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Vibrational spectroscopy of mantle minerals

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Abstract—Vibrational spectroscopy has been used extensively to characterize the high pressure minerals important in the Earth's mantle. The results of IR and Raman studies complement structural information obtained from diffraction experiments, for example in providing information on [6]-coordinated silicon in high-pressure phases such as stishovite and $MgSiO_3$ perovskite, on the tetragonal distortion of $MgSiO_3$ garnet, and on the presence of the inter-tetrahedral SiOSi linkage in β-Mg_2SiO_4. Such measurements provide detailed information on phase transitions and tests of *ab initio* and empirical calculations of mineral properties. *In situ* studies at high pressure and/or temperature have been used to study soft-mode behaviour associated with displacive phase transitions, as demonstrated recently for stishovite. The presence of OH in natural minerals and synthetic candidate high-pressure phases has been demonstrated by IR spectroscopy, permitting the identification of potential storage sites for hydrogen in the mantle. *In situ* high *P-T* Raman spectroscopy has demonstrated the stability of magnesite ($MgCO_3$) to mantle temperatures and pressures, important in determining the carbon budget within the deep Earth. Micro-Raman and (more recently) micro-IR spectroscopies have proven very useful for non-destructive, *in situ* analysis of minerals in complex natural and experimental sample assemblages. Experimental vibrational data have been used to construct and constrain models for calculation of thermodynamic parameters such as heat capacity and entropy. These have been useful in establishing *P-T* phase diagrams for mantle mineral assemblages. We summarize these results and collect together vibrational spectra obtained to date for principal mineral phases of the mantle. We also discuss both limitations and future directions of the techniques.

INTRODUCTION

OUR KNOWLEDGE of the internal structure of the Earth has been largely gleaned from analysis of seismic and other geophysical data, bounded by cosmological constraints on its composition (ANDERSON, 1989; POIRIER, 1991; GILLET, 1995; BINA and HEMLEY, 1996). Some direct sampling of mantle minerals has been possible, from examination of ultramafic xenoliths brought to the surface in kimberlites or alkali basalts, or as inclusions in diamonds (SAUTTER and GILLET, 1994). However, most of our present understanding of mantle mineralogy is based on experimentally determined phase relations and thermophysical properties of candidate minerals and assemblages. Vibrational spectroscopy has played an important role in this work (MCMILLAN and HOFMEISTER, 1988; MCMILLAN, 1989). Such measurements provide detailed information on structure and bonding in materials, thereby complementing direct structural studies by diffraction techniques and spectroscopy of electronic transitions. Vibrational spectroscopy provides a straightforward means for identifying phase transitions, as well as the mechanism of such transformations (*e.g.,* soft modes and order parameters). Minerals can be analyzed both as microscopic grains and in thin sections of multiphase natural samples as well as in experimental charges quenched from high pressures and temperatures. Finally, vibrational data have been used extensively for modeling the thermodynamic properties of mantle minerals. This has been an important part of this research because such vibrational data in many cases have provided the first, and in some cases the only, constraints on the thermodynamic properties of such materials at high *P-T* conditions corresponding to the deep Earth.

We review here the uses of Raman and infrared vibrational spectroscopy in the study of mantle minerals. We begin with an overview of the kinds of information that can be obtained from such measurements and their relevance to the Earth's mantle. We discuss in some detail the vibrational properties of the major mantle minerals, summarizing the available vibrational data for each phase. Our motivation has been to collect the spectra obtained to date in a single set of figures, for convenience of comparison and for identifying areas where further work is needed. This then extends and complements earlier and more general reviews of the applications of Raman and IR spectroscopy to Earth and planetary sciences (HEMLEY *et al.,* 1987a; MCMILLAN and HOFMEISTER, 1988; MCMILLAN, 1989; SHARMA, 1989, 1990). We also discuss vibrational spectroscopic studies of the role of water and carbon in the mantle. A brief description of future directions is given in the concluding remarks. The review is limited to crystalline minerals. Vibrational spectroscopy has demonstrated that large structural changes take place in silicate glasses at high pressures (and by inference melts), but this is beyond the scope of the present article and is reviewed elsewhere (MCMILLAN and WOLF, 1995). We also discuss results of theoretical studies of the vibrational dynamics of mantle minerals; excellent reviews of theoretical techniques and the calculation of other properties have been written by COHEN (1994), BUKOWINSKI (1994), and CHIZMESKHYA *et al.*, (1994).

