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Key Points:

- Direct measurements of methane's thermal conductivity to 25.1 GPa show linear increase punctuated by a spike at the I-A phase boundary
- First-principle calculations for solid methane to 100 GPa and 1200 K provide parameters for thermodynamic modeling of planetary interiors
- Conductivity-velocity-density crossplots supply a framework to constrain internal thermal structure and composition of icy planets

Supporting Information:

Supporting Information may be found in the online version of this article.

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Thermal Conductivity and Compressional Velocity of Methane at High Pressure: Insights Into Thermal Transport Properties of Icy Planet Interiors

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Abstract Methane is a primary component of the "ice" layers in icy bodies whose thermal transport properties and velocity-density profiles are essential to understanding their unique geodynamic and physiochemical phenomena. We present experimental measurements of methane's thermal conductivity and compressional velocity to 25.1 and 45.1 GPa, respectively, at room temperature, and theoretical calculations of its equation of state, velocity, and heat capacity up to 100 GPa and 1200 K. Overall, these properties change smoothly with pressure and are generally unaffected by the imposed atomic structure; though we observe a discrete spike in conductivity near the I-A phase boundary. We cross-plot the thermal conductivity and compressional velocity with density for the primary "ice" constituents (methane, water, and ammonia) and find that methane and water are the upper and lower bounds, respectively, of conductivity and velocity in these systems. These physical properties provide critical insights that advance the modeling of thermo-chemical structures and dynamics within icy bodies.

Plain Language Summary Neptune, Pluto, and Uranus all belong to an important subclass of objects in our solar system, and beyond, known as icy planetary bodies. These systems commonly have an internal "ice" layer, consisting of water, methane, and ammonia, that controls the outward flow of heat from the core. The dynamics within this layer contribute to the intriguing behaviors, such as supercritical subsurface oceans and odd magnetic fields, present in these systems. To understand these dynamics, we collected unique measurements under extreme pressure on methane's thermal conductivity, the fundamental property defining the rate of energy transport through a material. We quantified the rate of conductivity increase with pressure up to 25 gigapascals (GPa; 1 GPa $\approx 10^4$ atm) and captured an anomalous spike at a phase boundary that has never been previously observed. We combined this information with similar measurements on the other major "ice" components to constrain the composition and bulk physical properties of these layers. As our understanding of icy planetary bodies improves, primarily through remote-sensing, our research provides a framework to link surficial measurements to empirically-derived interior properties. This insight is critical for comprehending both the external and internal phenomena exhibited by icy bodies.

1. Introduction

Methane (CH₄) is the most abundant organic molecule in the universe (Spanu et al., 2009) and a major component of the "hot-ice" layers in gas-ice giants (e.g., Neptune and Uranus) (Guillot, 2005) and the subsurface oceans of icy satellites (e.g., Pluto and Enceladus) (Kamata et al., 2019). Structural models of these planetary bodies indicate that these layers comprise a significant portion (10%–40% of planetary radii) of the interior (Guillot, 2005; Nettelmann et al., 2013; Nimmo & Pappalardo, 2016). Meanwhile, compositional models suggest that methane, water, and ammonia are their primary constituents (Podolak & Hubbard, 1998), though exact compositions are poorly constrained. Due to their incredible difference in diameter and mass, however, the internal pressure and temperature (P-T) conditions for "hot-ice" layers (10–800 GPa; 2000–8000 K) (Maynard-Casely, 2009) are vastly different from those predicted for subsurface oceans (<3 GPa; <300 K) (Kamata et al., 2019; Robuchon & Nimmo, 2011).

Despite this range in P-T conditions, these "ice" layers likely impact the physical and magnetic structures of these planetary bodies. On gas-ice giants, convection within this layer may contribute to Neptune's and Uranus' non-dipolar, non-axisymmetric magnetic fields (Stanley & Bloxham, 2006). Meanwhile, a thin, thermally-insulating

© 2022. American Geophysical Union. All Rights Reserved. layer (potentially methane hydrate) present between the solid crust and liquid ocean on Pluto may help maintain the subsurface ocean (Kamata et al., 2019). Constraints on methane's lattice thermal conductivity (Λ_{CH_4}) and compressional velocity (V_{P-CH_4}) at high pressure and temperature can help us to better understand the physical and thermal structure of these systems.

Methane's physical properties are likely related to its phase behavior at high pressure, which has been refined using Raman and infrared spectroscopy and X-ray and neutron diffraction (e.g., Bini & Pratesi, 1997; Chen, P.-N. et al., 2011; Hirai et al., 2008; Maynard-Casely et al., 2010; Sun et al., 2009; Umemoto et al., 2002). At low temperature, methane exhibits a rich set of phases at both atmospheric (Phase-I and II at 90 and 21 K) and slightly elevated pressures (Phase-III, IV, V, and VI at 15 K and 0.1, 0.3, 0.65, and 1.3 GPa) (e.g., Bini & Pratesi, 1997; Umemoto et al., 2002). At room temperature (300 K) and elevated pressure (>1 GPa), experimental and modeling studies predict two phases (Phase-I and A at 1.6 and 5.2 GPa) beneath 12 GPa and up to four additional phases (Phase-B and various high-pressure phases) above (e.g., Bini & Pratesi, 1997; Chen, P.-N. et al., 2011; Nakahata et al., 1999; Sun et al., 2009).

