Vibrational Spectroscopy of Minerals at Pressure: Application to the Mantle

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ABSTRACT
Vibrational spectroscopy is a powerful tool to investigate the composition and thermal state of Earth's interior, as well as to study the basic properties of materials. Infrared (IR) data can be collected as a function of pressure (up to 100 GPa) from microsamples in a diamond anvil cell. Correct interpretation of these high-pressure spectra requires complete characterization of the sample at ambient conditions. Such data provide information on bonding and structure of materials, and allow calculation of thermodynamic and elastic properties, as functions of pressure and temperature, which are needed to establish the mantle geotherm. Current research involves measurement of IR spectra of phases in the MgO-FeO-SiO₂ system and their analogues as a function of pressure. Future endeavors will concern modification of the experiments to attain high temperatures during compression.

INTRODUCTION
A fundamental problem in geo-physics concerns deduction of the composition and thermal character of Earth’s interior from seismic data and from laboratory measurements of mineral properties. A major obstacle is the experimental difficulty of performing laboratory studies at appropriately high pressures (P) and temperatures (T) simultaneously. Determinations of the mantle's composition can be approached through accurate measurements of volume (V), thermal expansivity, compressibility, and higher P and T derivatives, which are obtained from the vibrational analysis of the equation of state (V(P,T)). However, progress in establishing the geotherm is severely impeded by (1) the impossibility of directly measuring thermodynamic properties such as heat capacity and entropy through calorimetry alone, and (2) the limited temperature range at which the thermodynamic properties of synthetic high-pressure phases are determined at 1 atm due to small sample sizes and metastability at low pressure. A new approach involves prediction of heat capacity and entropy at pressure from vibrational spectroscopy (Hofmeister et al., 1989; Chopelas, 1990a, 1990b) by use of a modified version of the model developed by Kieffer (1979) which is based on statistical thermodynamics. Here, I briefly describe this model, the theory of vibrations, and infrared (IR) and Raman spectroscopic methods. Current studies involve use of diamond anvil cells (Fig. 1) to collect high-pressure IR data from phases likely to occur in the mantle (e.g., olivine and its spinel polymorphs and pyroxene and its ilmenite, garnet, and perovskite polymorphs). Detailed studies at 1 atm of such phases and chemically or structurally related minerals are being done not only to provide reference data needed for high-pressure studies, but also to characterize these materials (e.g., Hofmeister et al., 1990a, 1990b).

Work at the University of California, Davis is coordinated with calorimetric experiments at high temperatures by P. Richet (Institut de Physique du Globe) and with Raman spectroscopic studies by A. Chopelas (Max Planck Institute) in order to refine the thermodynamic model so that it is sufficiently accurate (±3%) to be useful under mantle conditions. This report focuses on spectroscopic study of garnet at 1 atm and olivine at pressure, and applications of the results.

RELATION OF VIBRATIONS TO STRUCTURE, BONDING, AND THERMODYNAMIC PROPERTIES
All atoms oscillate about their equilibrium positions, except at the unattainable 0 K. Strictly speaking, this phenomenon can only be correctly described by quantum mechanics in terms of transition probabilities and selection rules, which is beyond the scope of this report. Instead, I use a classical analogy.

A vibrating material is crudely analogous to a set of balls (atoms) of different weights interconnected by springs (bonds) varying in length and stiffness. Any and all vibrations can be described as a combination of a limited

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number of compounds. The simplest possible vibrations are known as fundamental vibrations, each of which is related to the motion of an individual ion or group of atoms. A particular motion can be characterized by the amount of energy needed to drive it, which is typically described in terms of frequency (wavelength) in accord with the cyclic nature of oscillations. The classical analogy suggests that the harmonic properties of a given mode depend strongly on the masses, bond lengths, and bond strengths of the ions involved. This analysis appears to be valid in that various frequency regions are characteristic of certain species. For example, light mass and tight binding inside of SiO₂, tetrahedra make its bending and stretching motions occur at short IR wavelengths of 7 to 25 μm, whereas heavy mass and loose binding inside of Fe₂O₃, octahedra yield stretching modes at long IR wavelengths of 50 to 200 μm (e.g., McMillan and Hofmeister, 1988).