GENERAL CONSIDERATIONS

Overview of mantle mineralogy

The global structure of the mantle is defined by its major seismic discontinuities near 410 km and 660 km, which delineate the regions known as the upper mantle (20–410 km), transition zone (410–660 km), and lower mantle (660–2900 km) (Fig. 1). Based on extensive laboratory studies and theoretical modeling over the past two decades, it is likely that the dominant mineral phase in the lower mantle is a silicate perovskite with composition near $(Mg_{0.9}Fe_{0.1})SiO_3$, probably containing up to several per cent Al_2O_3 component, which co-exists with (Mg,Fe)O (magnesiowüstite) with the rock salt (B1) structure, and a nearly end-member $CaSiO_3$ perovskite (WILLIAMS *et al.*, 1989; ANDERSON, 1989; HEMLEY and COHEN, 1992; IRIFUNE, 1994). Free silica may be present as stishovite in basaltic regions trapped near the top of the lower mantle from subducted oceanic crust (KESSON *et al.*, 1994), which could give rise to aluminous phases (IRIFUNE *et al.*, 1991; YAGI *et al.*, 1994; AHMED-ZAID and MADON, 1995). A free SiO_2 phase near the base of the lower mantle has also been proposed (KNITTLE and JEANLOZ, 1991; JEANLOZ, 1993). The mineralogies of the transition zone and upper mantle are likely to be more complex (ANDERSON, 1989; GASPARIK, 1990; GILLET, 1995). The upper mantle is dominated by ultramafic minerals, principally olivine, pyroxene and garnet phases, but substantial amounts of plagioclase feldspar, kaersutitic amphibole, phlogopite mica, and many other accessory minerals may be found. The petrology is highly dependent on the type of province encountered, and the thermal and compositional regime involved. Many of these phases are volatile-rich, both providing host phases for water, CO_2 and F-, Cl- and S-bearing species degassing from deep within the Earth, or returning via subduction processes (THOMPSON, 1992; BELL and ROSSMAN, 1992a; GASPARIK, 1993; GILLET, 1993a; CARROLL and HOLLOWAY, 1994). In addition, this region is characterized by partial melting, so that the properties of molten silicates are important in the upper mantle, and perhaps even deeper within the Earth (WILLIAMS, 1990; ITO and KATSURA, 1992; WOLF and MCMILLAN, 1995). The transition zone is dominated by the mineralogy of refractory ultramafic phases including the β-(wadsleyite, or "modified spinel") and γ-(ringwoodite, spinel) forms of $(Mg,Fe)_2SiO_4$, along with the garnet and perhaps ilmenite phases of $MgSiO_3$ (GASPARIK, 1990). Both $MgSiO_3$ ilmenite and garnet contain [6]-coordinate silicon, and at least the majorite garnet will exist as a solid solution with Mg^{2+}, Fe^{2+} and Ca^{2+} substituting on the large ([12]-coordinate) site, Al^{3+}, Si^{4+} and Fe^{3+} on the octahedral site, and Si^{4+} and Al^{3+} on tetrahedral sites (IRIFUNE, 1994; KESSON *et al.*, 1994). All of these nominally anhydrous mantle minerals can contain significant amounts of dissolved H as "defect" OH species (BELL and ROSSMAN, 1992a; GILLET, 1993a). In addition, several high pressure hydrous phases, particularly within the system $MgO—SiO_2—H_2O$, may be present in the transition zone (KANZAKI, 1991; PREWITT and FINGER, 1992).