Molecular solids typically have a relatively low (<1 W m⁻¹ K⁻¹) thermal conductivity (Kannuluik & Carman, 1952; Lemmon & Jacobsen, 2004). To our knowledge, the only direct measurements of Λ_{CH_4} were taken at low-temperature (<140 K) and low-pressure (<0.23 GPa) within the Phase-I and Phase-II stability zones (Jezowski et al., 1997; Konstantinov et al., 1999; Krivchikov et al., 2007; Stachowiak et al., 2006). In the low-temperature form of Phase-I (21–90 K), Λ_{CH_4} ranges from 0.4 to 0.6 W m⁻¹ K⁻¹ with a maximum at ~55 K (Konstantinov et al., 1999). In Phase-II (<21 K), as the temperature decreases, Λ_{CH_4} increases quickly from 0.3 to 1.5 W m⁻¹ K⁻¹ at 5–10 K before dropping rapidly at temperatures approaching 0 K. The cause of this spike is debatable, though prominent theories include: (a) Molecular reorientation; (b) quantum effects (e.g., spin transitions and tunneling); and (c) phonon scattering, mean free path, and heat capacity interactions (Böer & Pohl, 2018; Briganti et al., 1978; Emtiaz et al., 2020; Gorodilov et al., 2005; Krivchikov et al., 2008; Stachowiak et al., 2006). These measurements provide an order-of-magnitude estimate of methane's thermal conductivity, though their applicability to icy bodies requires exploration into high P-T conditions.

In contrast, there are reliable measurements of V_{P-CH_4} at high-pressure. Hebert et al. (1987) measured the Brillouin frequency of methane at 300 K to 31.8 GPa. They found that the compressional velocity increased with pressure at a decreasing rate with no apparent anomalies. This lack of deviations, despite passing through multiple phase transitions, is intriguing and worth confirming with independent measurements.

In this study, we present data from six experiments on Λ_{CH_4} and V_{P-CH_4} at high pressure (1.8–45.1 GPa) and room temperature. We also use first-principles density functional theory (DFT) calculations to investigate the stability and physical properties of solid methane up to 100 GPa and 1200 K; specifically, we investigate four candidate high-pressure methane structures proposed by Gao et al. (2010) and Lin et al. (2011): P2₁2₁2₁, P2₁/c, Pnma, and Cmcm. Finally, we combine our thermal conductivity and compressional velocity results for methane, as functions of density, with historic data for water, ammonia hydrate, and methane hydrate to define systematics for these parameters in "ice" layers. Our results provide a framework to assist future studies in constraining the internal physical, compositional, and thermal structures in icy planetary bodies.

2. Methods

2.1. Experiment Execution

We performed six experiments in symmetric diamond anvil cells (DAC) where we compressed pure methane up to 45.1 GPa at 300 K to investigate its thermal conductivity and compressional velocity (Table 1). We pre-indented 250-µm-thick rhenium gaskets to an initial chamber thickness of 40–70 µm (15–25 GPa) and used an electronic drilling machine (Hylozoic Products, Seattle, WA, USA) to make a 160–300 µm diameter hole in the pre-indent (Table 1). After mounting the gasket onto the bottom DAC anvil, we loaded a small piece of borosilicate glass (Schott D263® T eco), coated with a thin (~80–100 nm) aluminum film, and a ruby ball into the bottom of the sample chamber (inset in Figure 1b). Finally, we filled the chamber with high-purity (99.999%) methane gas to 60–150 MPa and closed the DAC, using a mechanical gas-loading system.

We allowed the chamber pressure and temperature to equilibrate for at least 12 hr while tracking the internal pressure using calibrated ruby fluorescence (Mao et al., 1986); the pressure typically stabilized around 2 GPa after

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Experiment-Specific Parameters and Execution Information										
		Initial chamber dimensions				Max				
Experiment	Culet size (µm)	Diameter (µm)	Thickness (µm)	Gas loading pressure (MPa)	Initial pressure (GPa)	pressure (GPa)				
1	500	295	50	60	4.3	24.3				
2	400	195	55	120	2.4	6.6				
3	400				2.6	45.1				
4	400	195	41	120	2.2	44.7				
5	400	160	38	150	2.4	21.6				
6	500	305	70	150	1.8	10				

Note. The initial pressure was noted after the post-loading equilibration period (>2 hr). Errors in the pressure measurements are equivalent to the standard error measured during ruby pressure calibration (Section 2.3; ± 1.7 cm⁻¹; ± 0.2 –0.3 GPa).

the equilibration period (Table 1). During the compression and decompression cycles, we collected data every ~ 0.5 and ~ 2 GPa, respectively. Internal pressure alterations did not occur instantaneously, but rather changed over time at a decreasing rate. To account for this, we allowed the sample to equilibrate for at least 1 hour after changing its pressure before taking measurements; we found that this limited the pressure change during data collection to <0.2 GPa.

