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Thermal conductivity of MgO, MgSiO₃ perovskite and post-perovskite in the Earth's deep mantle

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A B S T R A C T

We report lattice thermal conductivities of MgO and MgSiO₃ in the perovskite and post-perovskite structures at conditions of the Earth's lower mantle, obtained from equilibrium molecular dynamics simulations. Using an advanced ionic interaction potential, the full conductivity tensor was calculated by means of the Green–Kubo method, and the conductivity of MgSiO₃ post-perovskite was found to be significantly anisotropic. The thermal conductivities of all three phases were parameterized as a function of density and temperature. Assuming a Fe-free lower-mantle composition with mole fractions $x_{MgSiO_3} = 0.66$ and $x_{MgO} = 0.34$, the conductivity of the two-phase aggregate was calculated along a model geotherm. It was found to vary considerably with depth, rising from 9.5 W/(m K) at the top of the lower mantle to 20.5 W/(m K) at the top of the thermal boundary layer above the core–mantle boundary. Extrapolation of experimental data suggests that at deep-mantle conditions, the presence of a realistic amount of iron impurities lowers the thermal conductivity of the aggregate by about 50% (Manthilake et al., 2011a). From this result and our thermal conductivity model, we estimate the heat flux across the core–mantle boundary to be 10.8 TW for a Fe-bearing MgO/MgSiO₃ perovskite aggregate and 10.6 TW for a Fe-bearing MgO/MgSiO₃ post-perovskite aggregate.

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1. Introduction

The thermal conductivity of minerals in the Earth's mantle is an important geophysical parameter which governs the heat flux from the core up to the surface and hence strongly influences mantle dynamics (Naliboff and Kellogg, 2007). Moreover, the thermal conductivity of minerals at the core–mantle boundary (CMB) determines the amount of heat extracted from the core, driving the convection of the liquid outer core and thus controlling the power available to the generation of the Earth's magnetic field (Davies, 2007; Aubert et al., 2009). Yet, measuring thermal conductivities at mantle pressures and temperatures is extremely challenging, and the experimental data are scarce. Several schemes exist to extrapolate thermal conductivities measured at lower pressures and temperatures to deep-mantle conditions (Ross et al., 1984; Hofmeister, 1999), but they are plagued with large uncertainties. Hence a computational approach is desirable to evaluate thermal conductivities directly at the relevant conditions. The aim of this study is to provide reliable values for the lattice thermal conductivities of MgO, MgSiO₃ perovskite (Pv) and

post-perovskite (PPv) at lower-mantle conditions and their variation with temperature and density (or pressure). These results can be directly applied to thermal transport in the lower mantle.

In deep-mantle minerals, heat is conducted by phonons and electromagnetic radiation. The importance of the radiative contribution to thermal transport in the Earth is under debate, and current estimates span a considerable range: while Goncharov et al. (2009) report a radiative thermal conductivity below ~ 0.5 W/(m K) across the lower mantle, Stamenković et al. (2011) predict ~ 5 W/(m K) at the CMB, and Keppler et al. (2008) even values of up to ~ 10 W/(m K), which is of the same order of magnitude as the lattice contribution. Moreover, the radiative conductivity seems to depend strongly on crystal grain size and on the iron content (Hofmeister and Yuen, 2007). In view of these difficulties, we focus on the lattice contribution in this study. If the radiative conductivity turns out to be significant, it can simply be added to the lattice part presented here.

Over the past years, different atomic-scale methods were developed to calculate lattice thermal conductivities. Stackhouse et al. (2010) applied the non-equilibrium or "direct" method (Müller-Plathe, 1997; Nieto-Draghi and Avalos, 2003) to derive the thermal conductivity of MgO, using molecular dynamics (MD) simulations based on density functional theory (DFT). In this approach, an energy current from the cold to the hot side of the simulation cell is imposed. From this current and the steady-state

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temperature gradient which builds up, the thermal conductivity is obtained via Fourier's law. While computationally rather efficient, the method suffers from strong finite-size effects, thus requiring extrapolation to infinite system size and introducing considerable uncertainties (Sellan et al., 2010). An approach based on phonon lifetimes, obtained from DFT, was used by de Koker (2009, 2010) and by Tang and Dong (2010) to calculate the thermal conductivity of MgO. Phonon lifetimes were either calculated from line widths in the Fourier transform of the velocity autocorrelation function (de Koker, 2009) or from anharmonic lattice dynamics (Tang and Dong, 2010). Combined with the Boltzmann transport equation for the phonon gas, they yield the thermal conductivity in the relaxation time approximation. This approach treats the anharmonicity of lattice vibrations perturbatively and is thus limited to temperatures where atomic displacements from the equilibrium positions are small enough for higher-order anharmonicity to be neglected.

A third approach, the Green–Kubo method, uses the Green–Kubo relations (Kubo, 1957) to obtain thermal conductivities from appropriate current correlation functions, which, in turn, are readily extracted from equilibrium MD trajectories. This method has been successfully applied to solids (e.g. Volz and Chen, 2000; Sellan et al., 2010; Esfarjani and Chen, 2011) and liquids (e.g. Galamba et al., 2007; Ohtori et al., 2009b; Salanne et al., 2011). In contrast to the non-equilibrium method, no concerns about leaving the linear-response regime arise for equilibrium MD. Moreover, the Green–Kubo method exhibits a weaker finite-size effect (Sellan et al., 2010), provides the full thermal conductivity tensor in one simulation and takes into account thermoelectric effects which can contaminate results of the non-equilibrium method for ionic conductors (Salanne et al., 2011). Unlike the lattice dynamics approach, the Green–Kubo method takes into account anharmonicity to all orders. Thus its validity is not restricted to low temperatures. In the light of these advantages, we decided to use the Green–Kubo approach to calculate thermal conductivities of MgO, MgSiO$_3$ Pv and MgSiO$_3$ PPv at conditions spanning a wide pressure and temperature range. We also determined conductivities at conditions where experimental data are available, and satisfactory agreement with these experiments makes us confident that our results are equally reliable at CMB conditions. A drawback of the method is that it requires long run durations (in the nanosecond range) to obtain reasonable statistical accuracy. Our calculations are based on classical MD simulations involving an interaction potential of first-principles accuracy (Jahn and Madden, 2007).