Structure and bonding

Although it is not a technique for direct structure determination, vibrational spectroscopy gives important insight into bonding in materials and structure-property relations, thereby complementing x-ray and neutron diffraction methods. Morever, vibrational spectroscopy has revealed transitions and structural changes that were not apparent from diffraction measurements (KINGMA *et al.*, 1995), although in other cases, such claims have not been supported by subsequent, and more accurate, direct structural investigations (*e.g.*, DOWNS *et al.*, 1996). Measurements as a function of pressure and/or temperature permit detailed identification of response of the structure to these thermodynamic variables (*i.e.*, changes in compression mechanisms in the absence of a thermodynamic phase transition). Vibrational spectroscopy has played an important role in characterization of mantle phases since the earliest days of experimental mantle petrology and mineralogy. Infrared spectroscopy confirmed the octahedral coordination of Si (or Ge in silicate analogues) in several of these high pressure phases (LYON 1962; TARTE and RINGWOOD 1964; WENG

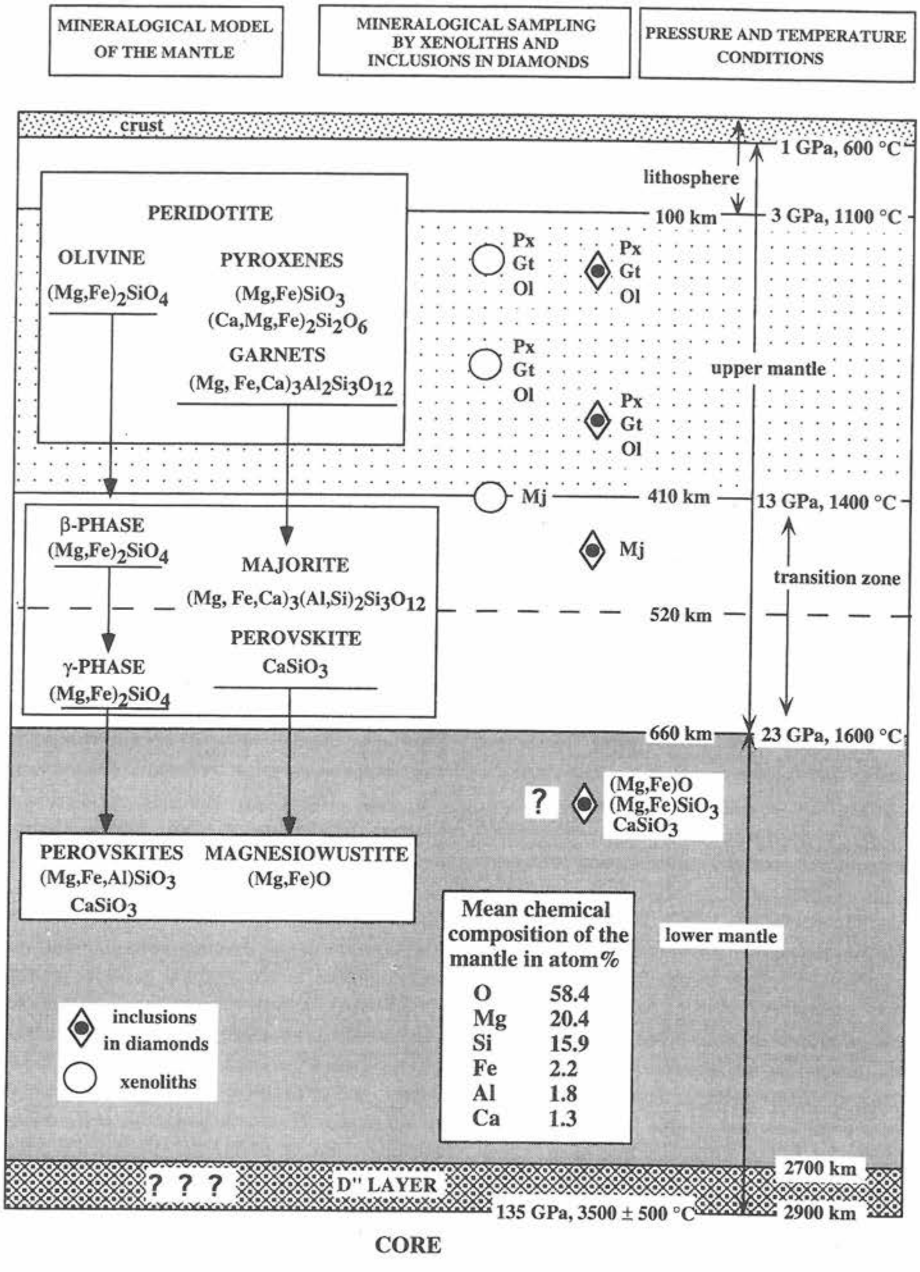


FIG. 1. Schematic (from GILLET, 1995) of the mineralogy of the Earth's mantle, inferred from results of high pressure-high temperature experiments, and natural sampling via xenoliths and inclusions in diamonds.