2.2. Physical Property Measurements

We used combined time-domain thermoreflectance (TDTR) and picosecond interferometry to collect reliable and rapid measurements of Λ_{CH_4} and V_{P-CH_4} (Hsieh et al., 2017). In this method, a 785-nm laser is split into a pump and a probe beam that are co-focused onto a point on the aluminum coating of a sample in a DAC chamber.



Figure 1. Raman spectroscopy results of methane at high pressure. Measurements were conducted from 1.6 to 45.1 GPa on thermodynamically (a) stable and (b) metastable methane phases (normalized to maximum intensity). Dashed lines highlight downshift in v_1 primary peak in the metastable phase, relative to the stable phase. Inset shows a diamond anvil cells chamber with aluminum-coated glass and a ruby ball surrounded by transparent, solid methane at ~5 GPa; there was no visual difference between stable and metastable phases. (c) Raman shift of the v_1 (circles) and v_3 (squares) primary peaks with pressure. Filled and hollow markers indicate compression and decompression measurements, respectively, on stable methane phases. Gray-filled markers indicate measurements on metastable methane phases.

Table 2

Thermal Model Parameters and Sources; No Source Indicates an Assumed Parameter

Name	Symbol	Value	Unit	Source
Laser modulation frequency	_	8.7 E+6	Hz	Set on equipment
Laser spot size	-	7.6E-4	cm	Set on equipment
Methane thickness	x _{CH4}	1E+0		_
Interface thickness	x _{int}	1E-7		-
Aluminum thickness	x _{Al}	~1E-5		Measured at ambient and then empirically-derived at pressure from EOS (Bercegeay and Bernard, 2005)
Substrate (glass) thickness	x _{sub}	1E+0		-
Methane heat capacity	C _{p-CH4}	3.00	$J cm^{-3} K^{-1}$	Figure 3c
Interface heat capacity	C_{p-int}	0.1		_
Aluminum heat capacity	C_{p-Al}	2.44		Hsieh et al. (2009)
Substrate (glass) heat capacity	C_{p-sub}	2.06		-
Aluminum thermal conductivity	$\Lambda_{A}l$	200	$W m^{-1} K^{-1}$	_
Substrate (glass) thermal conductivity	$\Lambda_{ m sub}$	1.3~3.7		Figure S2 in Supporting Information S1

Note. The assumed methane and substrate thicknesses are considerably larger than their actual thicknesses ($\sim 10-30 \ \mu m$) in our experiments. This is common practice, however, as the thermal penetration depth (i.e., how deep the laser-induced heat wave reaches into a material) for both materials is only $\sim 1 \ \mu m$, so there is practically no difference between assuming 1 cm or 10 μm .

The pump beam is directed through an automated delay system that dynamically changes the delay time—the difference in arrival time between the pump and probe beams. A silicon photodiode and lock-in amplifier then measure and isolate the in-phase (V_{in}) and out-of-phase (V_{out}) components of the reflected probe beam. At each pressure point, we took 3–6 thermal conductivity measurements and 1–3 compressional velocity measurements from different parts of the sample (dependent on the sample size, aluminum coating integrity, and reflection strength). We then averaged each set of measurements at each pressure for presentation in Section 3 and provide all individual measurements in our associated data repository (Meyer et al., 2021).

2.2.1. Thermal Conductivity

For Λ_{CH_4} measurements, we collected the reflectance signal with linear spacing, from -20 to 80 ps delay times, and exponential spacing, from 80 to 4000 ps delay times (Figure S1 in Supporting Information S1). We used the data between -20 and 20 ps to correct the phase shift and time offset in the signal and then isolated the exponentially-spaced data for analysis. We compared the measured voltage ratio ($-V_{in}/V_{out}$) to the output of a bi-directional heat flow model of the aluminum reflectance with temperature (Hsieh et al., 2009; Schmidt et al., 2008); this model has been extensively described by Hsieh (2011).

Many of the model parameters were equipment-specific or empirically-derived, including the laser spot size and modulation frequency, the borosilicate glass thermal conductivity (Figure S2 in Supporting Information S1), and the aluminum coating heat capacity and thickness with pressure (Table 2). We also assumed that: (a) The methane and substrate thicknesses were sufficiently large as to be considered infinite; (b) the heat capacity and thickness of the material interface (e.g., methane-aluminum or aluminum-glass) were negligibly small; (c) the glass heat capacity and aluminum thermal conductivities were constant and equal to their ambient values; and (d) the methane heat capacity was constant and equal to the theoretically-calculated (Sections 2.4 and 4) value at the midpoint pressure (12.5 GPa; 48 J mol⁻¹ K⁻¹).

