Reports

Phonon Density of States and Specific Heat of Forsterite, Mg_2SiO_4

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The phonon density of states of the geophysically important mineral forsterite has been calculated with a rigid-ion model, which gives good agreement with an experimental measurement by inelastic neutron scattering. The density of states has been used to calculate the specific heat as a function of temperature, the results of which are in excellent agreement with calorimetrically measured values. The rigid-ion model takes account of the interatomic interactions and normal modes of vibration on a detailed microscopic basis, and is therefore more realistic than the Debye and other empirical models used previously.

Forsterite is the magnesium end-member of the olivine $(Mg,Fe)_2SiO_4$ series. Magnesium-rich olivine, $(Mg_{0.9}Fe_{0.1})_2SiO_4$, is considered to be the major component of the earth's upper mantle, whose thermoplasticity is responsible for the motion of the continental plates. Furthermore, the olivine-to-spinel phase transition at high pressure and high temperature is responsible for a major seismic discontinuity at a depth of 400 km. Hence, an understanding of the mechanical and thermodynamic properties of olivine has major geophysical importance. Ultimately, it is desirable to have a description of the olivine on an atomic scale, specifying the relative positions of the atoms and the forces between them. From such a description it is possible to predict its mechanical and thermal properties at temperatures and pressures that exceed those accessible in the laboratory. This knowledge is necessary to understand the thermodynamic behavior of magnesium-rich olivine in the earth's upper mantle.

Information about the detailed atomic positions can be readily obtained from x-ray diffraction studies, and such data exist for olivine under ambient conditions and also at high temperature and high pressure (*1–3*). Some information about the interatomic forces has been inferred from measurements of elastic (*4–6*) and dielectric (*7*) constants and specific heat (*8*), and compared with theoretical results from model calculations (*9–14*). However, these are all macroscopic properties representing various kinds of averages over the interatomic forces or the atomic motions that depend on them; detailed information on an atomic scale is lost. Optical spectroscopic studies have also been carried out on olivine (*11*), but these measurements give information about only a limited set of the atomic motions, the optically active, long-wavelength vibrations ("zone center" phonons).

Inelastic neutron scattering provides detailed microscopic information about the atomic motions that can be related to the interatomic forces via well-known expressions (*15*). In solids containing molecular ions such as $[SiO_4]^{4-}$ the relatively low-frequency intermolecular modes are best studied on single crystals by inelastic neutron scattering with a neutron beam of constant wavelength from a nuclear reactor. Measurements of this type have been carried out by us at Brookhaven National Laboratory and reported separately (*16, 17*). The high-frequency intramolecular modes require the higher energy neutrons found at pulsed spallation sources, and it is convenient to measure the frequency spectrum of these modes by means of a time-of-flight technique on a powder sample. This report presents results of such measurements and comparison of the data with results calculated from a model for the interatomic forces (*18*). As a further check, this model is used to predict the specific heat for comparison with calorimetric data (*8*). Because of the complexity of dealing with a mixed silicate system, this initial investigation was carried out on the magnesium end-member of the olivine series, Mg_2SiO_4 (forsterite) (Fig. 1).

A convenient point of comparison between experiment and theory is the one-phonon density of states or frequency distribution $g(\omega)$ (*14*), where $g(\omega)d\omega$ is the number of phonons, or normal modes of vibration, in the frequency interval $(\omega, \omega + d\omega)$. This has been calculated for forsterite (Fig. 2) with the use of a rigid-ion model with the interatomic potentials described in Table 1, in which the parameters have been optimized with respect to the known crystal structure and elastic constants. Inelastic neutron scattering from a powder sample yields a related quantity, the generalized density of states $G(E)$ (*19*), in which contributions from the different atoms are weighted by the squares of the vibrational amplitudes and

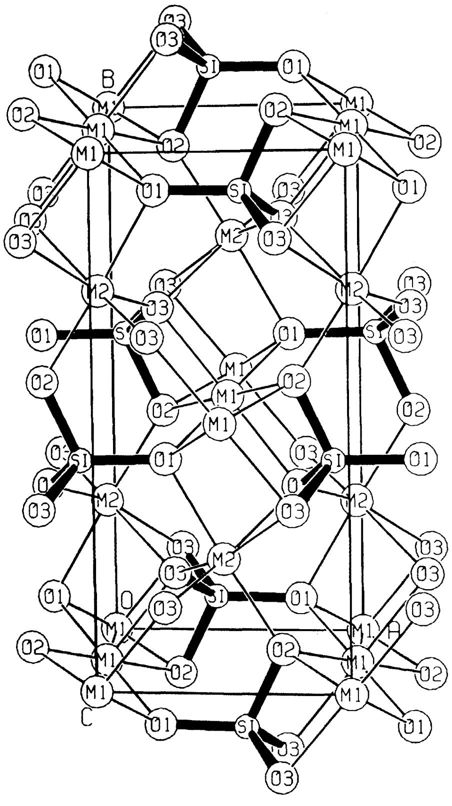

Fig. 1. Crystal structure of forsterite, Mg_2SiO_4 [after Matsui and Busing (*10*)].

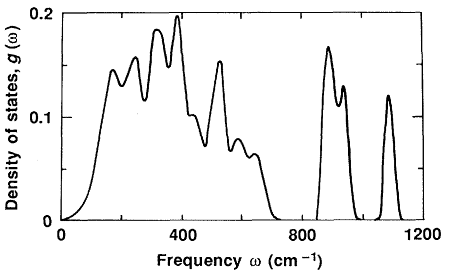

Fig. 2. Phonon density of states of forsterite, calculated from the rigid-ion model.