et al., 1983). In other cases, vibrational spectroscopy was used to reveal unusual structural features, such as the presence of the SiOSi linkage between tetrahedral SiO_4 groups in the β-("modified" spinel, or wadsleyite) polymorph of Mg_2SiO_4 (JEANLOZ, 1980; MCMILLAN and AKAOGI, 1987). Another example is the identification and characterization of ring structures in minerals such as coesite [SHARMA *et al.,* 1981]. This has been important in determining compression mechanisms in glasses as well as amorphization phenomena (HEMLEY *et al.,* 1994; MCMILLAN and WOLF, 1995).

Vibrational spectroscopy has also been essential for characterizing structural components such as hydrogen (bound stoichiometrically or as defects) which are difficult to study by other techniques, as discussed below.

Phase transitions

Because vibrational spectra typically provide a unique signature of crystal (and amorphous) structure, the measurement of such spectra has proven extremely useful for identifying phase transitions, particularly *in situ* at high pressures and/or temperatures. Moreover, such measurements can be used successfully to determine phase transitions mechanisms. A classic example is the study of soft modes and the identification of order parameters associated with displacive phase transitions (SCOTT, 1974; GHOSE, 1985, 1988; MCMILLAN, 1985, 1989; MCMILLAN and HOFMEISTER, 1988; SALJE, 1989). This includes both pressure-induced soft modes ($d\nu/dP < 0$) as well as the more commonly studied temperature-induced soft modes ($d\nu/dT < 0$). Both types of modes are known to occur for materials with the perovskite and rutile structures as functions of pressure and temperature (SAMARA and PEERCY, 1973; SCOTT, 1974), including the $MgSiO_3$ perovskite analog $CaTiO_3$ (GILLET *et al.,* 1993a,b). Early *ab initio* calculations suggested that such critical transitions might be important for $MgSiO_3$ perovskite under mantle *P-T* conditions (WOLF and BUKOWINSKI, 1987; BUKOWINSKI and WOLF, 1988). However, no soft mode behaviour has been observed experimentally in the Raman spectrum of metastable $MgSiO_3$ perovskite at ambient pressure (DURBEN and WOLF, 1992), consistent with more recent theoretical calculations (STIXRUDE and COHEN, 1993), as discussed below. A displacive phase transition associated with pressure-induced mode softening has been identified by Raman spectroscopy in stishovite, which undergoes a transition to a $CaCl_2$ structure at ~50 GPa (COHEN, 1992; KINGMA *et al.,* 1995).

Phase identification and multiphase assemblages

An important recent application is the identification of minerals in experimental samples, in particular, in polyphase assemblages quenched from high pressures and temperature. Micro-Raman has been used in most of these studies because of its high spatial resolution (~1 μm or the diffraction limit of visible light) (HEMLEY *et al.* 1987a). More recently, new micro-IR spectroscopic techniques have been developed (REFFNER *et al.,* 1994), which permit detailed IR mapping of complex samples with spatial resolution approaching the diffraction limit. FEI *et al.* (1991) used the micro-Raman technique to distinguish β- from γ-$(Mg,Fe)SiO_4$ in a study of the phase relations in the $MgO—FeO—SiO_2$ system. ZHANG *et al.* (1993) identified SiO_2 phases in experimental changes quenched from high *P-T* to determine the phase relations in the system to 2800°C at 9–14 GPa. More recently, BERTKA and FEI (1996) used the technique to identify a large number of different silicates in a high-pressure phase equilibrium study of the mineralogy of the martian mantle.

