Vibrational Spectroscopy of Minerals at Pressure: Application to the Mantle

Anne M. Hofmeister
Department of Geology, University of California, Davis, CA 95616
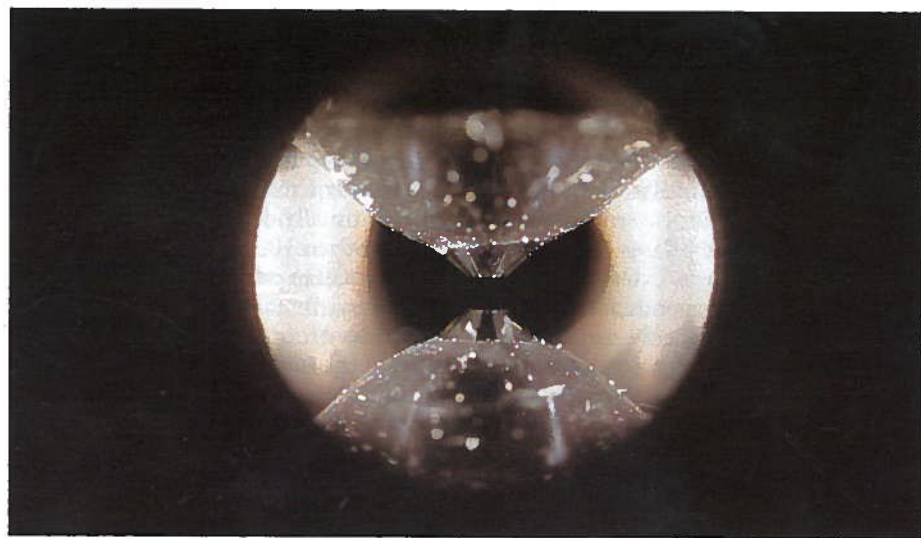
Figure 1. Opposing diamonds in a Mao-Bell piston-cylinder diamond anvil cell. Diameter of the tips is 0.6 mm.
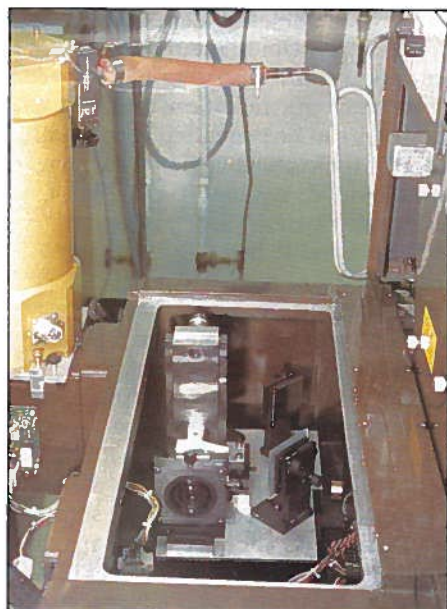

Figure 2. Experimental configuration used in IR studies at pressure. The evacuable sample compartment of our state-of-the-art Fourier Transform Infrared spectrometer (Bomem Model DA 3.02) contains a diamond anvil cell (lower middle). The mirrors are used to enhance light transmission. The gold-coated cylinder is a liquid-helium dewar containing three ultra-sensitive detectors for study of fundamental bands from 7 to 5000 μm in minerals and glasses.

Figure 3. A pair of type I diamonds used for far-IR studies. Largest diameter is 3 mm. Diameter of the tip is 0.6 mm.

Figure 4. Fayalite maintained at 320 kbar in a Mao-Bell diamond anvil cell. Sample thickness is about 5 μm. Light streaks to the right are reflections from the diamond facets.

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-SiO_2 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 geophysics 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 measurement of volume *(V)*, thermal expansivity, compressibility, and higher *T* and *P* derivatives, given a reasonable approximation for 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 at pressure, 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 (±1%) 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 weight interconnected with springs (bonds) varying in length and stiffness. Any and all vibrations can be described as a combination of a limited

Editor's Note:
Each year the David and Lucile Packard Foundation awards 20 Fellowships for Science and Engineering in a national competition to promising young scientists and engineers working in fields that receive relatively less popular attention than high-energy physics, space, and medicine. Each Packard Fellowship provides $100,000 per year for five years to the Fellow's institution, $90,000 of which is for use of the Fellow to support his/her research work. These young researchers are truly among the "best and the brightest" in the United States. The science article in this issue—"Vibrational spectroscopy of minerals at pressure: application to the mantle," by Anne M. Hofmeister—is the first of several in which Packard Fellows in earth science will report on research in their field.

