Abstract No.: Fran0539

The melting curve, bulk modulus and thermal expansivity of Ice VII to 65 GPa.

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Beamline: X17C

Introduction: A recent study [1] obtained data on the melting curve of Ice VII up to 13.09 GPa and claimed the melting curves determined by others [2-4], all of which are congruous, are erroneous. The difference is not slight, with melting a projected melting temperature difference of ~300 K at 40 GPa. The study presented here sought to determine the *PVT* properties of Ice VII at pressures > 20 GPa and especially along the melting curve at high-pressures to further constrain the equation of state of fluid H_2O and to test the models of previous workers derived from low-pressure data and extrapolated to high-pressures.

Methods and Materials: A Mao-Bell type diamond anvil cell with an external heater was used in this study. The temperature of the experiment was determined by placing a type-S thermocouple (Pt-$Pt_{0.9}Rh_{0.1}$) between the diamond anvil and Re-gasket, directly against the surface of the diamond. Temperatures were kept constant to ±5 K during data collection, whereas the uncertainty associated with the thermocouple itself is ±2 K over the range of temperatures in this study. The diffraction pattern of H_2O and gold were monitored during the experiment. The unit cell of gold determined from the diffraction lines was used in conjunction with a previously established *PVT* equation of state [5] so that gold acted as an internal pressure calibrant. The 111, 200 and 220 diffraction lines of gold and 110 line of Ice VII were present in most analyses.

Results: The 110 diffraction line was the strongest diffraction line for Ice VII under almost all conditions and was the primary line used in calculation of the unit cell volume, however, the 200 diffraction line was also used, in addition to the 110 line, whenever possible. There was good agreement in the Ice VII unit cell volumes calculated from each of the diffraction lines. The compression data were collected for Ice VII from 6.57 to 60.52 GPa and were fit to a third-order Birch-Murnaghan equation of state (Birch, 1978) where K_{T0}, K'_{T0} and V_0 are the isothermal bulk modulus, its pressure derivative and the volume (cm^3/mol) at zero pressure and room temperature, respectively. The results indicate V_0 = 12.3±0.1 cm^3/mol, K_{T0} = 24.1±0.2 GPa, and K'_{T0} = 4.1±0.1 and are in good agreement with previous studies [2, 6-7].

The diffraction lines and molar volume of Ice VII were monitored as a function of pressure and temperature up to the melting temperature at any given pressure. The methodology employed in this study was to use the disappearance of the diffraction pattern of Ice VII to monitor the melting of Ice VII in the system. The melting curve of Ice VII was monitored predominately by using the disappearance of the 110 peak as evidence of the minimum melting temperature. The melting curve for Ice VII can be well represented in *PT* space by the following Simon equation:

$$(P-2.16)/0.764 = (T/355)^{4.32} - 1$$

where P is pressure (GPa) and T is temperature (K). The results suggest that some of the previous melting curve determinations underestimated the melting temperature at any given pressure [2-4], whereas others overestimated the melting temperature [1].

Conclusions: The study presented here sought to determine the *PVT* properties of Ice VII along the melting curve at pressures > 20 GPa using the a Mao-Bell type diamond anvil cell with an external Mo-wire resistance heater. Previous melting curve work extended to <20 GPa whereas we were able to extend the pressure range up to ~ 45 GPa. Comparison of these results suggests that the previously stated work on the melting curve of Ice VII is cannot be extrapolated up to high pressure accurately.

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