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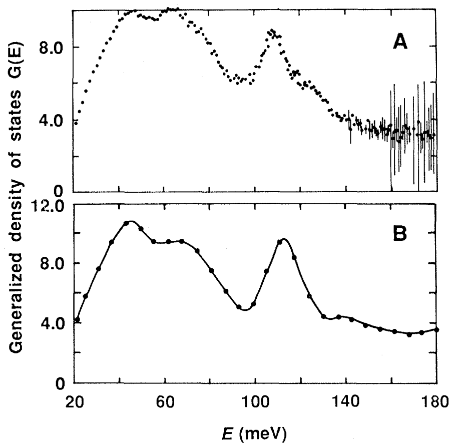

Fig. 3. Phonon density of states of forsterite at 300 K: comparison of results from experimental determination by inelastic neutron scattering (**A**) and theoretical calculation based on rigid-ion model (**B**). Resolution broadening and multiphonon contributions are included in both cases. In the experimental curve, energies below 20 meV could not be observed because of overlap with elastic scattering.

neutron scattering lengths. This quantity has been measured with the low-resolution medium-energy chopper spectrometer (LRMECS) at the Intense Pulsed Neutron Source, Argonne National Laboratory, with neutrons of 200-meV incident energy. The experimental data for $G(E)$ ($E = \hbar\omega$) are shown in Fig. 3A. The corresponding quantity calculated from the model described in Table 1 is shown in Fig. 3B. The latter includes the effects of multiphonon processes (neutrons creating or annihilating two or more quanta of normal modes of vibration) but not the interference effects associated with coherent nuclear scattering, which are believed to be small at these energies, as in SiO_2 (*19*). The excellent agreement between experiment and theoretical prediction shown in Fig. 3 gives a high degree of confidence in the interatomic force model (Table 1).

A simplified calculation (*13, 14*), using the interatomic potentials of Table 1 and treating the $(SiO_4)^{4-}$ ions as rigid "molecular" units, gives good agreement with the low-frequency intermolecular modes measured with reactor neutrons (*16, 17*), and also with the reported values of the elastic constants (*4–6*), but not with the spectrum of Fig. 3A. This is to be expected, since the molecular model neglects the intramolecular modes of the tetrahedral $(SiO_4)^{4-}$ group that contribute the peaks at 900 and 1100 cm^{-1} in Fig. 2 and the corresponding features in the calculated scattering spectrum at 100 and ~140 meV.

The density of states for the rigid-ion model (Fig. 2) can now be used to calculate the specific heat C_v, through the standard relation

$$C_v = \qquad (1)$$

$$Nk_B \int \frac{\hbar\omega\ (k_BT)^2\ \exp(\hbar\omega/k_BT)}{[\exp(\hbar\omega/k_BT) - 1]^2} g(\omega) d\omega$$

where N is the number of lattice sites, k_B is Boltzmann's constant, T is the temperature, $\hbar$ is Planck's constant, and ω is the vibrational frequency. The result is compared with the experimental data (*8*) in Fig. 4, which are seen to be in excellent agreement. The corresponding result with the molecular model fits the low-temperature region very well but fails to fit the high-temperature region above 150 K, again because it does not take the high-frequency modes into account. A calculation based on the Debye model, using a Debye temperature obtained from the observed elastic constants, gives a poor fit. An empirical model proposed by Kieffer (*12–14*), fitted to the elastic constants and the optically active modes measured by optical spectroscopy, gives results very close to those derived from Fig. 2. This is so because Eq. 1 contains an integral over the phonon density of states and so the specific heat is not very sensitive to its detailed behavior. However, our calculation includes the contribution of a low-frequency zone-center phonon at 104 cm^{-1}, observed by inelastic neutron scattering from a single crystal for the first time, which is optically (infrared, Raman) inactive (*17*).

In conclusion, inelastic neutron scattering data taken at incident energies high enough to sample the entire spectrum of vibrational modes, internal as well as external to the $(SiO_4)^{4-}$ molecular units, and in conjunction with reactor data taken at lower energies, provide confirmation of a detailed microscopic model of the interatomic forces in forsterite. This model yields a specific heat in good agreement with the measured specific heat over a wide temperature range. Such a model can also be used to predict mechanical and thermodynamic properties. The procedures used here in the case of forsterite can now be applied to the geophysically more important mineral, magnesium-rich olivine.

Table 1. Effective ionic charges $Z(Kk)$ and ionic radii $R(Kk)$. The interatomic potential function used for the rigid-ion model calculation for the external modes is

$$V(r) = \frac{e^2}{4\pi\epsilon_0} \cdot \frac{Z(Kk)Z(K'k')}{r} + a \exp\left\{-\frac{br}{R(Kk) + R(K'k')}\right\}$$

where a and b are constants equal to 1822 eV and 8.5, respectively, r is the radius, ϵ_0 is the vacuum permittivity, e is the electron charge, K is the rigid unit, and k is the atom. For internal modes covalent Si-O and O-O interactions were taken into account.

Atom	$Z(Kk)$	$R(Kk)$
Mg (1)	1.60	1.15
Mg (2)	1.80	1.185
Si	1.0	0.685
O (1)	−1.2	1.062
O (2)	−1.0	0.993
O (3)	−1.10	1.03

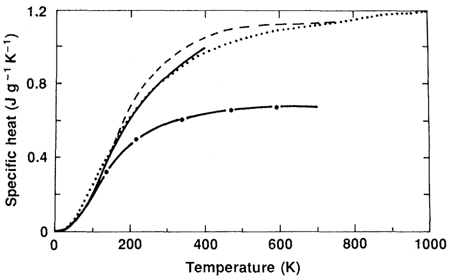

Fig. 4. Comparison of specific heat calculated from rigid molecular ion model (·—·), rigid-ion and Kieffer's models (····), and Debye model (– – –) with that from experimental measurements (——).

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