Thermal conductivity of compressed H₂O to 22 GPa: A test of the Leibfried-Schlömann equation

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The Leibfried-Schlömann (LS) equation, a commonly assumed model for the pressure dependence of thermal conductivity Λ, is tested by measurements on compressed H₂O using a combination of the time-domain thermoreflectance method with the diamond anvil cell technique. The thermal conductivity of ice VII increases by an order of magnitude between 2 and 22 GPa, reaching $\Lambda \approx 25$ W m^{-1} K^{-1}. Over a large compression range of $\approx$4%–33%, the LS equation describes the pressure dependence of Λ of ice VII to better than 20%.

Thermal conductivity Λ plays an important role in planetary evolution. Of particular relevance is the effect of pressure on Λ under the conditions of Earth and planetary interiors, where materials may be compressed by more than 50%. Measuring Λ of compressed materials is challenging: typically, the volume of compressed materials is extremely small in comparison to what is used in thermal conductivity experiments at ambient pressure. As a result, measurements of high-pressure Λ have been rare for compression exceeding 10%.[1,2]

H₂O, in its diverse forms of vapor, liquid (water), and solid (ice), is among the most abundant substances in the solar system. Compressed H₂O is prevalent inside icy planets and moons and governs their evolution and dynamics.[3] With at least 13 polymorphs and the diversity of the hydrogen bond, the behavior of H₂O under pressure is also a subject of considerable interest in the physics of condensed matter.[4,5] Data on the thermal conductivity of compressed H₂O are available to a maximum pressure of only 2.4 GPa.[6]

For dielectrics such as H₂O ices, oxides, and silicates, thermal conduction is largely controlled by phonon transport. The Leibfried-Schlömann (LS) formula[7,8] is among the most widely used schemes to describe the pressure dependence of Λ. The LS equation is based on a detailed theoretical analysis of phonon transport[8] but it has not been experimentally tested over a range of pressures sufficient to change the Debye frequency, density, and elastic constants of a crystal by large factors. Furthermore, since the LS equation is based on the assumptions that acoustic phonons are the dominant carriers of heat and that the dominant scattering mechanism for acoustic phonons is three-phonon interactions between acoustic modes, its applicability to crystals with multiple atoms per cell has been questioned.[9,10] Our previous work[11] showed that the pressure dependence of the cross-plane thermal conductivity of layered muscovite crystal could be adequately described by the LS equation when we assumed that the effective value of the Debye frequency varies as the square root of the cross-plane elastic constant C_{33}. Muscovite is highly anisotropic, however, and the applicability of the LS equation in this case is not strictly valid.

This study aims to measure the thermal conductivity of H₂O over a pressure range that was not accessible previously. The data on ice VII, a cubic crystal with a relatively small bulk modulus, allow us to test the LS equation over a large compression ratio. Our method combines the time-domain thermoreflectance (TDTR) method[12] in a diamond anvil cell (DAC) with density functional theory (DFT) calculations of the vibrational density of states (DOS). At room temperature, cubic ice VII (space group $Pn\bar{3}m$) is stable between 2.1 and $\approx$60 GPa.[13,14] With its extrapolated zero pressure bulk modulus $K_0 = 21.1 \pm 0.5$ GPa and the pressure derivative $K_0' = 4.4 \pm 0.1$,[15] ice VII is compressed by more than 30% at 22 GPa.

Symmetric DACs with 600-μm-culet diamonds and steel gasket were used to compress distilled H₂O to 22 GPa. Pressure was determined from ruby fluorescence.[16] An 80-nm-thick Al film, coated on a 20-μm-thick sheet of muscovite mica [KAl₂(Si₃Al)O₁₀(OH)₂, grade V-1 from SPI Supplies], was loaded in the DAC and served as a transducer in the TDTR measurements. The mica sheet provides a substrate and thermal insulation for the Al film.

The beam from a mode-locked Ti:sapphire laser was split into a pump beam and a probe beam, with a time delay between the two. The pump beam heats the surface of the Al film and the probe beam monitors the temperature of the Al film through small changes in the optical reflectivity. The in-phase V_{in} and out-of-phase V_{out} components of the intensity of the reflected probe beam were measured by a photodiode detector and rf lock-in amplifier.