The two remaining unknown variables were the thermal conductivities of methane (Λ_{CH_4}) and the material interfaces (Λ_{int}). As such, we determined both values using an automated grid-searching algorithm that incrementally changed the model inputs, Λ_{CH_4} and Λ_{int} , to minimize the mean average percent error (MAPE) between the modeled and measured ratios. Both variables were allowed to change dynamically during the grid-search, but Λ_{int} was limited to a maximum of 0.5 W m⁻¹ K⁻¹. Above this point, Λ_{int} had little effect on the model output (e.g., an increase from 0.2 to 0.4 W m⁻¹ K⁻¹ and 0.4 to 0.6 W m⁻¹ K⁻¹ results in average decrease in modeled $-V_{in}/V_{out}$ of <5% and <2%, respectively), but greatly increased the time to find an optimal solution. Finally, we filtered the



individual thermal conductivity measurements by two quantitative data quality metrics (V_{in} at 80 ps delay time >10; MAPE <5%) and averaged the remaining data points to determine Λ_{CH_4} at each pressure.

2.2.2. Compressional Velocity

For V_{P-CH4} measurements, we collected reflectance signals from 0 to 500 ps delay times at 1 ps intervals (Figure S3a in Supporting Information S1) to track V_{in} oscillations caused by heating-induced strain wave interference (Hsieh et al., 2009). We did not use quantitative filters to eliminate any velocity measurements, but did remove several with qualitatively poor signals. We then picked and applied a baseline to each data set, to isolate the interference oscillations, and used Matlab's Fast Fourier Transform function to extract the signal frequency (Figures S3b and S3c in Supporting Information S1). Since we employed a backscattering geometry with methane in contact with the reflector (i.e., Al-coated glass), the extracted signal frequency represents the Brillouin frequency (f_B) of methane (Polian, 2003). As such, we can calculate V_{P-CH4} from $f_B = 2NV_{P-CH4}/\lambda$ (Polian, 2003), where N is methane's index of refraction (Hebert et al., 1987; Sun et al., 2006) and λ is the laser wavelength. We determined N above and below 12 GPa from two, pressure-dependent empirical relationships (Hebert et al., 1987; Sun et al., 2006), using a first-order Murnaghan equation of state (Hebert et al., 1987) to calculate the methane density.

2.3. Raman Spectroscopy Procedures

We used a Raman spectrometer (Horiba Jobin-Yvon LabRam HR circa 1998) outfitted with a 532-nm laser (Coherent SAPPHIRE 532–300 SW CDRH) to measure the internal DAC pressure and characterize the methane in our experiments. We calibrated the spectrometer daily using the silicon peak at 520.4 cm⁻¹ and collected a zero-pressure ruby calibration spectra prior to each measurement to reduce errors in the pressure calculation; the average zero-pressure ruby peak position was 4391.2 ± 1.7 cm⁻¹ (equivalent to ± 0.2 and ± 0.3 GPa at 1 and 45 GPa, respectively).

We collected high-resolution methane Raman spectra using a 1200 groove/mm grating, 100% laser power (\sim 32 mW after filters), variable exposure time (0.5–2.5 min; signal strength dependent), and 3–5 averaged replicates to optimize the output data quality. At each pressure, we recorded two successive spectra within a \sim 580-cm⁻¹ range centered on 3,000–3,200 cm⁻¹, depending on the methane peak locations. The first set included the signal from an integrated neon lamp (OceanOptics NE-2), while the second was taken without the neon signal.

Neon produced many spectrographic lines within our region of interest and we used the two lines that encompassed the observed methane spectra to determine a linearly-interpolated frequency correction (Fang et al., 2018). We calculated and applied individual corrections (average absolute correction: $3.7 \pm 1.8 \text{ cm}^{-1}$) to each methane peak to determine their actual position. This process reduced peak position errors associated with instrumental fluctuations and improved comparability between spectra taken at different pressures and times.

After data collection, we processed and analyzed our Raman spectra using LabSpec5 (Horiba Scientific). We applied a baseline correction to remove the accumulated low-intensity noise that occurred with our extended exposure times and then used the integrated peak-fitting function (Gaussian-Lorentzian mixed distribution curve) to extract peak locations for both the ν_1 and ν_3 vibrational modes. For complex methane spectra (without neon), we manually-defined peak positions, full-width-half-maximums, and intensities prior to using the auto-fitting capability of the peak fit function. Meanwhile, in the combined neon and methane spectra, we only picked the two neon peaks and any other methane peaks needed to get decent fits.