Vibrational spectroscopy, in particular micro-Raman spectroscopy, has been useful for the analysis of mineral specimens in thin section, in some cases providing identification that was not possible by standard petrographic techniques (MAO *et al.,* 1987). These techniques have played a role in studying natural mantle xenoliths as well as deep crustal samples. GILLET *et al.* (1984) used Raman spectroscopy to identify coesite inclusions within pyrope grains in metasedimentary rocks from subducted continental crust (CHOPIN, 1984), placing constraints on the *P-T* history of the assemblage. Similarly, identification of coesite in a clinopyroxene from Norwegian eclogites demonstrated that the rock formation pressure exceeded 3 GPa (SMITH, 1984; BOYER *et al.,* 1985). Micro-Raman spectroscopy has been used to identify coesite in eclogites from central China (WANG *et al.,* 1989). SOBOLEV and SHATSKY (1990) and SHUTONG *et al.* (1992) used the technique to identify diamond crystals included in zircons and garnets, in high grade (>100 km) metamorphic rocks. The technique was also applied to study exsolution of garnet from clinopyroxene in high pressure rocks (MALEZIEUX, 1990), and to investigate eclogitic garnets included in diamonds (LIU *et al.,* 1990). Infrared spectroscopy has been useful in the study of fluid inclusions in diamonds (NAVON *et al.,* 1988), and was used to demonstrate the presence of solid CO_2 in one sample, fixing the entrapment depth at 220–270 km (SCHRAUDER and NAVON, 1993). Vibrational spectroscopy of solid inclusions in diamonds are giving further valuable information on the volatile content of the mantle (D. R. BELL, unpublished).

Characterization of impurities and defects

Vibrational spectroscopy has also been very useful for the identification of impurities, such as dissolved H in nominally anhydrous mantle minerals. Quantitative infrared absorbance measurements on nominally anhydrous minerals such as olivines, pyroxenes and garnets have revealed the presence of often substantial (up to 0.1 wt%) OH contained in defect sites within the structure (see BELL and ROSSMAN, 1992a), with implications for the possible water content of the mantle. The OH sites in hydrous phases in the system $MgO—SiO_2—H_2O$ have been characterized by Raman and infrared spectroscopy (AKAOGI and AKIMOTO, 1986; FINGER *et al.*, 1989; MCMILLAN *et al.*, 1991), and the importance of hydrogen-bonding in stabilizing such high pressure hydrous phases has been discussed (WILLIAMS, 1992). These materials may store large amounts of water within the mantle. SMYTH (1987) has suggested that the wadsleyite (β-) phase of Mg_2SiO_4 might provide an important storage site for H in the mantle. This possibility has been confirmed by vibrational spectroscopy (MCMILLAN and HOFMEISTER, 1988; MCMILLAN *et al.*, 1991; YOUNG *et al.*, 1993). Quantitative IR absorbance measurements have been used recently to investigate the OH content of the α-, β- and γ-phases of Mg_2SiO_4 as a function of composition and synthesis pressure by KOHLSTEDT *et al.* (1996). Finally, the H content and structural position of OH groups contained in defect sites in synthetic stishovite and $(Mg,Fe)SiO_3$ perovskite have been examined using such techniques (PAWLEY *et al.*, 1993; LU *et al.*, 1994; MEADE *et al.*, 1994).

Thermodynamic properties

Thermodynamic modeling based on vibrational spectroscopic data has played an important role in the development of our present knowledge of the properties of mantle minerals. A systematic and highly successful approach to this problem for minerals was developed by KIEFFER (1979a,b,c, 1980, 1982, 1985). This method permits the heat capacity and vibrational entropy of a mineral phase of interest to be calculated from a model density of states function, constructed from experimental infrared and Raman data, along with acoustic velocities. This application spurred many measurements of the IR and Raman spectra of high pressure silicates (AKAOGI *et al.*, 1984; NAVROTSKY, 1985, 1989; MCMILLAN and ROSS, 1987; HOFMEISTER *et al.*, 1989; FEI *et al.*, 1990; CHOPELAS, 1990a,b, 1991a,b; HOFMEISTER and CHOPELAS, 1991a,b; HOFMEISTER and ITO, 1992; CHOPELAS *et al.*, 1994). The resulting thermodynamic models have proven useful in establishing phase diagrams consistent with direct phase equilibrium data (AKAOGI *et al.*, 1984, 1989; NAVROTSKY, 1985, 1989; FEI *et al.*, 1990; SAXENA *et al.*, 1993).

