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A HIGH PRESSURE SPECTROSCOPIC STUDY ON THE ICE III – ICE IX, DISORDERED – ORDERED TRANSITION

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ABSTRACT

The only published data on the disordered-to-ordered ice III to ice IX transition refers to measurements of dielectric constant. Raman spectra of ice III and ice IX were recorded under a pressure of 0.3 GPa for temperatures in the ramge 250 to 130 K. They clearly show a transition that is predominantly of the disordered-ordered type. Raman spectra in the frequency range 15–4000 cm^{-1} will be shown but special attention will be given to two translational lattice modes at about 190 cm^{-1} and 65.5 cm^{-1} which show somewhat unusual behaviour. Small discontinuities in the frequency versus temperature plots suggest that there is a small discontinuous decrease in the volume during the ice III to ice IX transition.

INTRODUCTION

Ice III and ice IX are thought to be orientationally disordered and ordered versions of the same structure. Ice III is the most accessible high pressure form of ice. It can be made in a variety of ways, the most usual one being from ice I_h by raising the pressure to about 0.21 GPa at a temperature below the liquid-ice I_h-ice III triple point (Fig. 1). Ice IX can be obtained by cooling ice III at a rate not less than 1-2 K/min to a temperature below about 170 K (Fig. 1.).

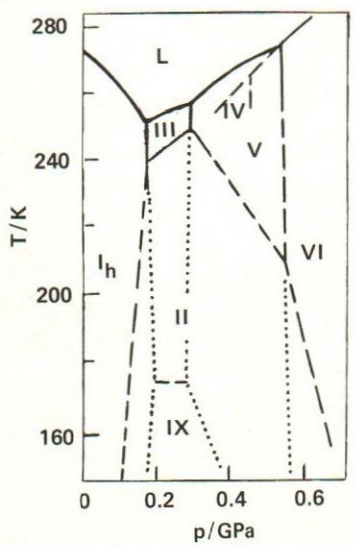

Fig. 1. Details of the phase diagram of H_2O

Ice III, the high temperature disordered form was distinguished from ice IX, the low temperature ordered form by measuring the dielectric properties of ice III (ref.1) at a constant pressure (0.3 GPa) in the temperature range between 260 K and 120 K. A gradual transition from orientationally disordered, ice III to an orientationally ordered phase was found. The new phase was designated as ice IX.

As a part of the general study on the high pressure forms of ice in their true thermodynamic regions of stability (refs.2,3) we have recorded the Raman spectra of ices III and IX of H_2O, D_2O and $H_2{}^{18}O$ and dilute solutions of H_2O in D_2O and D_2O in H_2O. In this paper we report the spectroscopic evidence for the gradual transition of disordered ice III to ordered ice IX. The ice III – ice IX transition was studied as a function of temperature at a constant pressure of about 0.3 GPa.

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A plot of frequencies versus temperature showed a discontinuity in most of the curves which indicated a discontinuous decrease in the volume during the ice III to ice IX transition.

EXPERIMENTAL

A specially designed high pressure, low temperature liquid Raman cell (described in ref. 3.) was used for pressures up to about 1.0 GPa and temperatures down to 130 K. A termocouple and oil pressure gauge were used for temperature and pressure measurements. The pressure was cheked against the frequency shift of the R_1 ruby fluorescence band, which gave a pressure determination in our experiments to an accuracy of $\pm$ 0.02 GPa.

Raman spectra were recorded with a Spex Ramalog 5M System with a Spectra Physics Ar^+ ion laser, using the 488.0 nm line at powers up to 1.2 W.

H_2O ices were made from redestilled, deionized water. D_2O ices were made from 99.8 % D_2O supplied by GOSS Chemicals Ltd.

