

Thermal Conductivity Systematics in Olivine and Spinel

By

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Abstract Systematic of thermal conductivity with change in chemical composition and with polymorphic phase transformations has been constructed for compounds of M_2SiO_4 ($M=Mg, Fe, Co, Ni$). The thermal conductivity (λ) changes with the molar volume (V) logarithmically at a fixed temperature along a relationship, $-\partial \ln \lambda / \partial \ln V \sim k$ (constant). The constant k has a value of about 10 for both olivine and spinel structure. On the other hand, this is 4 or 5 for the polymorphic change from olivine to spinel. Using this relationship, thermal conductivity of modified spinel, β - Mg_2SiO_4 is estimated to be $7.3 \text{ W m}^{-1} \text{ K}^{-1}$ at 373 K.

1. Introduction

According to comprehensive models (e.g. ITO and TAKAHASHI, 1987; IRIFUNE and RINGWOOD, 1987) for the constitution of the Earth's mantle, the dominant mineral phase in its upper part has olivine composition, $(Mg, Fe)_2SiO_4$. For more than two decades high pressure research in Earth sciences has elucidated that the olivine (α - M_2SiO_4 ; low-pressure phase) transforms to denser phases with increasing pressure. This phase transformation could occur in the transition region of the Earth's mantle, and thereby would contribute to the steep seismic velocity gradient with depth in this region. It has been established that the olivine (α -(Mg, Fe) $_2SiO_4$) begins to transform into modified spinel (β -(Mg, Fe) $_2SiO_4$) at the depth of 400 km, then after completing this, spinel (γ -(Mg, Fe) $_2SiO_4$) emerges around 550 km depth, and finally the spinel dissociates into silicate perovskite ((Mg, Fe) SiO_3) and rocksalt type oxide ((Mg, Fe)O) below 650 km.

Heat transfer in the Earth is an important issue for the evolution of this planet or for the thermal state in the layered interiors. Experiments on the thermal properties for candidate materials of the Earth's interior are vital approach to this problem. *In situ* measurements, i.e. those under high pressure and high temperature prevailing within the Earth's interior must be ideal. However, there are many difficulties of measuring physical properties of Earth's materials under high pressure. Then we still have another way of approach: to measure the properties of a variety of materials analogous to those of the Earth, to find relationships among them, and then to predict the physical constants of the Earth's materials. Here I attempt to construct a systematics of thermal conductivity in the olivine and spinel structure compounds, and to show a way of estimating the thermal conductivities of the important mantle minerals.

2. Relationships among the thermal conductivities of olivine and spinel

2.1. Thermal conductivities of olivine and spinel reduced from thermal diffusivities

Thermal conductivities of olivine and spinel here have been reduced from thermal diffusivities using the relation, $\lambda = \rho \cdot c \cdot a$, where λ is thermal conductivity, ρ is density, c is heat capacity per unit mass and a is thermal diffusivity. The heat capacities of mantle minerals including olivine and spinel were determined by WATANABE (1982) using a scanning calorimetry from 350 K to 700 K. The thermal diffusivities of small sintered were measured by the Angstrom method from 300 K to 500 K or to 600 K (except for γ -Mg₂SiO₄); description of the samples and details of the method will be reported elsewhere.

Table 1 shows some thermophysical properties of the olivine, spinel, and modified spinel structure compounds. Olivine and modified spinel are of orthorhombic crystal symmetry; the thermal diffusivity or the thermal conductivity of olivine represents the value for the aggregates of the anisotropic crystal.

Table 1. Some thermophysical properties of olivines, spinels and modified spinels.

