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Scale aspects of heat transport in the diamond anvil cell, in spectroscopic modeling, and in Earth's mantle: Implications for secular cooling

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ABSTRACT

Examining length and time scales reveals ruinous problems in diverse determinations of thermal conductivity (k) involving the diamond anvil cell (DAC). (1) Conditions in laboratory experiments are optically thick (diffusive) for low-frequency phonons, but optically thin (ballistic) for high-frequency photons. Because speeds of photons are about $\times 10^5$ those of phonons, ballistic photons transport heat over the short length and time scales of pulse-heating measurements in the DAC intended to measure phonons. Ballistic transport was confirmed by conducting pulse-heating experiments under various conditions. Not accounting for this time-dependent effect produces fallacious values for the lattice contribution to k. (2) In DAC optical spectroscopy, strong refraction was misinterpreted as sample absorption and its affect on path length went unnoticed, resulting in invalid calculations of the radiative diffusive component of k. Better estimates of lower mantle k are summarized. Scaling aspects point to the controls exerted by radiative transfer early in Earth's history and the importance of mantle layers to Earth's present thermal state. Diffusion of radiation is fast, making retention of primordial heat improbable: thus today's Earth is in quasi-steady-state, wherein its emitted heat is derived solely from current radiogenic contents.

1. Introduction

Heat transfer involves scales of length and time, and therefore of speed, which is a crucial aspect of dynamic behavior. Scale is relevant to all models and experiments involving heat flow. Heat transport is complicated because diverse scales pertain and not only do competing processes exist either in parallel or in series, but conditions can be transient or steady-state, and moreover may or may not be diffusive. Modeling macroscopic cooling of our immense Earth utilizes small-scale laboratory experiments as well as inferences of microscopic processes based on spectra obtained from tiny samples. Multiple crossings of scales (Yuen et al., 2000; Barth et al., 2002) and the above complexities not only necessitate careful execution of experiments and interpretation of results, but furthermore require deciphering conditions under which said results can be extrapolated to Earth's mantle. Approximations or trade-offs are necessarily involved, and must be understood for extrapolations to be valid.

This report centers on how length, time, and speed scales affect both heat transfer measurements and spectral data acquisition in the diamond anvil cell (DAC). My analysis permits evaluation of reliability and accuracy, beyond that nominally reported, regarding heat transport properties of mantle candidate materials. In ultra-high-P studies geared to generate conditions relevant to the Earth's interior (e.g., Beck et al., 2007; Goncharov et al., 2006, 2008, 2009; Keppler et al., 2007, 2008), scale aspects of the physical processes involved in heat transfer were misunderstood, leading to baseless values of thermal conductivity. Better founded values presently available are summarized. Heat transport in Earth's mantle with time is discussed from scaling perspectives, leading to the conclusion that a large proportion of secular cooling in the current heat budget is impossible, due to immense speed at which radiation diffuses.

2. Experimental

2.1. Samples

Synthetic MgO was purchased from Material Technology International (MTI) Corp.; NaCl from Janos and International Crystal

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Laboratories; $SrTiO_3$ from Morion Corp. Glass of $CaAl_2Si_2O_6$ was synthesized as described by Hofmeister et al. (2009). Sizes of the slabs were 10–12.7 mm across by 0.8–1.6 mm thick.

2.2. Spectroscopy

An evacuated Bomem DA3.02 Fourier transform interferometer with a SiC source, and InSb or HdCdTe detectors and CaF_2 or KBr beamsplitters covers frequencies (ν) of ~500–8000 cm^{-1}. Instrumental accuracy is 0.01 cm^{-1}. About 2000 scans were collected near 298 K from polished samples at a resolution of 2 cm^{-1}.

2.3. Pulse-heating experiments

Closely related, laser-flash measurements with a LFA 427 manufactured by Netzsch Gerätebau, Germany, of the samples studied here, and calibration procedures, have been previously described (Hofmeister, 2004, 2007a; Hofmeister et al., 2007, 2009; also see citations therein). The sample sits on top of a graphite tube and is heated with a GGG laser from below, while the emissions are collected by an InSb detector located above the sample. A high-temperature furnace surrounds the sample. Fused silica and CaF_2 windows permit light to enter and exit the furnace, respectively.

For the present study, samples were lightly sand blasted and a Quorum Technologies SC-7620 mini-sputter coater was used to apply Pt coatings of about 1 μm thick on one side *only*. The same LFA apparatus was used to record emissions at 298 K as a function of time after pulse heating with our GGG laser of our single-coated samples. Laser powers used were lower than in standard LFA experiments, which raise sample temperature by about 4 K. For some samples, the Pt-coated side was sprayed with graphite adding a C layer <0.5 μm thick: resulting *t*–*T* curves were essentially the same.

3. Theory: scales in heat flow

3.1. Microscopic mechanisms of heat flow and associated speeds

All processes have an associated length scale, which is linked to a specific physical law. Microscopic processes differ regarding wavelength (connected with transition energies), attenuation distances (arising from strengths of interaction), and speed.