To extract information on the thermal conductivity of H₂O, we fitted the measured ratio $V_{\text{in}}/V_{\text{out}}$ as a function of delay time to a thermal model that considers heat flow into H₂O and the muscovite.[17] Representative spectra and fitting are shown in Fig. 1. The thermal effusivity, i.e., the square root of the product of Λ and C_P, of H₂O, is the only significant unknown in the thermal model; Λ of compressed muscovite at room temperature has been determined in a separate study.[11] The C_P of Al and the thermal conductance of the muscovite/aluminum and H₂O/aluminum interfaces were estimated following Hsieh *et al.*[11] The C_P of liquid H₂O at high pressures is based on published data.[18] C_P of ice VII is determined from our *ab intio* calculations of the lattice dynamics of ice VIII and that of ice VI is calculated according to the thermodynamic relationship discussed by Tchijov.[18]

The heat capacity per unit area of the Al film is an important parameter in the thermal model. We calculate the changes in the thickness of the Al film with pressure by assuming
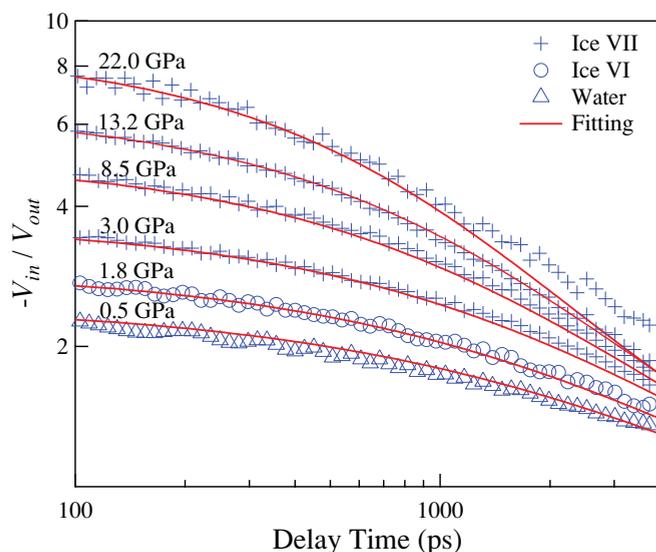
FIG. 1. (Color online) Time-domain thermoreflectance data (blue symbols) and the fitted curves (red lines) for H_2O at 300 K.

that the Al film adheres well to the mica substrate and that the Al film deforms plastically to accommodate differences in lateral compression of the Al film and the mica substrate. Under these assumptions, the thickness of the Al film decreases by 3.1% at 5 GPa, 5.5% at 10 GPa, and 7.5% at 20 GPa. (In our previous work,[11] we made the mistake of neglecting this change of Al film thickness with pressure, resulting in a thermal conductivity of mica that is ≈23% too high at the highest pressure used in the experiment, 23.5 GPa. This error is comparable to the experimental uncertainties and does not change the conclusions of Ref. 11. We used the corrected Λ of muscovite in our analysis of the data for ice VII (Table I)).

To analyze the TDTR data, we need to know C_P, the heat capacity per unit volume of ice VII for constant pressure, as a function of pressure. In our computational work, we use ice VIII as a surrogate for ice VII because proton-ordered ice VIII requires much less computational time to analyze than proton-disordered ice VII and, as we argue below, we do not expect that disorder in the proton arrangements will produce a significant change in the heat capacity. Our approach is to (i) calculate the phonon DOS of ice VIII at 0 K; (ii) evaluate the constant volume heat capacity C_V at 300 K using Bose-Einstein statistics; and (iii) determine C_P by calculating a correction to C_V using the thermodynamic relationship between C_P and C_V and experimental values for the thermal expansion coefficient and bulk modulus from Fei *et al.*[21]