2. Theory

The thermal conductivity tensor λ is defined by Fourier's law, $\mathbf{j}_Q = -\lambda \nabla T$, under the constraint that no mass or electric currents are present. This constraint is relevant to electronic or ionic conductors, where thermoelectric effects occur (Callen, 1985). Fourier's law is of linear-response type and relates the heat current density $\mathbf{j}_Q$ to the temperature gradient ∇T. For cubic and orthorhombic crystals, λ is diagonal if the coordinate axes are along the crystal axes, and direction-dependent conductivities can be defined by

$$\lambda_\alpha = -j_Q^\alpha / \nabla_\alpha T, \quad \alpha \in \{x,y,z\} \tag{1}$$

In the framework of non-equilibrium thermodynamics (Callen, 1985; de Groot and Mazur, 1984), the thermal conductivity can be expressed in terms of kinetic coefficients L_{AB}, as is done in Eqs. (3) and (4). They determine the linear response of the system to deviations from equilibrium, i.e. energy and mass flows resulting from thermal and chemical gradients. The gist of the

Green–Kubo method is that the kinetic coefficients L_{AB}, although representing non-equilibrium behavior, are linked to fluctuations in thermodynamic *equilibrium* via the fluctuation–dissipation theorem. The kinetic coefficients, and hence the thermal conductivity, can therefore be obtained from equilibrium MD by means of appropriate Green–Kubo formulae, which relate the linear response of a system with volume V to current correlation functions in thermodynamic equilibrium

$$L_{AB}^{\alpha\beta} = \lim_{\tau \to \infty} \left[\frac{1}{k_B V} \int_0^\tau dt \langle J_A^\alpha(t) J_B^\beta(0) \rangle \right] \tag{2}$$

where k_B is Boltzmann's constant, and J_A^α are the Cartesian components of the energy current ($A=U$) or of the mass currents ($A = 1, \ldots, N-1$, where N is the number of chemical species in the system), with respective dimensions of energy or mass times velocity. Angular brackets denote an ensemble average. We assume that the center of mass is at rest, hence there are only $N-1$ independent mass currents for a system with N chemical species. Then, for a system with two species, the thermal conductivity is given by Galamba et al. (2007)

$$\lambda_\alpha = \frac{1}{T^2} \left(L_{UU}^{\alpha\alpha} - \frac{(L_{U1}^{\alpha\alpha})^2}{L_{11}^{\alpha\alpha}} \right), \quad \alpha \in \{x,y,z\} \tag{3}$$

and for a system with three species by Salanne et al. (2011)

$$\lambda_\alpha = \frac{1}{T^2} \left(L_{UU}^{\alpha\alpha} - \frac{(L_{U1}^{\alpha\alpha})^2 L_{22}^{\alpha\alpha} + (L_{U2}^{\alpha\alpha})^2 L_{11}^{\alpha\alpha} - 2L_{U1}^{\alpha\alpha} L_{U2}^{\alpha\alpha} L_{12}^{\alpha\alpha}}{L_{11}^{\alpha\alpha} L_{22}^{\alpha\alpha} - (L_{12}^{\alpha\alpha})^2} \right) \tag{4}$$

It is worth noting that Eqs. (3) and (4) are written here in terms of mass currents, whereas they were originally derived in terms of ionic currents.

3. Simulation details

We performed equilibrium molecular dynamics simulations in the NVT ensemble, with a time step of 1 fs for the integration of the equation of motion and a Nosé–Hoover thermostat (Nosé, 1984; Hoover, 1985) maintaining the system at the desired temperature. The cell dimensions were chosen as the average cell size in a previous NPT run at the desired pressure P, maintained by a barostat (Martyna et al., 1994). The interactions between atoms were described by an advanced ionic interaction potential which was parameterized non-empirically, using DFT as a reference (Jahn and Madden, 2007). This potential has been shown to reliably predict properties of minerals of the system CaO–MgO–Al$_2$O$_3$–SiO$_2$ over a wide temperature and pressure range, with accuracy comparable to DFT. In particular, the ionic interaction potential used in this study was shown to describe MgO and the MgSiO$_3$ phases perovskite and post-perovskite well, predicting lattice constants to within 1% and elastic constants mostly to within 10%, compared to DFT results (Jahn and Madden, 2007). The elastic constants determine vibrational modes of the crystal in the limit of long wavelengths (Ashcroft and Mermin, 1976). These modes close to the Brillouin zone center, in turn, are expected to make the largest contribution to the thermal conductivity of the crystal (Tang and Dong, 2010). Therefore, we expect the interaction potential to produce accurate lattice dynamics and thermal transport properties. For MgO, MgSiO$_3$ Pv, and MgSiO$_3$ PPv, we used cubic or orthorhombic supercells containing 512, 960, and 720 atoms, respectively. For each composition, temperature, and pressure, we generated trajectories of at least 0.5 ns and up to 2.4 ns.

At each time step of the MD run, the mass currents for each species and the energy current were extracted for later calculation of