RESULTS AND DISCUSION

The Raman spectra of ice III and ice IX (H_2O) in the region of the O–H stretching vibrations and in the region of rotational and translational vibrations are shown on Fig. 2. Similarities in these spectra clearly indicate that the vibrations retain the same character in the two phases. A detailed assignment of the Raman and infrared spectra of ice IX at atmospheric pressure and temperature between 100 K and 25 K (refs. 4, 5) has been published recently using normal coordinate, bond moment and bond polarizability calculations.

Our Raman spectra of ice III and ice IX have particular value for testing and developing the theories on optical spectra of orintationally disordered crystals proposed and developed in the last ten to fifteen years by Whalley, Bertie and Klug (refs. 6, 7, 8). The disordered-to-ordered transition, ice III – ice IX, seems to be perfect example to test and extend this theory.

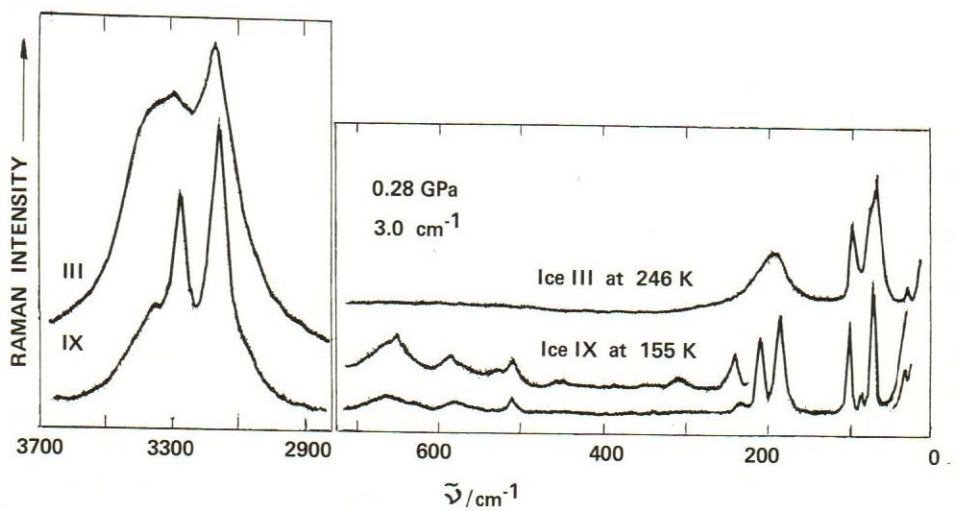

Fig. 2. The Raman spectra of ice III(H_2O) and ice IX(H_2O), at pressures, temperatures and resolutions as indicated.

Unusual behaviour* of the bands at about 190 cm^{-1} and 65.5 cm^{-1} in ice III (H_2O) (Fig. 2.) suggests that those two bands are the most instructive to observe during the ice III – ice IX transition. The influence of the ordering is the most apparent in the change of the shape in these bands during the ice III – ice IX transition (see Fig. 2 and Fig. 3).

Raman spectra showing the gradual transition of ice III to ice IX for both H_2O and D_2O are shown in Fig. 3 for the region of the translatory vibrations. Those spectra clearly confirm the previous results of the dielectric measurements of the ice III – ice IX transition, (ref. 1), in which it was found that the limiting low–frequency dielectric constant of ice III drops rapidly between 210 K and 165 K.

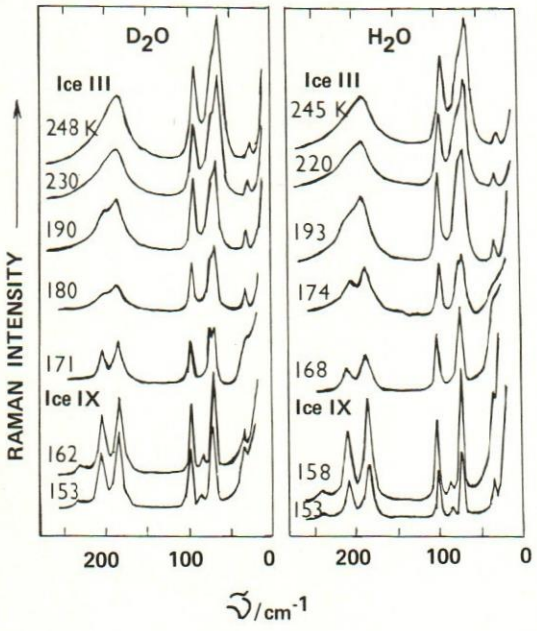

Fig. 3. The Raman spectra of ice III to ice IX transition in the region 0–250 cm^{-1} at pressures and temperatures as indicated (res. 3.5 cm^{-1}).