	Molar weight	Density	Molar volume ¹⁾	Heat capacity at const. pressure (373 K)	Thermal ²⁾ diffusivity (373 K)	Thermal ³⁾ conductivity (373 K)	Thermal Debye temperature
	<i>M</i>	ρ	<i>V</i>	<i>c_p</i>	<i>a</i>	λ	θ_{Dh}
	10 ⁻³ kg mol ⁻¹	10 ³ kg m ⁻³	10 ⁻⁶ m ³ mol ⁻¹	10 ³ J kg ⁻¹ K ⁻¹	10 ⁻⁶ m ² s ⁻¹	W m ⁻¹ K ⁻¹	K
Olivine							
α-Mg ₂ SiO ₄	140.69	3.225	43.62	0.958		5.38**	914
α-Fe ₂ SiO ₄	203.78	4.393	46.39	0.730	0.89	2.9	691
α-Co ₂ SiO ₄	209.95	4.708	44.59	0.726	1.14	3.9	616
α-Ni ₂ SiO ₄	209.48	4.928	42.51	0.694	1.85	6.3	769
Spinel							
γ-Mg ₂ SiO ₄	140.69	3.549	39.64	0.907	2.51***	8.1	1012
γ-Fe ₂ SiO ₄	203.78	4.848	42.03	0.702	1.22	4.2	781
γ-Co ₂ SiO ₄	209.95	5.170	40.61	0.699			706
γ-Ni ₂ SiO ₄	209.48	5.346	39.18	0.666	2.70	9.6	835
Modified spinel							
β-Mg ₂ SiO ₄	140.69	3.467	40.58	0.921			993
β-Co ₂ SiO ₄	209.95	5.043	41.63	0.704			685

* WATANABE (1982).
** KINGERY *et al.* (1954).
*** OSAKO and ITO (1988).
1) $V = M/\rho$.
2) with 5% uncertainty.
3) $\lambda = \rho \cdot c_p \cdot a$.

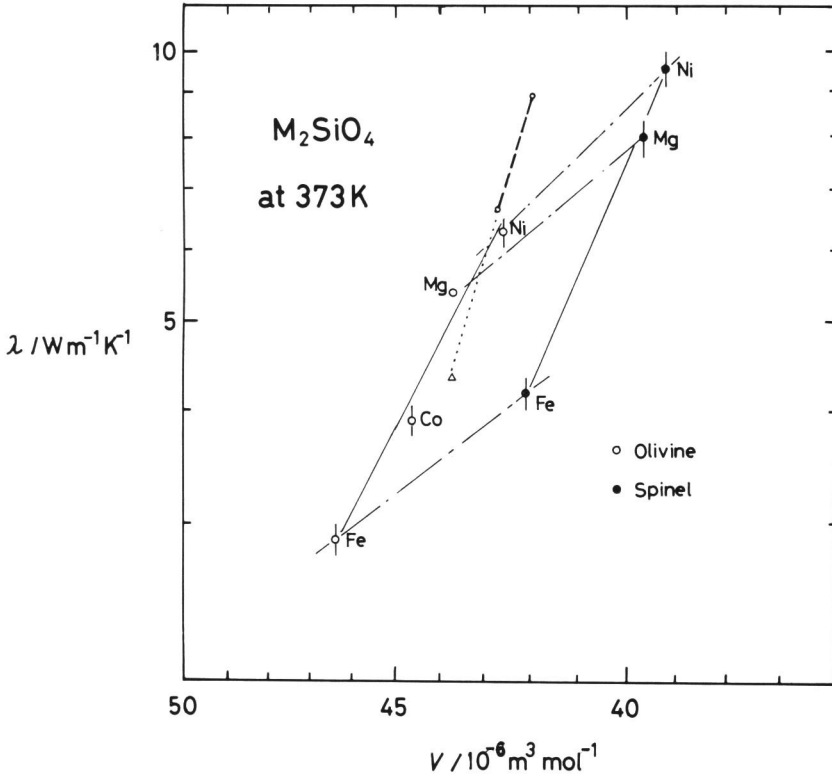


Fig. 1. Thermal conductivity (λ) of olivine and spinels at 373 K versus molar volume (V). Open circles indicate data for olivines and closed circles for spinels. Symbols of element represents that of cation M in the formula, M_2SiO_4 . The vertical bars correspond to the error derived from thermal diffusivity measurement. Isostructural lines (solid) and polymorphic change lines (dash-dotted) can be drawn in this λ - V planes on logarithmic scales. The solid dashed line shows the change in thermal conductivity of α - Mg_2SiO_4 with compression by increasing pressure from 3.0 GPa to 5.0 GPa at 500 K. This line seems to be connected to the point of zero-pressure value (triangle) at the same temperature.

