well potential barrier and is no more negligible compared to \( J \). This causes proton delocalization at a critical pressure above which it is not possible to stabilize the ordered solid even at low temperature. This pressure boundary which very likely extends above \( 100\) K as shown in Fig. 1 corresponds to the transformation to a quantum paraelectric solid characterized by strong proton quantum fluctuations. This solid does not differ from ice VII concerning the oxygen sublattice, as demonstrated by x-ray diffraction.\(^10,11\) Provided that the proton zero-point energy is still smaller than the barrier height, the proton density function in this range may have two maxima. Due to the effect of the zero-point motion, this function would be peaked at the bond center at higher pressure. This second step is closer to the expected ice X structure (Cu\(_2\)O). The approach of the cuprite structure following these two steps (disordered X–X) was proposed through various theoretical approaches.\(^12,13\)

Investigations with Raman scattering in the region of ice VII, showed no observable Raman feature above \( 50\) GPa. On the other hand infrared spectroscopy was found to be very useful in this range and recent results seem to confirm the above scheme.\(^14,15\) Specifically at \( 300\) K, very broad bands which suggest rather a symmetric loosely bonded solid are observed around \( 62\) GPa; these bands become better resolved at \( 90\) GPa.\(^14\) It is to be noted that the treatment of our x-ray data shows a slight anomaly around \( 70\) GPa which is very likely to be related to this transformation.\(^11\) Till now no significant feature was observed using powder x-ray diffraction at higher pressure where the transformation to ice X is expected. However a strong increase in infrared absorption was observed at \( 150\) GPa,\(^15\) also in this range specific features were observed using single crystal x-ray diffraction on ice at room temperature.\(^16\)

The Raman and x-ray investigations were performed with J.C. Chervin, B.Canny, E. Wolanin, M. Gauthier (Physique des Milieux Condensés, Paris), D. Häusermann, M. Hanfland (ESRF, Grenoble) and the neutron diffraction experiments by J.M. Besson, S. Klotz (Physique des Milieux Condensés, Paris), G. Hamel (Département Hautes Pressions, Paris), R. J. Nelmes, J.S. Loveday (Department of Physics and Astronomy, Edinburgh).

I am indebted to W. Holzapfel for helpful discussions.
Figure 1.
Ice VII-VIII transition line, pressure p(GPa) as function of temperature (K).
Hollow squares : experimental points for H2O.
Solid line : fit.
Dashed-dotted line : D2O.
(1), (2) and (3) : orientational disorder, classical regime, and quantum regime respectively.
Stars : locus of the features observed with powder x-ray diffraction.
Hatched zones : transition regions between regimes (1), (2), and (3).
IR : locus of the features observed with IR spectroscopy.14
X : expected pressure range for a proton density function peaked at the O-O center.13

References
2 G.A. Samara, Physica B 150, 179 (1988) and ref. therein.
3 G.A. Samara, P.S. Peercy, Solid State Phys. 36, 1 (1981) and ref. there in.
7 Ph. Pruzan, E. Wolanin, M. Gauthier, J.C. Chervin, B. Canny, D. Häusermann, M. Hanfland, J.
cference AIRAPT 16 & HPCJ 38 (Kyoto, Aug. 25-29, 1997).
11 E. Wolanin, Ph. Pruzan, J.C. Chervin, B. Canny, M. Gauthier, D. Häusermann, M. Hanfland,
13 M. Parrinello (this conference)
15 R. Hemley (this conference),
A.P. Goncharov, V.V. Struzhkin, M.S. Somayazulu, R.J. Hemley, H.K. Mao, Science, 273,
218 (1996).
16 P. Loubeyle, R. Le Toullec, M. Hanfland, D. Häusermann, Joint conference AIRAPT 16 & HPCJ
38 (Kyoto, Aug. 25-29, 1997).