IN THIS ISSUE

Vibrational Spectroscopy of Minerals at Pressure: Application to the Mantle
page 117

---

number of components. The simplest possible vibrations are known as fundamentals or modes, 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 (or wavelength) in accord with the cyclic nature of oscillations. The classical analogue suggests that the frequency of a given mode should depend strongly on the masses, bond lengths, and bond strengths of the ions that are involved. This analogy appears to be valid in that various frequency regions are characteristic of certain species. For example, light mass and tight bonding inside of SiO_4 tetrahedra make its bending and stretching motions occur at short IR wavelengths of 7 to 25 μm, whereas heavy mass and loose bonding inside of FeO_6 octahedra yield stretching modes at long wavelengths of 50 to 200 μm (e.g., McMillan and Hofmeister, 1988). Because a fundamental primarily 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. Therefore, vibrational data on glasses can be used to infer coordination and polymerization.

For crystalline solids, the number of fundamental modes is determined by, and diagnostic of, its space group, because the atoms must move in directions consistent with the symmetry (e.g., Farmer, 1974). For example, MgO has six modes, spinel has 42, and olivine has 83, whereas garnet has 240. Thus, spectroscopic data are useful in studying phase transformations. The combination of the number of modes, which is controlled by the crystal structure, 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 the mineral is then calculated according to statistical thermodynamics from the sum of the thermally weighted energies of all of the different fundamental vibrational modes and converted to integral form. (See Reif, 1965, for details.) Functions like heat capacity C_V or entropy S are then derived from E by classical thermodynamics, for example, $C_V = (\partial E/\partial T)_V$. As a result,

$$C_V = k \int_0^\infty \frac{e^{h\upsilon/kT}}{(e^{h\upsilon/kT}-1)^2}\left(\frac{h\upsilon}{kT}\right)^2 g(\upsilon)\, d\upsilon, \quad (1)$$

where h is Planck's constant, k is Boltzmann's constant, υ is the frequency, and $g(\upsilon)$ is the distribution of modes over frequency. Only two input values are required to determine C_V or S: temperature and $g(\upsilon)$. The distribution of modes $g(\upsilon)$ is assembled from spectroscopic data as follows. Three modes originate from translations of the lattice and can be obtained from sound velocities or elastic deformation of a mineral. (Elastic properties for a wide variety of compounds were compiled by Sumino and Anderson, 1984.) A parabolic function is used for their contribution to $g(\upsilon)$: this is a Debye

model (see Kieffer, 1979, for further discussion). Otherwise, $g(\upsilon)$ consists of delta functions (spikes) or a box-shaped function placed at optically active frequencies derived from IR and Raman spectroscopies. These models were derived by Albert Einstein and by Susan Kieffer. The symmetry of the mineral is used to arrive at the proper number of modes—i.e., to account for the fact that a given vibrational frequency may represent more than one atomic motion (Hofmeister, 1987).

Elastic properties also can be calculated from vibrational frequencies by using the fact that both of these properties can be described in terms of the interatomic potentials ϕ_i of a solid. By arranging the two equations (υ_i as a function of ϕ_i and compressibility as a function of ϕ_i) and to eliminate the potentials, Brout (1959) showed that bulk modulus—i.e., the inverse of compressibility—for the rock-salt structure is

$$K_T = -\left[\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T\right]^{-1} = \frac{\mu}{18r_0}\sum_i \upsilon_i^2, \quad (2)$$

where μ is the reduced mass and r_0 is the bond length. Similar formulas have been derived for the structures in which high-pressure phases crystallize, and the derivation was extended to relate the pressure dependence of K_T to the pressure dependence of the vibrational frequencies for these substances (A. M. Hofmeister, in prep.). Thus, the compressibility of a solid and its pressure derivatives can be calculated easily from only ionic masses, bond lengths, and vibrational frequencies as a function of pressure. These data are needed to determine the mantle's composition. Such relations provide a simple way to correlate macroscopic elastic properties with microscopic spectroscopic parameters, without use of complicated computer routines such as those needed to calculate interatomic potentials.

