Thermoelastic properties of MgSiO₃ perovskite using the Debye approach

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ABSTRACT

MgSiO₃ perovskite is shown to be a Debye-like mineral by the determination of specific heat, Cᵥ, entropy, S, and thermal pressure, ΔPᵥ, using the Debye theory up to 1800 K. Sound velocities and bulk moduli at ambient conditions published by Yeganeh-Haeri were used to find the ambient acoustic Debye temperature, Θ_D. The variation of Θ_D with T was assumed to be a curve parallel to the Θ_D vs. T curves previously found for Al₂O₃, MgO, and MgSiO₃, enabling Θ_D(T) to be given up to 1800 K. To determine Cᵥ, the thermal expansivity, α, and the isothermal bulk modulus, Kᵢ, are needed. After considering several sets of α(T), the α(T) data of Funamori and his colleagues were chosen. Using the ambient Kᵢ and the values of (αKᵢ/αT)ᵥ vs. T reported by Jackson and Rigden, Kᵢ(T) up to 1800 K was found. Then Cᵥ(T) up to 1800 K was found assuming quasiharmonicity in Cᵥ. The data behind the Cᵥ(T) calculation are also sufficient to find the Grüneisen parameter, γ(T), and the Anderson-Grüneisen parameters, δᵥ and δᵢ, up to 1800 K. The value of q = (α ln γ/α ln Vᵥ) was found, and with γ and p, ΔPᵥ vs. V and T was determined. The three sound velocities, vᵥ, vᵢ, and vₛ = (3Kᵢ/ρ)¹/³, were then determined to 1800 K. From vᵥ and vᵢ, Poisson’s ratio and the isotropic shear modulus, G, were found to 1800 K. MgSiO₃ perovskite is one of a small, select group of Debye-like minerals for which thermoelastic properties and the equation of state (EOS) are calculable from acoustic data.

INTRODUCTORY REMARKS ON DEBYE THEORY

Thermoelastic properties for a Debye solid, such as Cᵥ vs. T, at P = 0 can be easily calculated from standard Debye tables. A Debye solid is a monatomic solid (typically a metal) in which thermoelastic properties are a function of only one characteristic frequency, ω₀, which is equivalent to one characteristic temperature, Θ_D (Debye 1912). The specific heat, Cᵥ, of a Debye solid is defined as (Kittel 1971)

\[ Cᵥ = 3R \theta_D \frac{\Theta_D}{T} \]  

(1)

where Θ_D is the Debye temperature; R is the gas constant; and \( \theta_D(\Theta_D/T) \) is the Debye function for specific heat found from tables. Most solids of interest to geoscience are not monatomic. Debye theory may be applied usefully to certain polyatomic minerals, provided the vibrational phonon density of states is well approximated by a Debye frequency spectrum (Kittel 1971),

\[ g(\omega) = \omega^2 \quad \omega \leq \omega_0 \]

\[ = 0 \quad \omega > \omega_0 \]  

(2)

where \( \omega_0 \) corresponds to Θ_D.

Equation 2 does not work as a substitute for the phonon density of states if the solid has a wide band gap, as found in NaI, α-quartz, or calcite. Polyatomic solids in which Equation 2 is a useful substitute for the phonon density of states are called Debye-like solids; these include NaCl, MgO, Al₂O₃, and, as we shall see, MgSiO₃ perovskite. Minerals are rarely Debye-like solids because their thermoelastic properties are not usually a function of a single characteristic temperature. Note that there is no consideration of optic modes in a Debye-like solid.

The pertinent parameters are vᵥ, vᵢ, and vₛ, the shear and longitudinal sound velocities, and the maximum phonon frequency, \( \omega_0 \) (or temperature, Θ₀). The value of Θ₀ is found from the sound velocities as given by the relation between Θ₀ and the mean sound velocity, \( v_m \) (Poirier 1991)

\[ \Theta₀ = 251.2 \left( \frac{\mu}{M} \right)^{1/3} v_m \]  

(3)

where \( \mu = M/p \) is the mean atomic mass; \( M \) is the molecular mass; \( p \) is the number of atoms in the vibrating cell (\( p = 2 \) for NaCl or MgO); and \( \rho \) is the density. \( v_m \), the mean sound velocity, is related to the measured sound velocities by

\[ \frac{3}{v_m^3} = \frac{2}{v_p^3} + \frac{1}{v_s^3} \]  

(4)

\( v_m \) is only slightly larger than \( v_s \), as seen when Equation 4 is written as

\[ v_m = v_s \left( \frac{3}{2 + (v_s/v_p)^3} \right)^{1/3} \]  

(5)