2.2. Relationships among the thermal conductivities at a fixed temperature

The thermal conductivities of olivine and spinel at 373 K versus molar volume (V) are shown in Fig. 1, where both of the variables are plotted on a logarithmic scale; slope of a line on the plane indicates a logarithmic rate of change $-\partial \ln \lambda / \partial \ln V$. The thermal conductivity increases with decreasing the volume both for the olivine structure compounds (α - M_2SiO_4 : $M=Mg, Fe, Co, Ni$) and for the spinel structure compounds (γ - M_2SiO_4 : $M=Mg, Fe, Ni$). Thus an 'isostructural' line of the thermal conductivity can be drawn for the exchange of M-ion both in olivine and in spinel. The slope of this line $-\partial \ln \lambda / \partial \ln V$ is about 10.

The volume will also change with increasing pressure. To illustrate this effect

on the λ - V plane the change of thermal conductivity by compression is calculated, using the data of thermal diffusivity measured under high pressures (FUJISAWA *et al.*, 1968). The change of volume is calculated by a Murhnan's equation, $V/V_0 = \{(K_0'/K_0)P + 1\}^{-1/K_0'}$, where K is incompressibility and K' is its pressure derivative and P is pressure, and the suffix of 0 denotes the zero-pressure value. For α - Mg_2SiO_4 K_0 is 120 GPa and K_0' is 5.6 (OLINGER, 1977). The result for 500 K, represented as a dashed line in Figure 1, shows that the change rate $-\partial \ln \lambda / \partial \ln V$ with compression is slightly larger than that with the exchange of cations in the olivines. Moreover, this line seems to be just connected smoothly to the zero pressure value (KINGERY *et al.*, 1954) at the same temperature. However, the data from experiments under high pressure have greater uncertainty than those under the ambient condition. In addition, the absolute value is less reliable than the relative change. Thus this smooth connection might be a fortuitous coincidence. Further measurements should be needed to see whether these two kind of volume change: compression by increasing pressure and lattice contraction by exchanging of cations, have equal effect of thermal conductivity or not.

The phase transformation from olivine to spinel enhances the thermal conductivity. For three compounds, Mg_2SiO_4 , Fe_2SiO_4 and Ni_2SiO_4 the change of thermal conductivity with this phase transformation is also shown in Fig. 1. The change $-\partial \ln \lambda / \partial \ln V$ along these 'polymorphic change lines' with a slope of 4 or 5 is more moderate than that along the isostructural line for olivine or spinel. With the aid of this relation, the thermal conductivity of β - Mg_2SiO_4 could be estimated to be $7.3 \text{ W m}^{-1} \text{ K}^{-1}$ (373 K) at the cross point of the polymorphic change line for Mg_2SiO_4 with the molar volume of β - Mg_2SiO_4 , $40.58 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$.

From a Debye-Grüneisen model, RUOFOSSE and JEANLOZ (1983) derived the change in thermal conductivity of insulating crystals as the similar expression, $\partial \ln \lambda / \partial \ln \rho \sim f$ ($f=7$). They showed that this expression predicts fairly well the change of thermal conductivity on compression, however, it fails in predicting the dependence of conductivity on crystal structure. As also elucidated here, the constant f could no longer have the universal value but would be a variable depending on the modes of volume change, that is, copression with increasing pressure, volumetric change by exchanging of ions in isostructure and density increase with phase transformation.