EXPERIMENTAL TECHNIQUES

All minerals have IR modes. These modes are excited by direct absorption of long-wavelength light ($\lambda > 1 \mu$m), if the energy of the incident light matches that of the vibration, and if the magnitude or direction of the dipole moment between the atoms is changed during their vibration. Absorption peaks are observed at various frequencies, each with a width and height that are characteristic of the particular motion and types of atoms involved. Peaks can equally well be measured by reflection of IR light because of similar interactions with atoms near the surface.

A closely related method is Raman spectroscopy, which involves stimulation of vibrations during scattering of short-wavelength light, usually blue light emitted from a laser. The existence of Raman peaks is tied to momentum conservation, and requires a change in the shape of the ionic group (i.e., its polarizibility) during the vibration (McMillan and Hofmeister, 1988, and references therein). The difference in energy between the peaks in the scattered light and the incident light give the Raman frequencies. The Raman effect is obviously based on quantum mechanics, because the connection with momentum requires that both the light and the vibrations be treated as particles (photons and phonons). Most, but not all, structures possess Raman peaks. The Raman peaks usually result from atomic motions differing from those associ-

ated with IR peaks; thus, these two techniques offer complementary information (e.g., Farmer, 1974; Karr, 1975). One advantage of the IR technique is that peak intensities are absolute and provide quantitative information on optical properties such as the dielectric functions; an advantage of Raman scattering is that spectra can be acquired from samples as small as 1 μm.

IR spectroscopy in the past has revolved around qualitative absorption measurements from powder dispersed in a matrix like KBr that is transparent over a wide wavelength range. Quantitative results require reflection measurements from a single crystal, with polarized light if the structure is not cubic. Common occurrence of weak and overlapping modes in many structures requires additional absorption measurements on crystals thinned to 1 μm or less. Recent technological advances, such as Fourier Transform Infrared (FTIR) spectrometers, have made quantitative study of complicated minerals feasible. Commercially available IR microscopes and state-of-the-art detectors (Fig. 2) provide for collection of data until the diffraction limit is reached when the wavelength of incident light equals the sample's diameter. IR peaks usually occur at wavelengths λ shorter than 100 μm, which is sufficiently small to permit complete study of many synthetic high-pressure phases. These advances permit data to be collected at the longest IR wavelengths (the far-IR), which involve cations other than Si and thus reveal microscopic behavior connected with solid solutions in minerals.

The high sensitivity of modern instruments also allows collection of IR data from samples compressed in a diamond anvil cell. Numerous types exist (Hazen and Finger, 1982; Jephcoat et al., 1987), but all operate under the same principles (Fig. 3): diamonds are strong and transparent to most electromagnetic radiation, and high pressures can be generated with small forces if the contact area between the two diamonds is small (Fig. 1). At UC Davis, the piston-cylinder design of H-K. Mao and P. Bell (Fig. 2) is used. For this type of diamond anvil cell, pressures of IR studies are limited by diffraction. For example, the difficult far-IR measurements are possible at mantle pressures of up to 100 GPa, because attaining this pressure requires small (~100 μm) samples that diffract light with $\lambda > 100$ μm. Figure 4 shows a fayalite crystal used in such a study.

Pressure is calibrated by means of a ruby fluorescence spectrometer (Mao et al., 1986), which takes advantage of the fact that compression moves electronic orbitals closer together. Thus, for ruby, compression alters the transition energies between d electron levels of Cr^{3+} impurity ions and thus changes the color. This systematic increase in frequency of emitted light with pressure has been calibrated through comparison with shock-wave experiments.

CHARACTERIZATION OF GARNETS AT AMBIENT CONDITIONS

Complete single-crystal IR reflectance and Raman spectra have been obtained for five natural end-member garnets (Hofmeister and Chopelas, 1991a), in order to characterize vibrations of this structure and to develop an accurate thermodynamic model for this ubiquitous mineral family. (IR measurements for geologically relevant binary and ternary solid solutions involving the dodecahedral site are part of a Ph.D. thesis by Timothy

Fagan.) Applying the thermodynamic model developed for the end members (see below) to these results will enable accurate calculation of mixing properties, and hence improvement in garnet geobarometers and geothermometers.