2.4. First-Principles Calculations

In this work, we performed structural optimizations and phonon calculations (based on density functional perturbation theory) using the Quantum ESPRESSO codes (Giannozzi et al., 2020). We computed vibrational free energies by combining phonon spectra and the quasi-harmonic approximation (QHA) and then derived thermal parameters and the equations of state at nonzero temperatures ($T \neq 0$). We then fit our results to the third-order Birch-Murnaghan equation of states, as implemented in the QHA package (Qin et al., 2019). In our calculations, we adopted the PBE-type generalized-gradient approximation (Perdew et al., 1996) and norm-conserving pseudopotentials (NCPPs) available on PseudoDojo (van Setten et al., 2018).





Figure 2. Methane thermal conductivity (Λ_{CH_4}) and compressional velocity (V_{P-CH_4}) results as a function of pressure for stable (black circles) and metastable (red hollow circles) phases of methane. (a) Λ_{CH_4} of up to 25.1 GPa. Gray-shaded area highlights the anomalous thermal conductivity; magnified in inset. Black and red dashed lines indicate best linear fits to the stable and metastable data, respectively, excluding the shaded region. (b) V_{P-CH_4} measurements from this study (circles) compared to those from Hebert et al. (1987) (squares).

In the PseudoDojo NCPPs, the cutoff radii of carbon (C) and hydrogen (H) were 1.25 and 1.0 bohr, respectively. Their sum was slightly larger than the C-H bond length in CH_4 . To check the effects of cutoff radii, we performed additional calculations using the projected augmented wave (PAW) PPs (Kresse & Joubert, 1999), with the cutoff radii of 1.1 and 0.8 bohr for C and H, respectively, adopted in the Vienna Ab initio Simulation Package (VASP). The differences between the PAW and NCPP results at 100 GPa and 300–1200 K were within 0.1%, 1.3%, and 1.7% for volume, heat capacity, and bulk sound velocity, respectively.

3. Experimental Results

3.1. Methane Raman Spectra

All methane Raman spectra we collected at low pressure (<12 GPa), and most at high pressure (>12 GPa), mirror the behavior previously reported (Chen, P.-N. et al., 2011; Hirai et al., 2008). In particular, the ν_1 and ν_3 peak positions shifted to higher frequencies with pressure, exhibited a positive discontinuity (~5 cm⁻¹) at 12 GPa, and underwent peak-splitting at 12, 33, 37, and 42 GPa (Figures Ia and Ic). Some spectra, however, were continuous at 12 GPa (Figure 1c) and remained broad and bimodal, without peak-splitting, up to 45 GPa (Figure 1b); Proctor et al. (2017) observed a similar behavior, but did not specifically distinguish it as atypical. We interpreted that the methane in the former case was fully thermodynamically stable, while that in the latter was thermodynamically metastable. This distinction is important, as we measured physical properties on both the stable and metastable phases. Additional information on methane's spectrographic behavior and the predicted fits for all the peaks in the full spectra of its stable phase are available in the Supporting Information (Text S1 and Figure S4 in the Supporting Information S1).

3.2. Thermal Conductivity

We measured thermal conductivity between 1.6 and 25.1 GPa, on both the stable and metastable methane phases. The stable phase measurements (Figure 2a: black circles), from 1.8 to 24 GPa, increased linearly from 0.2 to 3.4 W m⁻¹ K⁻¹ at an average rate of 0.120 W m⁻¹ K⁻¹ GPa⁻¹ (Figure 2a: black dashed line). This trend, however, was punctuated by a spike in conductivity near the I-A phase boundary (4.7–8.0 GPa; Figure 2a: shaded area) where the conductivities were 4–5 times greater than background. Meanwhile, the metastable phase measurements from 12 to 25.1 GPa (Figure 2a: red circles), increased at a similar rate as the stable phase (0.113 W m⁻¹ GPa⁻¹; Figure 1a: red dashed line), but were 5%–10% lower.



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Figure 3. Theoretical calculations of methane's molecular volume (V), isobaric heat capacity (C_p), and bulk sound velocity (V_{ϕ}) at high pressure and room temperature (300 K). (a) High-pressure atomic structures of CH₄ used in the calculations. (b) V, (c) C_p , and (d) V_{ϕ} up to 100 GPa for each methane structure: Cmcm (black lines), P2₁/c (red lines), Pnma (green lines), and P2₁2₁2₁ (blue lines); the four curves in 3b are essentially identical. Unit cell volume data (3b; circles) are taken from Hazen et al. (1980), Nakahata et al. (1999), and Sun et al. (2006), for various structures based on X-ray diffraction analyses.