Heat-energy is transported by lattice vibrations, because all atoms in a solid are linked thru chemical bonds. Quantized vibrations (phonons) exist as two types, optic and acoustic, which are closely related (see discussions of Brillouin zone folding and dispersion relations, e.g., Burns, 1990). In optic modes, atoms move in opposite directions, so interactions are strong, vibrations are highly damped and fairly localized. In acoustic modes, atoms translate together within the unit cell, so interactions are weaker, allowing propagation over long distances, even huge distances, when large energies are involved, such as in Earthquakes. Both types occur as transverse and longitudinal varieties, but acoustic modes are generally described as shear or compression waves, due to ties with deformation of solids.

In complex structures such as silicates, optic phonons are important to energetics being an order of magnitude more numerous than acoustic modes and having higher energies, i.e., in the infrared (IR) range of the electromagnetic (EM) spectrum, known as "heat" in the vernacular. Although previous models considered acoustic modes to dominate carriers heat transport (e.g., Morelli and Slack, 2006), this cannot be correct because heat is attenuated much more strongly than sound and all such models fail to describe the change in *D* or *k* across solid solutions. That optic phonons are crucial to lattice heat transport is demonstrated for a variety of structures by strong correlations of IR peak widths with thermal diffusivity, taking sound speeds and the number of atoms in the primitive unit

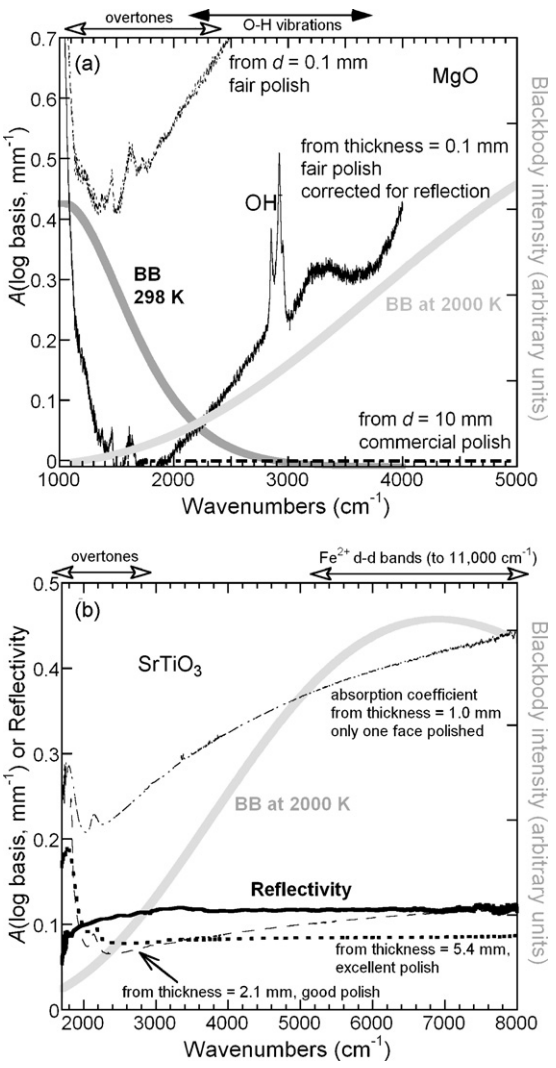

Fig. 1. Comparison of spectral features in magnesiowustite and perovskite structures to blackbody curves at ambient and mantle temperatures, showing how imperfect polish creates an artificial UV rise. Grey lines = blackbody curves on arbitrary scales. Arrows above the frame indicate frequency ranges associated with types of transitions found in minerals. (a) Absorption coefficients for MgO calculated on a log basis. Dots = spectra obtained for a sample with *d* = 0.1 mm. Solid = spectra of this same small sample, corrected for reflections. Dot–dash = spectra scaled from commercially polished MgO with 10 mm thickness. See Hofmeister et al. (2003) for additional reflectance and absorbance data on MgO. (b) Spectra of colorless, cubic perovskite $SrTiO_3$. Broken light lines = absorption coefficients calculated from absorbance of slabs of varying thickness and polish, as labeled. Heavy line = $SrTiO_3$ reflectivity.

cell into account in the damped harmonic oscillator model (Giesting and Hofmeister, 2002; Hofmeister et al., 2007; Hofmeister, 2004, in review).

Optic modes occur not only as fundamentals but also as higher energy overtones, which participate in lattice heat transfer. However, overtones rapidly loose strength with order, and do not exist as distinct entities above ~3rd order, ~3000 cm^{-1} for silicates (Mitra, 1969; Hofmeister and Mao, 2001) but ~1500 cm^{-1} for simple oxides (Fig. 1a), leading to extreme transparency in the spectral region known as the near-IR, and a clear demarcation between vibrational and optical transfer of heat, discussed further below.

Heat disturbances involving lattice vibrations propagate over short distances (inside the unit cell) at the (compressional) speed of sound (u_p), which can be understood by considering the example of the diatomic chain (Hofmeister, in review), and also stems from shear (TA) modes not possessing a definable Gruneisen parame-