Thermodynamic properties of the end members pyrope and grossular have been calculated from their complete vibrational spectra using our modification of Kieffer's (1979) model. The calculations (Hofmeister and Chopelas, 1991b) reproduce experimental heat capacity and entropy at 1 atm for pyrope within 0.5% from ~100 to 1300 K. We show that the calorimetrically determined entropy for grossular at 300 K is 5% low, probably due to hydrous impurities. This result solves the decade-long controversy over why entropy measured for grossular at 300 K was higher than that for pyrope, in contrast to expectations. Correct values for entropy are needed for calculation of phase equilibria involving grossular (e.g., Koziol and Newton, 1988). The excellent agreement of our results with calorimetric measurements on pyrope of Tequi et al. (1991) and their extrapolations to higher temperatures suggests that spectroscopically based calculations based on single-crystal data are reliable at geologically relevant temperatures, and thus can be used to calculate phase boundaries. Calculations based on powder data are not sufficiently accurate for these applications.

IR SPECTROSCOPY OF OLIVINE AT MANTLE PRESSURES

The response of far- and mid-IR bands to pressures of up to 42.5 GPa for ferro-magnesian olivines (Fig. 5; Hofmeister et al., 1989) are typical of low-pressure silicate phases. Mid-IR bands associated with Si-O bonds shift linearly with pressure (not shown), whereas far-IR band shifts associated with Mg (or Fe) gradually become smaller as pressure increases (Fig. 5). The different slopes can be used to validate assignments of peaks to atomic motions, and hence to improve upon our thermodynamic calculations. These differences between Si-O and Mg-O vibrations are due to the fact that the more loosely bonded octahedra are more compressible than the tetrahedra with very strong bonds. These data are important because the second derivative of frequency with respect to pressure is related to the second pressure derivative of the bulk modulus. K is difficult to measure directly but is needed to compare laboratory measurements to seismic data. Near 10 GPa, the IR and Raman peaks of olivine change in intensity and number, as well as position, indicating that a phase transformation occurs (Hofmeister et al., 1989; Chopelas, 1990a).

