Effect of mass disorder on the lattice thermal conductivity of MgO periclase under pressure

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Thermal conductivity of mantle materials controlling the heat balance and thermal evolution of the Earth remains poorly constrained as the available experimental and theoretical techniques are limited in probing minerals under the relevant conditions. We report measurements of thermal conductivity of MgO at high pressure up to 60 GPa and 300 K via diamond anvil cells using the time-domain thermoreflectance technique. These measurements are complemented by model calculations which take into account the effect of temperature and mass disorder of materials within the Earth. Our model calculations agree with the experimental pressure dependencies at 300 and 2000 K for MgO. Furthermore, they predict substantially smaller pressure dependence for mass disordered materials as the mechanism of scattering changes. The calculated thermal conductivity at the core-mantle boundary is smaller than the majority of previous predictions resulting in an estimated total heat flux of 10.4 TW, which is consistent with modern geomodeling estimates.

Recently, there has been a great deal of experimental and theoretical activity in determining heat transport properties of the mantle minerals1–6 as these parameters have been realized to be critically important for geomodels aiming to better understand the Earth’s thermal history and geodynamics7–9. Central to this knowledge is the determination of various energy contributions to the Earth’s overall energy balance. These can be estimated based on heat flow across the most distinct physical and chemical planetary interfaces -- the Earth’s surface, which is well constrained and the core-mantle boundary (CMB), which remains to be more precisely determined10. Knowledge of the overall energy balance gives access to various phenomena within Earth’s interior such as radiogenic heating, dynamics of thermal plumes in the mantle, and also to the Earth’s history, in particular to the extent to which deep mantle melting previously occurred11.

Earth’s mantle consists of simple and ternary (perovskite) oxides of Mg, Si, and Ca doped with Fe and Al. These materials are electrically insulating, thus thermal transport is governed by phonons. Other contributions to the heat transport, including radiative conductivity and convection, are not considered in this paper. Perovskite, (Mg,Fe)SiO3, is the primary component within the Earth’s mantle, while ferropericlase (Fe,Mg)O is the second most abundant mineral in the mantle. The experimental determinations of the lattice thermal conductivities of these materials are numerous1–5,12–15, but limited in pressure and temperature and also in experimental accuracy. Thus, estimates of the thermal conductivity at the conditions of the CMB are based on phenomenological extrapolations16,17 and on theoretical first-principle calculations18–20, both of which are not validated experimentally. Moreover, since the major mantle minerals are solid solutions and have mass disorder, their thermal conductivity is greatly affected21. This effect has been theoretically estimated in the case of isotopic substitution19, but has not been examined for large mass disorder in mixed crystals such as ferropericlase. Until now, the effect of mass disorder could only be estimated through experimental investigations that were limited to low pressure1. Pressure dependence of thermal conductivity in the case of disordered materials has never been addressed.

Here we present data on the thermal conductivity of MgO - a prototype oxide- up to 60 GPa to establish a baseline for the pressure dependence of thermal conductivity. We used the time domain thermoreflectance technique22,23, which offers a non-contact, optical method for extending thermal transport measurements of mantle materials to higher pressure and temperature. To account for mass disorder and the effects of elevated temperature, we applied a Debye-Callaway-Morelli (DCM) model24, which closely described the experimental...
Results

Figure 1 shows example data for the in-phase ($V_{in}$) and ratio ($-V_{in}/V_{out}$) signals of the TDTR measurements on the MgO coated with Al film at ambient condition. The thermal conductivity of MgO was determined by comparing the ratio $-V_{in}/V_{out}$ as a function of delay time with the calculation of a thermal model that takes into account the heat flow into the MgO substrate as well as the heat flow into the Ar medium. Since the thermal penetration depth in MgO at the modulation frequency of pump beam (10 MHz) is ~0.7–1.2 μm, small compared to the radius of the laser spot size, ~7.5 μm, the heat flow in our sample geometry is predominantly one-dimensional. The parameters of the thermal conductivity model are given in supplementary materials.

The DCM model, which we have used to calculate the effects of mass disorder and temperature effects, is derived from the Boltzmann transport equation for an isotropic and linear phonon dispersion, and assumes functional forms for the normal and resistive phonon relaxation rates for the longitudinal and transverse modes. For each mode we assume a truncated Debye dispersion, with cutoff frequency set by the acoustic phonon frequency near the [100] zone edge as a linear function of MgO density (see Ref. 2, Suppl. Materials). As such, this calculated $k_{DCM}$ includes only acoustic modes, so to account for the optical modes our model is actually $k_{MgO} = k_{DCM} + k_{min}$, where $k_{min}$ is the minimum thermal conductivity (in the limit of an amorphous solid) from Ref. 29. Further details of our DCM model are given in supplementary materials.