3.3. Compressional Velocity

We collected compressional velocity measurements from 1.6 to 45.1 GPa on both stable (Figure 2b: black circles) and metastable (Figure 2b: red circles) methane phases. Overall, the velocity ranged from 3.9 to 13.7 km s⁻¹ and matched well with those taken by Hebert et al. (1987) (Figure 2b: white squares). In contrast to the anomalous thermal conductivity (Figure 2a: shaded area), the velocity increased smoothly and appeared unaffected by the numerous high-pressure phase transitions. We found, however, that metastable methane had an acoustic velocity 1%-3% lower than stable methane between 12 and 25 GPa, similar to the behavior observed in methane's thermal conductivity (Figure 2a).

4. Theoretical Calculations

While the crystal structure of solid CH₄ beyond 25 GPa remains experimentally unverified, several candidate structures have been proposed (Figure 3a), including P2₁2₁2₁, P2₁/c, Pnma, and Cmcm (Gao et al., 2010; Lin et al., 2011). We computed the Gibbs free energy (G), molecular volume (V), bulk sound velocity (V_{ϕ}), and heat capacity (C_p) of these high-pressure phases up to 100 GPa and 1200 K using the first-principles calculations described in Section 2.4. From the Gibbs free energy calculations at room temperature (Figure S5 in Supporting Information S1), P2₁2₁2₁ appears stable from 25 to 85.3 GPa, before transitioning to Pnma at higher pressure; these results are consistent with those from Gao et al. (2010).

Initially, we investigated the effect of the imposed crystal structure upon compression at 300 K on these physical properties (Figure 3). As described in Section 1, methane undergoes a series of structural transitions upon compression. Interestingly, the experimentally-derived molecular volumes (Figure 3b: circles) up to 100 GPa





Figure 4. Theoretical calculations of methane's molecular volume (V), bulk sound velocity (V_{ϕ}), and isobaric heat capacity (C_p) at high pressure and temperature. (a) V and (b) V_{ϕ} of methane's $P2_12_12_1$ structure (Figure 3a) up to 100 GPa at 0 K (black lines), 300 K (red lines), 600 K (blue lines), and 1200 K (green lines). Although not shown here, all structures exhibit similar absolute values and temperature-dependencies for V and V_{ϕ} ; we focus on the $P2_12_12_1$ results as that is the predicted high-pressure stable structure. (c) C_p of methane up to 100 GPa at 100 K, 300 K, 600 K, and 1200 K for each methane structure (Figure 3a): Cmcm (black lines), $P2_1/c$ (red lines), Pnma (green lines), and $P2_12_12_1$ (blue lines). At 600 and 1200 K, results are limited by the pressure-dependent melting curve (Hirai et al., 2009; Lobanov et al., 2013); dashed sections for 1200 K data indicates the uncertainty in the melting pressure at this temperature.

(Hazen et al., 1980; Nakahata et al., 1999; Sun et al., 2009) can be well fitted with a single compression curve, suggesting negligible volume anomalies across these structural transitions. Our computed compression curves of the four structures (Figure 3b: lines) agreed well with these experiments and were nearly identical to each other. In addition, the isobaric heat capacity (Figure 3c) and bulk sound velocity (Figure 3d) exhibited little dependence on the crystal structure.

We then examined the effects of temperature on these physical properties (Figure 4), while accounting for methane's pressure-dependent melting curve; at 600 and 1200 K, methane solidifies at 8 GPa and between 30 and 70 GPa, respectively (Hirai et al., 2009; Lobanov et al., 2013). Generally, methane's V (Figure 4a) and V_{ϕ} (Figure 4b) increased and decreased with temperature, respectively. The change, however, was limited to less than 5% and diminished at higher pressures for both properties (e.g., V increases 5% at 30 GPa, 3% at 50 GPa, and 1.6% at 100 GPa between 300 and 1200 K). In contrast, methane's C_p (Figure 4c) was highly dependent on the temperature, increasing more than 10-fold between 100 and 1200 K across the entire pressure range. At each temperature, however, the structural effect on C_p was still very limited.

The most striking observation from all our theoretical calculations (Figures 3 and 4) was that all output parameters (e.g., molecular volume, bulk sound velocity, and isobaric heat capacity) were generally unaffected by the atomic structure across the entire range of P-T conditions. From this, we interpret that, within the reasonable limits of our theoretical calculations, these results can be reliably applied to all methane phases across this range, including phases A, B, or other uncharacterized phases.



5. Discussion

5.1. Physical Properties

Thermal conductivity (Λ), a parameter describing the rate at which thermal energy flows through a material, is often modeled via the expression, $\Lambda = 1/3Cv = 1/3Cv^2\tau$ (Kittel, 1976); *C*, *v*, *A*, and τ are the heat capacity, group sound velocity, and phonon mean free path (MFP; = $v\tau$) and scattering time, respectively. Within this framework, we interpret our experimental measurements of methane's thermal conductivity below.

With the exception of the anomalous region (Figure 2a: shaded zone), Λ_{CH_4} increases steadily with pressure (Figure 2a: black dashed line). Since its compressional velocity (Figure 2b), molecular volume (Figure 3b), and heat capacity (Figure 3c)—All proxies for major parameters in the generic Λ -equation—Change smoothly with pressure, the continuous background increase in Λ_{CH_4} is expected. However, the lack of discontinuities in these parameters despite intersecting multiple phase boundaries is intriguing.