Changes in peak positions with pressure measurably affect the thermodynamic properties, which are calculated by incorporating the pressure shifts into the 1 atm model of olivine by Hofmeister (1987). The calculated results match extrapolation of calorimetrically determined C_v from 1 atm to C_v at pressures, within the uncertainty of the equation of state used for extrapolation. At 200 kbar, the heat capacity at 298 K drops to 94% of its 1 bar value, whereas that at 1200 K decreases by only 0.5%. Thus, at mantle conditions, the thermodynamic parameter most affected by temperature is volume. Accurate measurements of
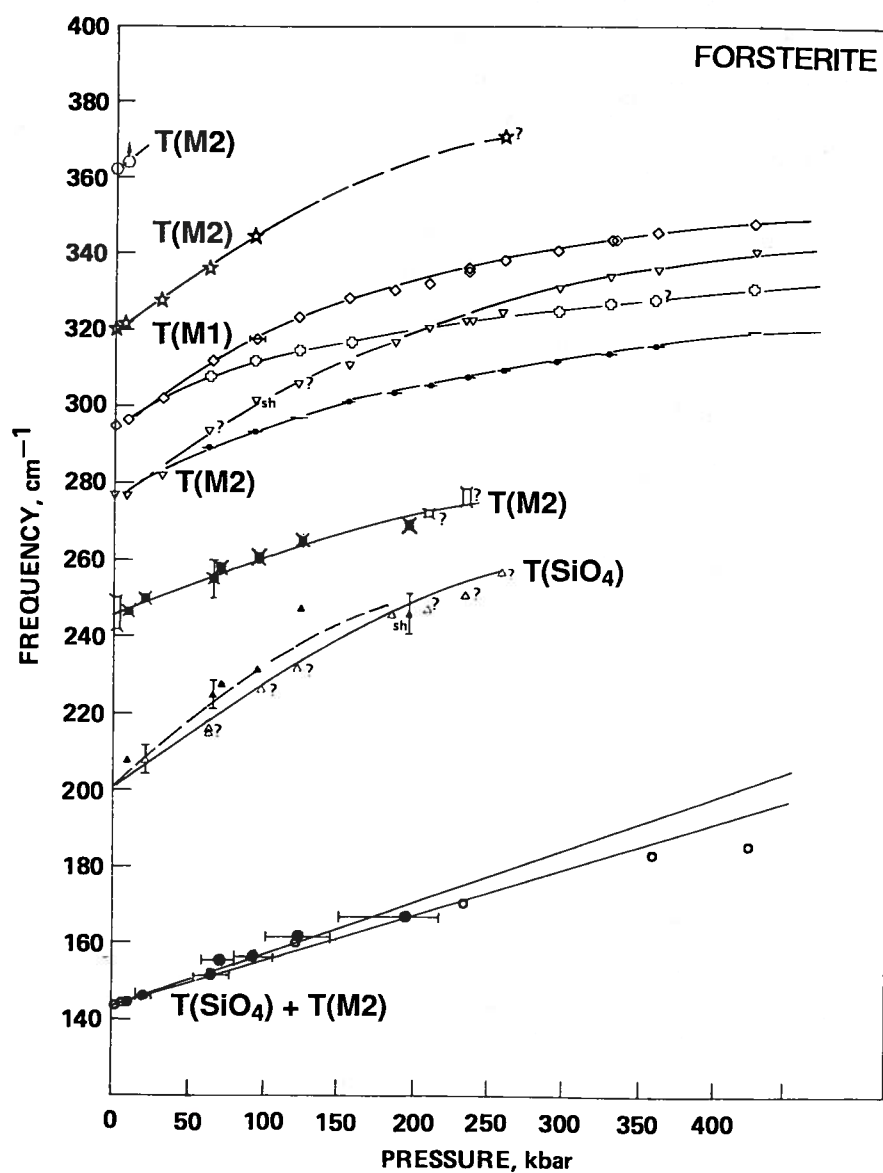
Figure 5. Pressure dependence of the far-IR peaks of forsterite, from Hofmeister et al. (1989). Symbols denote individual peaks, which may represent more than one mode. $T(SiO_4)$ indicates that the mode involves a translation of the SiO_4 tetrahedron. $T(M1)$ or $T(M2)$ indicate translations of the Mg ion in either the M1 or M2 sites. Intensities of most of these peaks decreased during compression such that many peaks could not be tracked above 20 GPa.

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 to ensure that American law keeps pace with changes in technology. Many of the subcommittee's activities are designed to promote the technological leadership, international competitiveness, 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 improving productivity and increasing the flow of information, but they also create new vulnerability and new opportunities for abuse. It is important to update our laws to stay abreast of rapid changes in computer technology and in 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 computer "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 Senate 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 establish 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 plaguing 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. The law was drafted so that it would become the worldwide standard, and it included incentives for other countries 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 expires in July. I am working with the Subcommittee on Technology and the Law on legislation that would extend the authority of the secretary to issue temporary protection to countries that are making adequate progress toward laws protecting U.S. chips.

The semiconductor industry is vital to the economic welfare and national security of the United States. The Semiconductor Chip Protection Act has helped stimulate research and preserve jobs by reducing the international piracy that was plaguing the semiconductor industry. ∎

thermal expansivity are sorely needed to interpret seismic profiles and to establish the geotherm. Chopelas (1990a) has used spectroscopic data in conjunction with adiabatic compression measurements (Boehler, 1982) to constrain dependence of forsterite's thermal expansivity on pressure.

APPLICATIONS TO THE MANTLE AND CURRENT PROJECTS

Entropy and Phase Transformations. Measurements of entropy for very high pressure phases 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

$$\frac{\partial P}{\partial T} = \frac{\Delta S}{\Delta V} \qquad (3)$$

gives slopes for reactions involving $MgSiO_3$ ilmenite that match those of experimentally determined phase boundaries (Hofmeister and Ito, 1991). A number of other phases have reaction boundaries that are poorly constrained (e.g., transformations involving stishovite, and β- or γ-Mg_2SiO_4; Fei et al., 1990). Ongoing spectral measurements of these phases should provide independent knowledge of reaction slopes from equation 3 for phase tranformations important to mantle petrology.