In these calculations, anharmonic effects have generally been taken into account by using a quasiharmonic C_p-C_v correction ($C_p = C_v + TV\alpha^2K_T$) from the measured bulk modulus and thermal expansivity (KIEFFER, 1979b; 1985). This approach ignores the effects of intrinsic mode anharmonicity; *i.e.*, variations in vibrational mode frequencies with temperature at constant volume due to phonon-phonon interactions (GILLET *et al.* 1989a, 1990, 1991, 1992, 1993a; HEMLEY, 1991; STIXRUDE and HEMLEY, unpublished). LIU (1993) has in fact suggested that such anharmonic effects are not present for minerals. However, there is ample experimental and theoretical evidence for the existence of intrinsic mode anharmonicity in many minerals (GERVAIS *et al.*, 1972, 1973; GERVAIS and PIRIOU, 1975; GERVAIS, 1983; WOLF and JEANLOZ, 1984; REYNARD *et al.*, 1992; WINKLER and DOVE, 1992), although anharmonic effects do tend to decrease with increasing pressure (*e.g.*, HEMLEY and GORDON, 1985). These anharmonic contributions permit the high temperature heat capacities to exceed the Dulong-Petit limit, and cause the C_p values calculated within the quasiharmonic approximation to be underestimated by several per cent at mantle temperatures (RICHET *et al.*, 1992). The magnitude of anharmonic corrections can be evaluated experimentally by separately measuring vibrational mode frequencies at high temperature and high pressure (SAMARA and PEERCY, 1973; MAMMONE and SHARMA, 1980; GILLET *et al.*, 1989a; 1990). However, it is also found that intrinsic anharmonic corrections to C_p do not substantially affect the calculated phase boundaries over a wide temperature range (AKAOGI *et al.*, 1987; NAVROTSKY, 1989; FEI *et al.*, 1990; YUSA *et al.*, 1993; AKAOGI and ITO, 1993a), and differences between calculations and experiment are likely to be associated with other uncertainties (*e.g.*, free energies of formation, thermal expansivity). The effects of intrinsic mode anharmonicities are important for calculating the high-temperature heat capacity and isotopic fractionation between minerals, properties that depend strongly on vibrational anharmonicity (GILLET *et al.*, 1996).

There have been suggestions to use experimentally determined vibrational frequencies to estimate mineral elastic properties such as the bulk modulus, since K_T is proportional to $\Sigma\nu_i^2/V^{1/3}$ in the quasiharmonic approximation (HOFMEISTER, 1991). The approach involves a large number of approximations for materials beyond highly symmetric structures but has nevertheless has been applied to several mantle phases (HOFMEISTER, 1991; LU *et al.*, 1994). LIU (1992) has suggested estimating the bulk modulus from the pressure shift of an easily observable vibrational mode; however, this approach suffers from an unfortunate circularity because it requires a prior determination of the mineral compressibility. Such applications of vibrational spectroscopy may be useful for exploring possible relationships between (high-frequency) optical modes and elastic properties (low-frequency acoustic modes). However, their predictive value may be questioned in view of the fact that high *P-T* elastic properties can now be measured directly with higher accuracy (ANDERSON *et al.*, 1993; DUFFY *et al.*, 1995). Moreover, first-principles theoretical calculations in many cases are more reliable (*e.g.*, COHEN, 1992).

Density of states and lattice dynamics

Perhaps of most concern in the construction of vibrational models for thermochemical calculation is the very incomplete nature of the vibrational data set available from infrared and Raman spectroscopy. These techniques give information on vibrational modes at the Brillouin zone centre, and generally give little or no insight into dispersion of vibrational frequencies (MCMILLAN, 1985). In addition, many zone center modes may not appear in IR or Raman spectra due to selection rules imposed by crystal symmetry, and others may not be observed experimentally due to low intensity (MCMILLAN and HOFMEISTER, 1988). Because the heat capacity and entropy are obtained as integrals over the entire vibrational density of states $g(\omega)$, the result is a vibrational model for calculating these which may be poorly constrained by experiment. In principle, this problem can be solved by directly determining $g(\omega)$ from inelastic neutron scattering; such measurements gives $S(\omega)$, the vibrational density of states weighted by an atomic participation factor in each vibration, and its neutron scattering cross section (*e.g.*, GHOSE, 1985, 1988). This technique, however, requires large samples (typically a few grams), and is not usually possible for high pressure silicates, especially *in situ* at high pressure. Alternatively, lattice dynamics calculations may be carried out using either *ab initio* (first-principles) or empirically derived interatomic potentials (CATLOW and PRICE, 1990; COHEN, 1994; BUKOWINSKI, 1994). Both approaches have been applied successfully to mantle minerals. The empirical calculations require experimental data as input, which may include vibrational spectroscopic data. It is of particular interest that both IR and Raman spectra of minerals can be obtained readily at high pressures and (most recently) high temperatures (HEMLEY *et al.*, 1987a; MCMILLAN and HOFMEISTER, 1988; CHOPELAS and BOEHLER, 1992), so that not only mode frequencies and relative intensities are available for comparison between theory and experiment, but also their changes with pressure and temperature. Recent developments in *ab initio* techniques permit calculation of mineral lattice dynamics and thermophysical properties with increasing accuracy (COHEN, 1994; BUKOWINSKI, 1994), and it appears that we are entering a new era of sophistication in modeling structure and dynamics of minerals under mantle *P-T* conditions. Infrared and Raman spectra obtained *in situ* at high pressures and temperatures are invaluable for evaluating and constraining the quality of these calculations.