2.3. Relationships among the thermal conductivities at the Debye temperature

The thermal conductivity of insulating crystal including silicate minerals has strong temperature dependence, inverse proportional to absolute temperature. Needless to say, specifying the temperature at which they are compared should be essential. In insulators heat is mainly transported by lattice vibration. Thus the comparison at the characteristic temperature relating to a lattice vibrational mode would have more physical meanings than that at a fixed temperature.

Figure 2 shows the thermal conductivities of olivine and spinel at the thermal

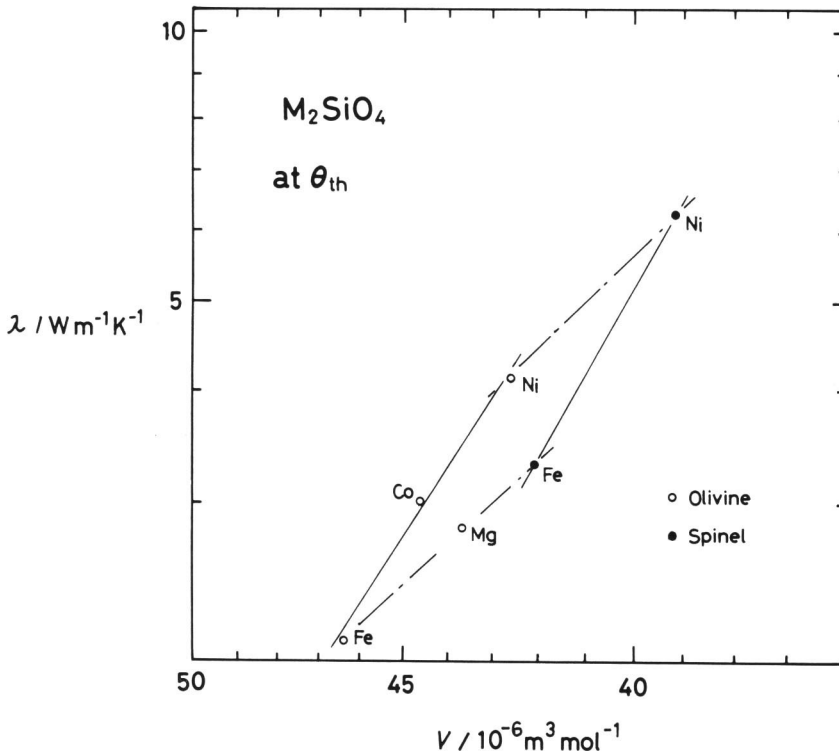


Fig. 2. Thermal conductivity of olivines and spinels at the thermal Debye temperature versus molar volume. Symbols are the same as in Fig. 1. Error bars are omitted; extrapolation of the measured thermal diffusivity to such higher temperatures yields considerable uncertainty, and the Debye temperatures reported have 10% ambiguity. The estimated thermal conductivity of γ - Mg_2SiO_4 at the Debye temperature would range from $3.8 \text{ W/m}^{-1} \text{K}^{-1}$ to $4.6 \text{ W/m}^{-1} \text{K}^{-1}$ (not shown). This uncertainty is due to the situation that the thermal diffusivity is measured at relatively low temperatures, up to 420 K compared with the Debye temperature, 1012 K.

Debye temperature versus molar volume. Although each plotted point has greater uncertainty, systematics similar to that in figure 1 could be seen. Nevertheless, unlike the comparison at a fixed temperature, Mg_2SiO_4 appears to be distinguished from the other compositions, Fe_2SiO_4 , Co_2SiO_4 and Ni_2SiO_4 . Considering that the extrapolation of thermal diffusivities to higher temperatures will yield large ambiguity, to conclude this distinction to be intrinsic might be premature. However it is likely that the presence of ions of transition element, Fe, Co and Ni in olivine or spinel could affect the lattice conduction, and thereby this would split the series of λ - V relation into two branches.

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