Phase transformations can also be observed directly in spectra as a function of pressure, because the number of bands depends on the space group of a mineral. Spectroscopic determination of the α- to γ-Mg_2SiO_4 transformation at room temperature and 10 GPa (Chopelas, 1990a; Hofmeister et al., 1989) falls on the same trend as the phase boundary established near 1000 K through phase equilibria experiments, suggesting that IR and Raman studies can provide important constraints on phase stabilities. Currently, a Ph.D. thesis by Ren Lu involves measurement of $\upsilon(P)$ for $MgSiO_3$ perovskite and analogues. An intriguing question to which this study should provide an answer is whether a cubic structure of one of the distorted orthorhombic or tetragonal polymorphs is stable in the mantle.

Equations of state. Laboratory studies of minerals cannot be related to seismic data without adequate knowledge of the relevant equations of state, $V(P,T)$ (e.g., Birch, 1952). Dependence of thermal expansivity on pressure has been determined for MgO and Mg_2SiO_4 through spectroscopy (Chopelas, 1990a, 1990b). Comparison with a variety of other compounds indicates that the relation is generally applicable to crystal structures found in the mantle (Anderson et al., 1990).

Available equations of state for $V(P)$ differ by an order of magnitude in their prediction of the second pressure derivative of the compressibility. The relations of vibrational frequencies to elastic properties (Hofmeister, in prep.) can be used to provide the first and second pressure derivatives of K_T and to distinguish which of the various formulations are appropriate. Ongoing IR measurements of solid-solution garnets can also be used to calculate elastic properties in an 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 heat capacity as a function of pressure because the adiabatic temperature gradient is given by

$$\left(\frac{\delta T}{\delta P}\right)_S = \frac{\alpha T V K_T}{K_S C_V}, \qquad (4)$$

where the bulk modulus K is defined in equation 2 and α is the thermal expansivity. Brown and Shankland (1981) generated a temperature profile from seismic data that is in accord with recent values for core temperatures of Boehler 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 requires a large data base of vibrational spectra at pressure. Currently, work at UC Davis focuses on pyroxene, spinel, and perovskite phases.

LIMITATIONS OF THE TECHNIQUE AND FUTURE DIRECTIONS

Single-crystal study at ambient conditions has reached the theoretical limit involving diffraction of light from small samples. Improvement in quality of IR data for synthetic high-pressure phases therefore rests on synthesis of untwinned crystals larger than 100 µm. 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, elevated temperatures and pressures simultaneously. In the near future, such advances are more likely for Raman than IR studies 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 calorimetric measurements of C_V, and complete vibrational data on a large variety of compounds. The gain for mantle studies is a more reliable prediction of heat capacity and entropy. This is especially important for very high pressure phases that are metastable. Accordingly, the main focus of our research group, now and in the future, is assembly of a spectroscopic data base, at ambient conditions, and as a function of pressure and temperature, of rock-forming minerals and mantle phases.

REFERENCES CITED

Anderson, O.L., Chopelas, A., and Boehler, R. 1990, Thermal expansivity versus pressure at constant temperature: A reexamination: Geophysical Research Letters, v. 17, p. 685–688.

Bass, J.D., 1986, Elasticity of uvarovite and andradite garnets: Journal of Geophysical Research, v. 91, p. 7505–7516.

Birch, F., 1952, Elasticity and constitution of the Earth's interior: Journal of Geophysical Research, v. 57, p. 227–240.

Boehler, R., 1982, Adiabats of quartz, coesite, olivine, and magnesium oxide to 50 kbar and 1000 K and the adiabatic gradient in the Earth's mantle: Journal of Geophysical Research, v. 87, p. 5501–5506.

Boehler, R., Von Bargen, N., and Chopelas, A., 1990, Melting, thermal expansion, and phase transitions of iron at high pressures: Journal of Geophysical Research, v. 95, p. 12,731–12,736.

Brout, R., 1959, Sum rule for lattice vibrations in ionic crystals: Physical Review, v. 113, p. 43–44.

Brown, J.M., and Shankland, T.J., 1981, Thermodynamic parameters in the Earth as determined from seismic profiles: Royal Astronomical Society Geophysical Journal, v. 66, p. 579–596.