Because a fundamental primary involves nearest neighbor interactions, its existence requires that similar structural units occur throughout the material but does not require a regular array of atoms, in contrast to X-ray diffraction. The derivation of vibrational data on glasses can be used to infer coordination and polymeric conformations. For amorphous solids, the number of fundamental modes is determined by, and diagnostic of, its space group, its overall structure must move in directions consistent with the symmetry (e.g., Farmer, 1974). For example, MgO adopts six modes, spinel has 42, and olivine has 83, whereas garnet has 240. Thus, spectroscopic data are useful in studying the distribution of the modes and the frequency, which is controlled by chemical composition, makes vibrational spectroscopy useful in mineral identification.

The activation of vibrations by heat intimately connects spectroscopic data with thermodynamic properties. In fact, atomic vibrations contain virtually all of the thermal energy of the solid; only a small amount is electronic or magnetic. Kieffer's (1979) model assumes that thermal excitation of a mode increases exponentially with temperature. The internal energy E of a solid, which is calculated from an analysis, is then a function of the different vibrational modes and con- verted to integral form (see Reif, 1965; for details). The oscillations like entropy S are then derived from E by classical thermodynamics, for example, Cₚ = d(E/ST). As a result,

\[ C_v = \left( \frac{\partial^2 E}{\partial T^2} \right)_{V = \text{const}} = \frac{\partial^2 E}{\partial V^2} \left( \frac{\partial V}{\partial T} \right) \]

where \( E \) is Planck's constant, \( k \) is Boltzmann's constant, and \( g \) is the distribution of modes over frequency. Only two input values are required to determine \( C_v \) and \( g \). The distribution of modes \( g \) is assembled from spectroscopic data (e.g., see Truhlar et al., 1985). These may originate from translations of the lattice and can be obtained from sound velocities, which are usually known for a particular mineral. (Elastic properties for a wide variety of compounds were compiled by Sumino and Sato, 1986.) The parabolic function is used for their contribution to \( g \); this is a Debye model (see Kieffer, 1979, for further discussion). Otherwise, \( g(\omega) \) consists of delta functions (spikes) or a box-shaped function placed at optical frequencies obtained from IR and Raman spectroscopies. These models were derived by Albert Einstein and by Sumino Kieffer. The symmetry of the mineral is used to arrive at the proper number of modes and to account for the fact that a given vibrational frequency may represent more than one atomic motion (Hoffman, 1987).

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Computer Legislation in the U.S. Senate Subcommittee on Technology and the Law

Craig M. Schiffries
GSA Congressional Science Fellow

The U.S. Senate Judiciary Committee established the Subcommittee on Technology and the Law in the 1997 session of Congress to ensure that American law keeps pace with changes in technology. The subcommittee's activities are designed to promote the technologically, internationally competitive, and economic growth of the United States.

I am serving on the staff of the Subcommittee on Technology and the Law during my tenure as the GSA Congressional Science Fellow. Many of my legislative responsibilities are concerned with computer technology. In this column, I discuss some of the computer legislation that will be introduced this spring by Senator Leahy (D-Vermont), chairman of the Subcommittee on Technology and the Law.

Computer Viruses

Innovations in computer technology create new opportunities for increasing productivity and increasing the flow of information, but they also create new vulnerabilities and new opportunities for abuse. It is important to update our laws to stay abreast of rapid changes in computer technology and its techniques of computer-system abuse.

The deliberate abuse of computer systems to cause damage and disruption has already posed significant burdens on numerous computer users. For example, thousands of scientists had their research interrupted when Robert Morris introduced a "worm" on the INTERNET computer network in November 1988. The program quickly replicated itself, clogged the network, and halted research throughout the country.