Phase transitions are accompanied by structural changes that, when significant and rapid, may cause physical property discontinuities. In methane's case, there are five proposed phases from 12 to 45 GPa: A, B, HP1, HP2, and HP3. The A-B transition is accompanied by a "sluggish", but considerable, structural change (Bini & Pratesi, 1997; Chen, P.-N. et al., 2011; Hirai et al., 2008; Maynard-Casely et al., 2014; Sun et al., 2009). In contrast, the other transitions are rapid, but only require minor structural changes or molecular reorientations (Hirai et al., 2008; Lin et al., 2011; Maynard-Casely et al., 2014; Umemoto et al., 2002). The details of methane's phases are still debatable (Chen, P.-N. et al., 2011; Hirai et al., 2008; Sun et al., 2009), but slow transitions or structural similarities between phases could explain the lack of observed physical property discontinuities.

Within the anomalous region, however, the dramatic increase in thermal conductivity at the I-A phase boundary is a truly unique result (Figure 2a). The absence of anomalies in the experimental measurements of V_{P-CH_4} from 2 to 12 GPa (Figure 2b) suggest that *v* is not driving this behavior. Phase transitions, however, can result in anomalous heat capacity fluctuations and complex phonon scattering factors (i.e., *A* and τ) that may alter the phonon scattering rate (τ^{-1}) and thermal conductivity.

Relative to methane's other high-pressure transitions, the I-A transition occurs rapidly and requires a significant structural reorganization (Maynard-Casely et al., 2010; Sun et al., 2009). These factors force an abrupt Gibbs free energy and phonon mean free path re-equilibration that may have unpredictable effects on the heat capacity and thermal conductivity. Methane's I-II phase transition at low temperature and pressure (21 K; 1 atm) is similarly complex and rapid and results in a comparable conductivity anomaly (Jezowski et al., 1997; Krivchikov et al., 2007). This behavior has also been observed in other non-metallic crystals (Berman, 1967) and may be attributed to complex interactions between the phonon mean free path and the material heat capacity as functions of temperature (Böer & Pohl, 2018). These interactions may be responsible for producing the observed spike in thermal conductivity in our experiments, though this requires confirmation through direct experimental observation. At this time, however, measuring heat capacity at high temperature and pressure is extremely difficult and beyond the scope of this study. We hope our related experimental findings will encourage future research into methane's heat capacity under extreme conditions.

5.2. Implications for Planetary Interiors

At a planetary scale, thermal conductivity is a key component controlling the transport of heat from the core to the surface via conductive and convective processes. On many icy bodies, thermal convection processes (e.g., plate tectonics, thermal plumes) are limited and conduction becomes the predominant mechanism in heat transport through the icy mantle (Guillot, 1995; Hussmann et al., 2006; McKinnon, 1998; Robuchon & Nimmo, 2011). These systems host a number of intriguing phenomena, such as subsurface oceans on icy satellites (e.g., Pluto, Enceladus) (Nimmo & Pappalardo, 2016; Robuchon & Nimmo, 2011) and anomalous magnetic fields around gas-ice giants (e.g., Neptune, Uranus) (Stanley & Bloxham, 2006). To understand these planetary-scale phenomena, it is essential to constrain the thermal conductivity profile under extreme conditions.

A very simple, yet useful, approach for analyzing velocity-density data of earth materials is Birch's law, which states that the compressional velocity of a material is linearly proportional to its density (Birch, 1961). This technique is traditionally applied to silicates, oxides, and metallic alloys for estimating Earth's internal velocity





Figure 5. Density (ρ) dependence of the thermal conductivity (Λ) and compressional velocity (V_p) for the major components of the "ices" on icy bodies. (a) Λ and (b) V_p as functions of ρ for methane (red dots), water (blue dots), methane hydrate (stars), and ammonia hemihydrate phase-II (AHH-II; green dots). Dashed lines indicate best fits for each Λ (power) and V_p (linear) relationship. Our experimental methane data is plotted against historical data for water (Ahart et al., 2011; Chen, B. et al., 2011; Polian & Grimsditch, 1984; Shi et al., 2021; Shimizu et al., 1995; Zha et al., 1998), methane hydrate (Beam et al., 2016; Waite et al., 2007), and AHH-II (Li et al., 2019). For our thermal conductivity measurements, we only plot stable-phase methane data outside the "anomalous region" denoted in Figure 2a. Densities of the compounds are calculated from their relevant equations of state (Datchi et al., 2006; Frank et al., 2004; Hebert et al., 1987; Loveday et al., 2001).

structure and composition (e.g., Boness & Ware, 2017; Lin et al., 2005; Sakaiya et al., 2014). Chung (1972) noted that this relationship is only valid within a specific density range that is inversely proportional to the material's average molecular weight. However, experimental studies on dense rare gases indicate that this relationship also holds at densities down to 0.5 g cm⁻³ (Loubeyre & Letoullec, 1990), compared to the typical 3–6 g cm⁻³.