We begin with the description of the experimental results for periclase. Two experimental runs to 32 and 59 GPa yielded consistent data sets. Figure 2 shows the high pressure thermal conductivity data up to pressures of 60 GPa compared to various phenomenological models for predicting the high pressure behavior of MgO. The ambient pressure thermal conductivity value (53(2) W/m/K) is in agreement with that found in literature, which showed single crystal MgO at 298 K in air to have a mean value of 55.2 ± 0.4 W/m/K. The experimental error bars determine the uncertainty of the fit to the experimental time series (Fig. 1) vary from 10% at low to 19% at high pressures. These uncertainties are comparable to those of the classical Angstrom method for the large press measurements and are better than those which have been reported recently by thermo-reflectance on the ns time scale.

Our high-pressure data for the thermal conductivity, $κ$ can be fit well by a linear function (Fig. 2), but can also be fit linearly on a log-log scale as a function of density (inset). This is useful in comparing with phenomenological descriptions, which usually assume the power law dependence as a function of density and temperature.

Figure 1 | Ambient pressure data: (a) In-phase($V_{in}$) signal as a function of time. The metallic transducer film thickness can be determined from the acoustic echo signal which is present within the $V_{in}$ signal. (b) Ratio ($-V_{in}/V_{out}$) signal as a function of time for epi-polished and hand polished MgO, along with fit to the thermal calculation.

Figure 2 | Thermal conductivity of MgO up to 60 GPa at room temperature. The open and dotted circles are our data on pressure increase for two different pressure runs; the filled circles are our data on pressure release. The inset shows the data plotted in a log-log scale; the solid curve is the linear fit. Gray thick line is the results of the DCM calculations from this work. Phenomenological predictions are shown by the long dashed line; dashed-dotted line, and short dashed line. The latter description coincides with that determined from the Leibfried-Schlomann equation $\kappa = AV^{1.13}v_D^{-1}\gamma^{-1}T^{-1}$, where $V$ is volume, $\omega_D$ is Debye frequency, $\gamma$ is the Grüneisen parameter, $T$ is temperature and $A$ serves as a fit parameter.
in some models. Use of the self-consistent thermodynamic models1,2 to that with natural isotope composition by nearly 50%19. The theor-

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proximity to the conditions of the geotherm in the lower mantle

temperature range of the lower interior requires

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closed circles with large error bars are experimental data from Ref. 34, the presence of the post-perovskite phase should increase the lattice conductivity (e.g., Ref. 3), but the radiative component diminishes. We have presented measurements of thermal conductivity for MgO up to pressures of 60 GPa within a DAC using an all-optical pump-probe technique at ambient temperature. The pressure dependence for the thermal conductivity of MgO was found to obey the power law of density with the power parameter \( g \) of 5.0(1), corresponding to an isothermal pressure coefficient of 2.1% GPa\(^{-1}\). We have also performed DCM calculations of the pressure dependence of pure and mass disordered MgO at 300 and 2000 K. The results show that mass disorder substantially reduces the value and the pressure dependence of the thermal conductivity. Using these results as a guide, we revisited the estimations of the heat flux through the CMB by extrapolating the pressure dependences of the thermal conductivities of mass disordered mantle minerals to CMB conditions. The result for the heat flux agrees with the majority of the previous estimates and lies in the middle of the current geophysical estimations. Future more careful estimations of the heat transport properties of deep Earth will require verification of the results of the calculations presented here.

**Methods**

Samples of (100) orientation MgO (SPI supplies) had a polish that is suitable for the epitaxial growth of other materials on the MgO as a substrate (epi-polished). They were heated to 1200 K for 15–30 minutes under vacuum to remove hydroxides and other volatile hydrocarbons from the exposed MgO surface. The substrates of MgO were then coated in situ with ~80 nm Al film via magnetron sputtering. The backside surface of the MgO (which was not coated) was then ground and polished to ~10 \( \mu \)m thickness and cleaved to 50 \times 50 \( \mu \)m\(^{2}\) pieces for sample loading into a symmetric piston-cylinder diamond anvil cell. The sample and a ruby ball were loaded into the cell with Ar as the pressure medium, so the Al film is sandwiched between the MgO sample and the Ar medium (Fig. 1S of supplementary materials).

The thermal conductivity of MgO at room temperature was measured by time domain thermoreflectance (TDTD), which utilizes sub-picosecond optical pulses to pump and probe the dynamics of thermal diffusion. In TDTD, the output of a mode-locked Ti:sapphire oscillator was split into pump and probe beams: the pump beam heats the Al surface and the probe beam subsequently monitors changes in the optical reflectivity of Al due to the temperature evolution. The in-phase (\( V_{in} \)) and out-of-phase (\( V_{out} \)) signals of the variation of the reflected probe beam was then measured by a Si photodiode and an rf lock-in amplifier. The details of our TDTD system are outlined elsewhere.

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**Author contributions**

A.F.G. and D.G.C. designed research. D.A.D., W.P.H. and A.F.G. conducted the experiments. G.T.H. and D.G.C. developed the mass disorder model. D.A.D., W.P.H., A.F.G. and G.T.H. wrote a manuscript. All authors reviewed the manuscript.

**Additional information**

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