Chopelas, A. (1990a) Thermal expansion, heat capacity, and entropy of MgO at mantle pressures: Physics and Chemistry of Minerals, v. 17, p. 142–148.

Chopelas, A., 1990b, Thermal properties of forsterite at mantle pressures derived from vibrational spectroscopy: Physics and Chemistry of Minerals, v. 17, p. 149–156.

Farmer, V.C., ed., 1974, The infrared spectra of minerals: London, Mineralogical Society, 525 p.

Fei, Y., Saxena, S.K., and Navrotsky, A., 1990, Internally consistent thermodynamic data and equilibrium phase relations for compounds in the system MgO-SiO₂ at high pressure and high temperature: Journal of Geophysical Research, v. 95, p. 6915–6928.

Hazen, R.M., and Finger, L.W., 1982, Comparative crystal chemistry: New York, John Wiley & Sons, 231 p.

Hofmeister, A.M., 1987, Single-crystal absorption and reflection infrared spectroscopy of forsterite and fayalite: Physics and Chemistry of Minerals, v. 14, p. 499–513.

Hofmeister, A.M., and Chopelas, A., 1991a, Vibrational spectroscopy of end-member silicate garnets: Physics and Chemistry of Minerals (in press).

Hofmeister, A.M, and Chopelas, A., 1991b, Thermodynamic properties of pyrope and grossular from vibrational spectra: American Mineralogist (in press).

Hofmeister, A.M., and Ito, E., 1991, Thermodynamic properties of MgSiO₃ ilmenite from vibrational spectra: Physics and Chemistry of Minerals (in press).

Hofmeister, A.M., Xu, J., Mao H-K., Bell, P.M., and Hoering, T.C, 1989, Thermodynamics of Fe-Mg olivines at mantle pressures: Mid- and far-infrared spectroscopy at high pressure: American Mineralogist, v. 74, p. 281–306.

Hofmeister, A.M., Horigan, J., and Campbell, J.A., 1990a, Infrared spectra of Ge O₂ rutile and prediction of inactive modes for rutile-type minerals: American Mineralogist, v. 75, p. 1238–1248.

Hofmeister, A.M., Xu. J., and Akimoto, S., 1990b, Infrared spectra of synthetic and natural stishovite: American Mineralogist, v. 75, p. 951–955.

Jephcoat, A.P., Mao, H.K, and Bell, P.M., 1987, Operation of the megabar diamond-anvil cell, in Ulmer, G.C., and Barnes, H.L., eds., Hydrothermal experimental techniques: New York, Wiley Interscience, p. 469–506.

Karr, C., Jr., ed., 1975, Infrared and Raman spectroscopy of lunar and terrestrial minerals: New York, Academic Press.

Kieffer, S.W., 1979, Thermodynamics and lattice vibrations of minerals: 3. Lattice dynamics and an approximation for minerals with application to simple substances and framework silicates: Reviews of Geophysics and Space Physics, v. 17, p. 35–39.

Koziol, A.M., and Newton, R.C., 1988, Redetermination of the anorthite breakdown reaction and improvement of the plagioclase-garnet-Al₂SiO₅-quartz geobarometer: American Mineralogist, v. 73, p. 216–223.

Mao, H-K., Xu, J., and Bell, P.M., 1986, Calibration of the ruby pressure gauge to 800 kbar under quasi-hydrostatic conditions: Journal of Geophysical Research, v. 91, p. 4673–4676.

McMillan, P., and Hofmeister, A.M., 1988, Infrared and Raman spectroscopy, in Hawthorne, F.C., ed., Spectroscopic methods in mineralogy and geology: Reviews in Mineralogy, v. 18, p. 99–160.

Reif, F., 1965, Fundamentals of statistical and thermal physics: New York, McGraw-Hill.

Sumino, Y., and Anderson, O.L., 1984, Elastic constants of minerals, in Carmichael, S., ed., Handbook of the physical properties of rocks: Boca Raton, Florida, CRC Press, p. 139–280.

Tequi, C., Robie, R.A., Hemingway, B.S., Neuville D., and Richet, P., 1991, Thermodynamic and melting properties of pyrope: Geochimica et Cosmochimica Acta (in press). ■