LOWER MANTLE MINERALS

(Mg,Fe)SiO_3 perovskite

Extensive studies of (Mg,Fe)SiO_3 perovskite have been performed in recent years because of its importance for lower mantle mineralogy (NAVROTSKY and WEIDNER, 1989; HEMLEY and COHEN, 1992). (Mg,Fe)SiO_3 perovskite was first synthesized by LIU (1974, 1975) and characterized in detail in subsequent years (see HEMLEY and COHEN, 1992). KNITTLE and JEANLOZ (1987) showed experimental evidence for its stability at *P-T* conditions corresponding to most of the lower mantle, indicating that the phase may be the dominant mineral in the Earth. The structure and thermodynamic properties of this phase are reviewed by WILLIAMS *et al.* (1989) and by HEMLEY and COHEN (1992). The infrared spectrum of a sample of pure $MgSiO_3$ perovskite, synthesized in the diamond anvil cell, was obtained by WENG *et al.* (1983), and the Raman spectrum was first recorded by WILLIAMS *et al.* (1987). The number of IR-active modes, and the appearance of a first-order Raman spectrum, confirmed the distortion from cubic symmetry of this phase (Fig. 2).

Perovskite with the ideal cubic structure (*Fm3m*) would have three IR-active modes and no Raman spectrum: from symmetry analysis,

$$\Gamma_{vib} = 3F_{1u}(IR) + F_{2u}(inactive). \qquad (1)$$

Within such a hypothetical cubic structure, the highest frequency mode involves asymmetric stretching of the octahedral groups (SiO_6), the mid-frequency vibration corresponds to a deformation vibration of the octahedra, and the lowest frequency IR mode involves translational motions of the alkaline earth cation in the dodecahedral site. Based on systematic infrared spectroscopy of other