Calculations of the vibrational density of states of ice VIII are performed with VASP,[22,23] a plane-wave density functional theory code. The Perdew-Wang 1991 (PW91) generalized-gradient approximation (GGA) for the exchange-correlation potential[24] with the projector-augmented wave potentials[25] for oxygen and hydrogen provide an accurate prediction of the ice VIII structure. The electronic wave functions are expanded up to a plane-wave cutoff of 800 eV, with an $18\times18\times18$ k-point mesh in the Brillouin zone and 0.1 eV Fermi-Dirac smearing of electronic occupancy. The forces on all ions are relaxed to

5 meV/Å, and the cell vectors relaxed to stresses that deviate by less than 2 MPa from the applied pressure; this determines the zero-temperature volume of ice VIII at 0, 10, and 20 GPa without accounting for zero-point motion. To compute the vibrational spectra, a direct-force method is used with a $2\times2\times2$ unit cell consisting of 32 oxygen and 64 hydrogen ions. The resulting forces produced by displacements of +0.01 and −0.01 Å in the x, y, and z directions approximate the harmonic response of ions; due to translational and rotational symmetry, only one oxygen and hydrogen atom is displaced in the unit cell. The extracted force constants are used to compute the phonon spectra on a $32\times32\times32$ k-point mesh in the Brillouin zone to determine the phonon DOS, and compute the vibrational contribution to the constant-volume heat capacity at 300 K.

Our calculated vibrational DOS spectra of ice VIII at 0, 10, and 20 GPa and 0 K agree well with experimental data[26] and previous calculations at 0 GPa.[27] Moreover, both experiments and theory suggest only a minor difference in vibrational density of states between ice VII and VIII.[26,27] Vibrational excitation of the proton sublattice contributes 30% of C_V at 0 GPa and 24% at 20 GPa. The effects of the random proton arrangements in ice VII would therefore have to be large to produce a significantly different C_V for ice VII.

We apply Bose-Einstein statistics to the phonon DOS of ice VIII at 0, 10, and 20 GPa and find $C_V \approx 3.04$ J cm^{-3} K^{-1} at $T = 300$ K independent of pressure. The correction to the pressure from atomic vibrations at 300 K is 2.1 GPa, also independent of pressure. The nearly constant value of C_V (J cm^{-3} K^{-1}) is a coincidence that results from the opposing

TABLE I. The thermal conductivity (W m^{-1} K^{-1}) and heat capacity (J cm^{-3} K^{-1}) of H_2O and muscovite at 300 K up to 22 GPa.

Phase[a]	P (GPa)		H_2O		Muscovite[d]	
			Λ[b]	C_P[c]	Λ	C_P
W	0.1	(.1)	0.54	(.07)	4.11	0.49	2.31
W	0.5	(.1)	0.70	(.05)	4.39	0.47	2.32
W	0.8	(.1)	0.84	(.02)	4.57	0.48	2.32
VI	1.8	(.1)	1.8	(.2)	2.89	0.59	2.34
VII	2.5	(.1)	3.8	(.4)	3.05	0.71	2.35
VII	6.6	(.1)	5.7	(.6)	3.05	1.46	2.43
VII	10.5	(.2)	8.7	(1.0)	3.05	1.79	2.50
VII	14.6	(.1)	12.1	(1.4)	3.04	2.45	2.56
VII	18.3	(.3)	17.8	(1.8)	3.04	3.55	2.62
VII	22.0	(.4)	24.8	(3.0)	3.04	4.65	2.68

[a]"W": liquid water; "VI": ice VI; "VII": ice VII.
[b]The numbers in parentheses are the uncertainties estimated from multiple measurements.
[c]C_P of liquid water is estimated from its density (Ref. 19) and by assuming C_P in J g^{-1} K^{-1} is constant and ≈3.979 (J g^{-1} K^{-1}), which is the C_P at 0.1 GPa and 300 K (Ref. 20); C_P of ice VII is derived from the DFT calculations of ice VIII and thermal expansivity of ice VII (Ref. 21); C_P of ice VI is estimated from the thermodynamics relations in Tchijov (Ref. 18).
[d]The thermal conductivity and heat capacity of muscovite are from Hsieh *et al.* (Ref. 11), used as input parameters to the thermal model.

effects of the decrease in the number of thermally excited vibrational modes and the increase in the atomic density with increasing pressure.

