Understanding Heat Transfer from the Perspective of IR to UV Spectroscopy

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Transport of heat occurs under non-equilibrium conditions, making this phenomenon difficult to understand. Systematic errors in experimental data on hard, partially transparent materials (many minerals) have masked true behavior over the past century. Correcting the basics requires extensive measurements and recognizing that "heat" and "light" are equivalent. My efforts center on the use of spectroscopic measurements to probe the interaction of "heat" with matter and on developing new phenomenological models. Thermal transport properties (k = thermal conductivity = $\rho C_P D$ and D = thermal diffusivity, where C_P = heat capacity and ρ = density) largely govern Earth's thermal state and evolution. Because mineral spectra vary with frequency, heat transport can be diffusional and/or ballistic (direct) depending on temperature, which is tied to frequency and path length. Providing and extrapolating reliable data under meaningful geophysical conditions is challenging.

Direct measurements of the vibrational component of diffusivity in semi-transparent materials as a function of temperature (T) are now accurately made with laser flash analysis, essentially a spectroscopic technique, due to recent advancements in sample coatings and mathematical models of the time-temperature curves. My group has published $D(T)$ data for the following structures: garnet, olivine, spinel, clinopyroxene, feldspar, silica, perovskite, B1 and B2, along with glass and melts of many compositions, and various rocks. These data are explained by phonon lifetimes obtained from available IR reflection spectra and acoustic speeds at ambient and elevated T. Speeds are acoustic because heat is propagated as a disturbance. Polarization behavior shows that optic modes transfer energy. We discovered that D^{-1} is proportional to αT where α = thermal expansivity. This relationship exists because α is anharmonic and depicts the role of the crystal lattice in vibrational transport. Disorder provides additional phonon scattering, and is quantified by peak widths. The above and depiction of the quasi-harmonic pressure response by the bulk modulus and Grüeneisen parameters permit both extrapolation and prediction based on measurements of spectra and/or physical properties. Measurements of $D(P)$ at high pressure are not yet accurate, but agree with this simple model.

Diffusive radiative transport cannot be measured, and therefore spectroscopic measurements and a realistic model are essential. At ambient pressure, near-IR to UV spectra are used because refraction errors in the diamond anvil cell cannot be accurately determined (perceived absorption is mostly the baseline) and because P is unimportant compared to T. Scattering and grain-size are included to account for effects well-known to spectroscopists. For low Fe contents, absorptions are low: from this behavior and integration in the model over frequency, the results do not strongly depend on sample character, permitting application to the mantle. What is important, however, is not the value of k for radiative transfer but the dominance of this process in transient heating events due to photon speeds.

References:
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