Last year, the United States unanimously passed a bill to clarify and strengthen the criminal laws against the intentional transmission of destructive computer viruses and related forms of computer system abuse. The House of Representatives did not consider the bill before the Congress adjourned. I am working with Senator Leahy to reintroduce the bill in the current Congress.

In crafting this legislation, we have sought to balance punishment of destructive conduct with the need to encourage legitimate experimentation and the free flow of information. There are important differences among computer incidents, and the legislation would not create a structure for treating such incidents—whether they are malicious, reckless or accidental—with appropriately balanced legal sanctions. The bill has been drafted and revised on the basis of careful review of issues raised in the subcommittee’s hearings. It has a great deal of popular support from both the scientific and legal communities, and it should move quickly through the legislative process.

Semiconductor Chips

Semiconductor chips lie at the heart of the worldwide computer revolution. These marvels of modern technology have propelled dozens of new industries toward the 21st century. Research and innovation are essential to the life and health of the American semiconductor industry. But research and innovation in the design of semiconductor chips were threatened by "chip piracy," the unauthorized copying and distribution of semiconductor chips. Neither patents nor copyrights provided adequate protection against piracy of computer chips.

The U.S. Congress passed the Semiconductor Chip Protection Act (SCPA) of 1984 to combat the piracy that was eroding innovation in the design of computer chips. The SCPA established a new form of intellectual property protection particularly suited to the needs and special characteristics of semiconductor chips.

The United States became the first nation to enact a law specifically to protect the design of semiconductor chips. It is important to note that it would become the worldwide standard, and it included incentives for others to enact equivalent protection. To encourage foreign nations to adopt laws protecting U.S. chips, the SCPA authorized the Secretary of Commerce to issue temporary protection to countries that are "making good faith efforts and reasonable progress..." toward reciprocal protection for U.S. chips. The reciprocal approach—we will protect your country's work so long as you make speedy progress toward laws protecting ours—has been very effective. Nineteen countries have been granted temporary protection, and most of these countries have enacted legislation that is substantially similar to the SCPA.

The authority of the Secretary of Commerce to issue temporary protection was removed July 1, 1991, when the Senate left the budget reconciliation bill without a provision to enact equivalent legislation. The Senate also passed the Semiconductor Chip Protection Act without a provision to enact equivalent legislation. The U.S. Geological Survey, which supports 47% of the program with a $12,000 grant.

Note: Craig Schiffries is the GSA Congressional Science Fellow for 1990-1991. He is serving on the staff of the Subcommittee on Technology and the Law of the Senate Judiciary Committee. He can be reached at (202) 224-3406. The one-paragraph bill (S. 1067) is available from the GSA or by the U.S. Geological Survey, which supports 47% of the program with a $12,000 grant.
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thermal expansivity are sorely needed to interpret seismic profiles and to establish the geotherm. Chapelas [3] uses high-temperature spectroscopic data in conjunction with adiabatic compression measurements (Boebl, 1982) to constrain geotherms for fold-thrust complex's thermal expansivity on pressure.

APPLICATIONS TO THE MANTLE AND CURRENT PROJECTS
Entrainy and Phase Transformations. Measurements of entropy for systems which are phase unstable is impossible because these phases are produced only in minute quantities and commonly revert at high temperature and 1 atm. Accurate calculation of entropy can be provided by spectroscopy, as shown by our garnet studies. Using the resulting entropy in a Clausius-Clapeyron equation
\[
\frac{dS}{dT} = \frac{\Delta V}{T} \frac{\Delta H}{\Delta V}
\]
gives slopes for reactions involving MgSiO₃ larnite that match those of experimentally determined phase boundaries (Boebl and Hro, 1991). A number of other phases have reaction boundaries that are poorly constrained, so that enthalpy determinations stishovite, and B- or Mg-SiO₂ Fei et al., 1989) and spectroscopic data provide independent knowledge of reaction slopes from 3 to 30 GPa for important mantle petrology.