Corresponding behaviour can be seen in the Raman spectra in Fig. 3. The sharpening of the bands during the transition (which clearly indicates disordered-to-ordered transition) and the appearence of new bands occurs over the similar range of temperature.

Our Raman spectra of ice III, ice IX and the ice III – ice IX transition suggest:

(i) Ice IX was obtained from ice III only when the cooling rate was not less than 1–2 K/min and the pressure was kept in the range 0.27 to 0.32 GPa, otherwise ice II was formed.

On heating, ice IX always transformed into ice III at a temperature of 180 K and then ice III always transformed into ice II between 190 and 210 K. This kind of behaviour has been also observed in the dielectric measurements (ref. 1). On further heating at a constant pressure, ice III reappeared at a temperature of about 250 K.

(ii) Occasionally during the ice III – ice IX transition, ice IX was accompanied by small amount of ice II. The existence of ice II was identified by the appearence of the band at about 150 cm^{-1}, which has a maximum intensity in the Raman spectrum of ice II (see Fig. V.6. in ref. 3).

(iii) In contrast with ice IX, ice III could be obtained in a variety of ways. Besides the ice I_h–ice III transition (Fig. 1), in which ice is usually made, it appears as an intermediate phase in ice I_h–ice II transition at temperatures as low as 210 K. Ice III was also formed in our experiments by de–pressurising ice V and by warming ice II.

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* All the results of the temperature and pressure measurements in ice III and in ice IX are collected and presented in details in Table V.2. in ref. 3.

Thus ice II was formed during the ice III – ice IX transition and, on the other hand, ice III was formed during ice I_h – ice II transition. This implies that the molecular arrangements within these different structures must have some special inter–relationships.

The breaks in the lines of the ν versus T curves (Fig. 4) during the ice III – ice IX transition are somewhat surprising, in that the O–H stretching frequency seem to suggest a slight increase in volume whereas the lattice modes seem to suggest a clear decrease. The lattice mode data seems to be the more convincing, but it is in disagreement with the reports by Whalley et al. (ref. 1) who have found an increase in volume of about 0.1 % in the ice III – ice IX transition.

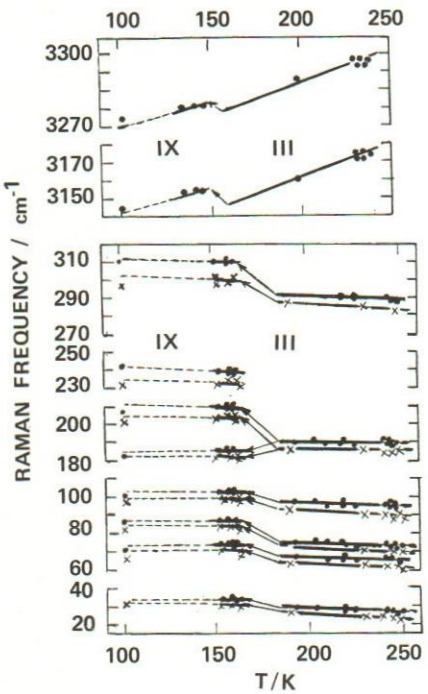

Fig. 4 Temperature dependence of the O–H stretching and translational vibrations in the ice III – ice IX transition at 0.28 GPa. ($\bullet$ – H_2O, $\times$ – D_2O).
Points at 100 K are from refs. 4 and 5.

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