To evaluate C_P, we use the thermodynamic relationship $C_P - C_V = T\alpha^2 K_T$,[28] where T is the temperature, α is the bulk thermal expansion coefficient, and K_T is the bulk modulus. The correction to C_V is extremely small: 0.7% at 2.1 GPa, 0.4% at 10 GPa, and 0.2% at 20 GPa. Our calculated values for C_P of ice VII (Table I) from 2.1 to 4.0 GPa are ≈24% smaller than the values from a thermodynamic analysis of the ice VII to water phase transition that were derived by extrapolating the equation of state of water and fitting the melting curve of ice VII in the pressure range $P < 5$ GPa.[18,21]

Our results (Fig. 2) show that Λ of liquid H_2O increases from 0.60 W m^{-1} K^{-1} at 1 bar to 0.83 (±0.06) W m^{-1} K^{-1} at 1.3 GPa; and Λ of ice VI is 1.8–1.9 W m^{-1} K^{-1} between 1.8 and 2.0 GPa. Water persisted beyond 1.05 GPa in our experiments due to steady-state heating ΔT of the sample by the average power of the pump and probe beam; for water, we estimate $\Delta T = 50$ K. The steady-state heating decreases to $\Delta T = 30$ K for ice VI and $\Delta T < 20$ K for ice VII. Within the uncertainty of the measurements ($\pm10\%$), the thermal conductivity of water and ice VI agree with the standard reference values of liquid water at 300 K,[29,30] and with the previously published values for ice VI at 300 K in Ross *et al.*[1] The agreement confirms the validity of the method, which opens up the capability to study thermal physics under extreme conditions. Upon transformation to cubic ice VII, Λ almost doubles, consistent with theoretical understanding of the effects of the change in density and structure at this phase transition.[31] Our results for ice VII are ≈28% higher than a single reported value of 2.7–2.9 W m^{-1} K^{-1} between 2.0 and 2.4 GPa (Fig. 2 and Table I).[1] The Λ of ice VII increases with pressure by about $(13 \pm 2)\%$ per GPa in the low-pressure regime, comparable to the rate of ≈20% per GPa reported by the previous study covering a limited pressure range of 2.0 to 2.4 GPa.[1]

The Leibfried-Schlömann equation is often used to model the pressure dependence of Λ,

$$\Lambda = f \frac{V^{1/3}\omega_D^3}{\gamma^2 T},$$ (1)

where V is the volume, ω_D is the Debye frequency, γ is the Grüneisen parameter, T is the temperature, and f is a parameter independent of pressure.[8] We use our data for the thermal conductivity of ice VII to test the accuracy of the LS equation for describing the pressure dependence of Λ over a much wide range of Λ than has been previously possible. To begin, we ignore the weak pressure dependence of $V^{1/3}$ and γ and consider only the pressure dependence of the Debye frequency. If we assume that the Poisson ratio and elastic anisotropy parameter are approximately independent of pressure, then $\omega_D \propto V^{1/6}\sqrt{K_T}$,[32] where K_T is the isothermal bulk modulus at pressure P. At constant T, the LS equation is then simply $\Lambda = A K_T^{3/2}$. The isothermal bulk modulus is defined as $K_T = -dP/d\ln V$. We extract K_T from the third-order Birch-Murnaghan equation of state (EOS) with three free parameters at $P = 0$, $V_0 = 12.4 \pm 0.1$ cm^3 mole^{-1}, $K_0 = 21.1 \pm 1.3$ GPa, and $K_0' = 4.4 \pm 0.1$.[15] The best fit
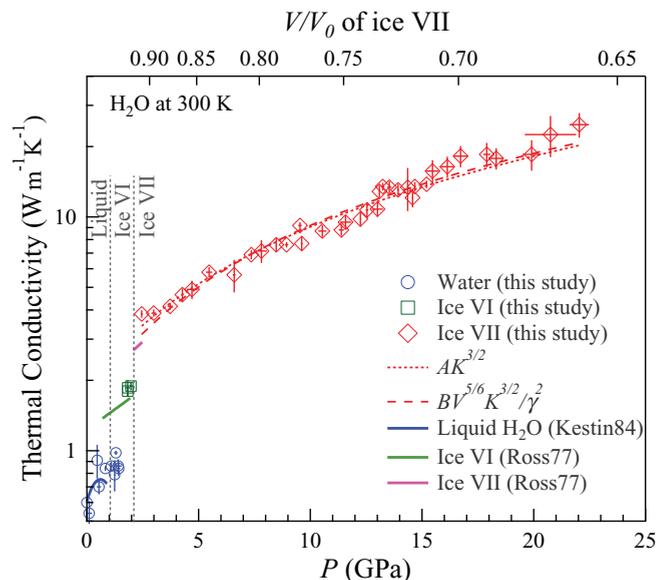