Thus, we extend the application of Birch's law to icy bodies by cross-plotting the thermal conductivities (Figure 5a) and compressional velocities (Figure 5b) of common "ice" layer constituents against their densities. We include our experimental results on methane (Figure 5: Red dots) and historical data for water (Figure 5: Blue dots), ammonia hydrate (Figure 5b: Green dots), and methane hydrate (Figure 5: Stars). Although these data were taken at room temperature, our theoretical calculations indicate that the temperature effect on some physical properties is limited, particularly at high pressure (Section 4; Figure 4). As such, our plots here may be applicable to high-temperature conditions.

The thermal conductivities of methane and water both increase with density according to power relationships (Figure 5a: Dashed lines). The difference between them, however, decreases from 13-fold to 4-fold as density increases from 1 to 2 g cm⁻³, indicating that the thermal conductivities converge at higher densities. Meanwhile, the compressional velocities of methane, ammonia hydrate, and water increase with density at rates of 13.2, 10.3, and 6.1 ($\partial V_P / \partial \rho$; Figure 5b), respectively, and continuously diverge. Although the available data only cover densities from 1 to 3 g cm⁻³, the thermal conductivity and compressional velocity of methane likely exceed those of water for the majority of icy layers. In this case, the methane (Figure 5: Red-dashed lines) and water (Figure 5: Blue-dashed lines) results represent endmembers within these regions.

Interestingly, methane hydrate (Figure 5: Stars) contains 15%–20% methane by mass, while its thermal conductivity and compressional velocity are both weighted 25%–35% toward the methane endmember. This finding suggests that the physical properties of icy layers can be estimated using linear-mixing models of the individual components. Therefore, as estimates of the compositions of these layers improve, our conductivity-velocity-density cross-plots can be used to constrain these layers' physical properties. Although the compositions of icy bodies are currently poorly constrained, rough estimates suggest that the "ice" layers are close to an even split between methane and water, with ammonia as the minority constituent (Podolak & Hubbard, 1998); this narrows the range of physical properties with density. Generally, however, methane-rich material will have higher thermal conductivity and compressional velocity than water-rich material, which allows for some fundamental insights into icy bodies. For example, icy satellites tend to have relatively low pressures and temperatures within their subsurface oceans (<3 GPa; <300 K), which suggests that the methane in those systems exists as a combination of Phase-I methane and mixed hydrates. In colder regions or satellites with higher pressures, however, Phase-A methane could be thermodynamically stable, which could produce narrow regions of anomalously high thermal conductivity. Also, in the case of Pluto, the compositional change between the thin layer of methane hydrate (~15% methane) at the bottom of the crust (Kamata et al., 2019) and the underlying ocean (>30% methane) could result in a 2 to 3-fold thermal conductivity contrast. These insights improve our understanding of the heterogeneous structure and physical properties of these systems and similar insights can be made wherever solid methane is present.

Overall, we provide a database of density-dependent thermal conductivity and compressional velocity for the key components in icy bodies to help constrain depth profiles of these parameters. As estimates of internal compositions improve, our results can be used to build thermal conductivity and compressional velocity profiles of these planetary bodies. In addition, inverse compositional models of icy bodies can be compared to our data to ensure their outputs are consistent with the behaviors we observe. As such, we have produced a new tool to assist in the investigation of icy planetary interiors.

6. Conclusions

We present a unique set of experimental data on the high-pressure thermal conductivity and compressional velocity of pure methane. Other than a spike in the thermal conductivity related to the I-A phase transition, both the conductivity and velocity increase smoothly with pressure up to 25.1 and 45.1 GPa, respectively. We also present theoretical calculations for four potential methane structures up to 100 GPa and 1200 K. The computed compression curves are in great agreement with previous experiments. In addition, our calculations indicate that the effect of atomic structure on the molecular volume and physical properties of solid CH_4 is negligible.

From our experimental results and historic data, we constructed cross-plots of thermal conductivity and compressional velocity as functions of density for methane, water, ammonia hydrate, and methane hydrate. From this we interpret that methane and water act as endmembers for the physical properties in the interiors of icy bodies, with methane-rich "ice" layers exhibiting higher velocities and conductivities than water-rich ones. This information provides an important first-order insight into the physical properties of planetary bodies such as Neptune, Uranus, Pluto, and Enceladus. As the internal compositions of these planets are better constrained, we can construct reasonable estimates of their velocity and conductivity profiles from our results.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

Our data are stored in the Zenodo repository: "Thermal conductivity and compressional velocity of methane at high pressure" (Meyer et al., 2021).

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