Phase transformations can also be observed directly in spectroscopy as a function of pressure, because the number of bands depends on the space group of the mineral. High-pressure spectroscopy of the n- to MgSiO₃ transformation at room temperature and 10 GPa (Chopelas, 1996b) for olivine (Chopelas et al., 1989) falls on the same trend as the phase boundary established near 1000 K through phase equilibria experiments, suggesting that it and Raman studies can provide important constraints on phase stabilities. Currently, a Ph.D. thesis by Ren Lu involves measurement of u(O) for MgSiO₃ perovskite and analysis of the question of whether the distance to which this study should provide an answer is whether a cubic structure of one end member (vertical) and tetragonal polymorphs is stable in the mantle.

Equations of state. Laboratory studies on minerals cannot be related to seismic data without adequate knowledge of the relevant equations of state, YD7 (e.g., Birch, 1952). Dependence of thermal expansivity on pressure has been determined for Mg and MgSiO₃ through spectroscopy (Chopelas, 1990a, 1990b). Comparison with a variety of other compounds indicates that the relation is generally applicable to cubic crystal structures found in the mantle (Anderson et al., 1990).

The determination of state for V/P differs by an order of magnitude in their prediction of the second pressure derivative of thermal expansivity. The relations of vibrational frequencies to elastic properties (Hofmeister, in prep.) can be used to derive a first and second pressure derivatives of K and to distinguish which of the various formulations is appropriate. Ongoing IR measurements of solid-solution garnets can also be used to calculate elastic properties. The sample in attempt to understand why compressibility depends linearly on composition for some garnet series, while for others it does not (e.g., Bass, 1986). Derivation of systematic relations is important because pressure derivatives of elastic properties are lacking for many minerals.

Calculation of the geotherm requires data on high-temperature spectroscopic data as a function of pressure because the adiabatic temperature gradient is given by
\[
\frac{dT}{dr} = \frac{\Delta T}{\Delta r} \frac{\Delta S}{\Delta V} \frac{\Delta V}{\Delta r}
\]
where the bulk modulus K is defined in equation 2 and is the thermal expansivity. Brown and Shankland (1981) estimated a temperature profile from seismic data that is in accord with recent values for core temperatures of Boebl et al. (1990). Geotherms calculated for forsterite based on spectroscopic data at pressure agree reasonably well with the seismic profile (current study). However, for a laboratory-based geotherm to be meaningful, the base of the mantle must be free of high pressure/temperature.

LIMITATIONS OF THE TECHNIQUE AND FUTURE DIRECTIONS
Single-crystal study of amphibolites contains a significant phase equilibrium involving dihafusion of light from small samples. Improvement in quality of IR data and collection of phase pressure phases therefore rests on synthesis of unstented crystals larger than 100 mm. Pressure studies have a similar intrinsic limitation (light is scattered by a hole smaller than the wavelength).

One area worthy of pursuit is study of spectra at elevated temperatures and, ultimately, evaluating pressure phases and pressures simultaneously. In the near future, such advances are more likely. Raman and IR data on mica, for example, become the pressure phases because the latter has wider band widths, which become even broader as temperature increases.

Another limitation is the accuracy of the thermodynamic model. Incorporation of additional terms may improve Kieffer's (1979) model. Refining the model requires increased accuracy of the heat capacity and entropy that are used as input to the thermodynamic model.

Primary crystal structure is highly sensitive to pressure and temperature. Therefore, pressure phases are meta-stable. Accordingly, the main focus of our research group, now and in the future, is assembly of uncorrelated spectroscopic data base, at ambient conditions, and as a function of pressure and temperature, of rock-forming minerals and mantle phases.

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REFERENCES CITED

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