FIG. 2. (Color online) Thermal conductivity of H_2O up to 22 GPa at 300 K (open symbols). The Λ of ice VII can be fitted approximately by considering only the change in bulk modulus (red dotted curve), where A equals to 0.020 (±0.001), or more accurately by also considering the pressure dependence of the unit cell volume V and the Grüneisen parameter γ (red dashed curve), where B equals 0.008 (±0.001) with 95% confidence level. The uncertainties in Λ are estimated from multiple measurements at the same pressure. The V/V_0 of ice VII was based on Frank *et al.* (Ref. [15]).

of to the thermal conductivity data gives $A = 0.020 \pm 0.001$ Wm^{-1} K^{-1} GPa$^{-1.5}$, Fig. 2.

The quality of agreement between theory and experiment does not change if we also consider the pressure dependence of V and γ in Eq. (1). Assuming that the Poisson ratio and elastic anisotropy are independent of pressure, the Grüneisen parameter γ, also known as the "Slater γ,"[33] can be derived from the pressure derivative of the bulk modulus $\gamma = \frac{1}{2}\frac{dK}{dP} - \frac{1}{6}$. Taking the pressure derivative of K_T of ice VII in the Birch-Murnaghan EOS,[15] the calculated γ decreases with P from $\gamma = 1.82$ at 2.1 GPa to $\gamma = 1.47$ at 25 GPa. The Λ of ice VII is well fitted by $\Lambda = B V^{5/6} K_T^{3/2}/\gamma^2$, where $B = 0.008$ (±0.001) $\times 10^5$ W mole$^{5/6}$ m$^{-3.5}$ K^{-1} GPa$^{-1.5}$ (see Fig. 2). It should be noted that γ was derived from the second derivative of volume with regard to pressure and thus requires accurate measurements of the EOS.

We conclude that the LS equation describes the pressure dependence of Λ of ice VII over a large compression range $(\Delta V/V_0)$ ≈4%–33% to better than 20%. When compressed from 2.5 to 22 GPa, Λ of ice VII increases by nearly one order of magnitude, from 3.8 to 25 W m^{-1} K^{-1} (Fig. 2), reaching a value that is comparable to the ambient pressure thermal conductivity of sapphire (Al_2O_3).[34]

The Leibfried-Schlömann equation is tested over a wide range of Debye frequencies, density, and elastic constants of a cubic crystal, ice VII. The pressure dependence of Λ can be adequately described by the LS equation of ice VII up to 22 GPa, confirming its usefulness as a model for the pressure dependence of Λ for dielectric crystalline materials. The theoretical predication is of important significance for

solid-state physics and geophysics. For instance, most of the planetary interiors are under extremely high pressure, where experimental measurements of Λ of its constitutive materials are generally not available. This relationship, if proved valid for most dielectric materials, could be adapted to predict the Λ at extreme conditions based on the thermal conductivity at ambient conditions and the equation of state. We point out, however, that the LS equation is formulated for pure crystals and may need to be modified to account for the effects of disorder in mixed crystals such as olivine $(Mg,Fe)_2SiO_4$ in the Earth's upper mantle, and perovskite and postperovskite $(Mg,Fe)SiO_3$ and ferropericlase $(Mg,Fe)O$ in the lower mantle.

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