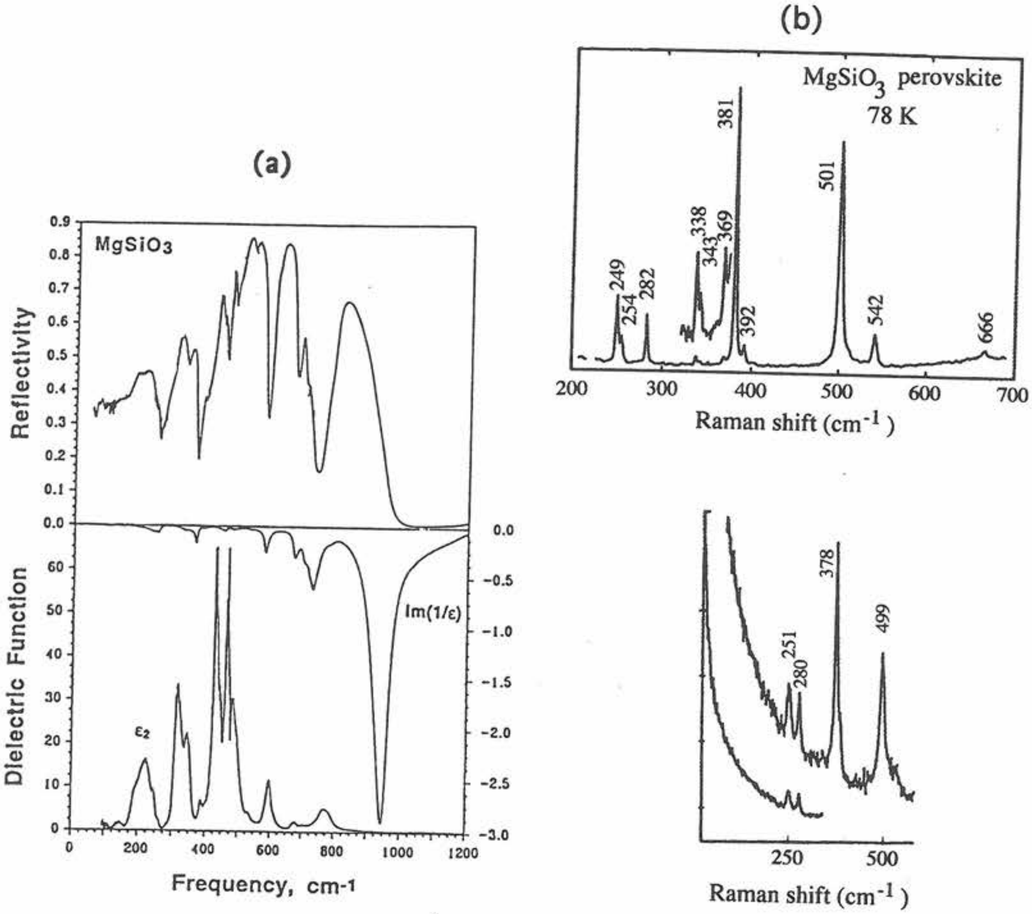


FIG. 2. (a) Infrared and (b) Raman spectra of $MgSiO_3$ perovskite. The infrared reflectivity data are redrawn from LU *et al.* (1994; Fig. 1, p. 11, 798). The peaks and minima in the dielectric functions $\epsilon_2(\nu)$ and $\mathrm{Im}(1/\epsilon(\nu))$ (middle left) indicate the positions of the TO and LO mode frequencies, respectively (LU *et al.*, 1994). The Raman spectrum at top is redrawn from DURBEN and WOLF (1992; Fig. 2, p. 891), for a sample cooled to 78 K. The spectrum at bottom (WILLIAMS *et al.*, 1987) shows the detail of the low-frequency region, to 30 cm^{-1}.

cubic perovskites, and calculations for hypothetical cubic $MgSiO_3$ perovskites, these modes would be expected to occur in the regions 750–1000 cm^{-1}, 500–700 cm^{-1}, and 250–400 cm^{-1}, respectively (WILLIAMS *et al.*, 1987; HEMLEY *et al.*, 1987b; LU *et al.*, 1994). Reduction of the symmetry to orthorhombic *Pbnm* with $Z = 4$ units of $MgSiO_3$ in the unit cell causes splitting of the IR-active modes, the occurrence of additional peaks in the IR spectrum, and the appearance of a first order Raman spectrum:

$$\Gamma_{vib} = 7A_g(R) + 7B_{1g}(R) + 5B_{2g}(R) + 5B_{3g}(R) + 8A_u(inactive) + 7B_{1u}(IR) + 9B_{2u}(IR) + 9B_{3u}(IR) \quad (2)$$

(WILLIAMS *et al.*, 1987; WOLF and BUKOWINSKI, 1987; HEMLEY *et al.*, 1989).

The mid-IR transmission spectra exhibited bands with maxima at 797, 683, 614 and 544 cm^{-1} (WENG *et al.*, 1983; WILLIAMS *et al.*, 1987). MADON and PRICE (1989) observed low frequency peaks at 390, 347, 320 and 282 cm^{-1}, and also suggested splitting in some of the higher frequency bands. The powder transmission minima correspond quite well with TO (transverse optic) mode frequencies obtained by LU *et al.* (1994) from their single crystal and powder reflectivity studies of pure $MgSiO_3$ and $(Mg_{0.9}Fe_{0.1})SiO_3$ samples, and several additional peaks were recognized in this study (Fig. 2). The frequencies of longitudinal (LO) modes were also deduced from the reflectivity data. WILLIAMS *et al.* (1987) observed Raman peaks at 251, 280, 378 and 499 cm^{-1}, which likely correspond to four of the seven expected A_g vibrations. Additional weak modes at 536 and 990 cm^{-1} were observed by HEMLEY *et al.* (1989). The best resolved spectrum obtained (at 78 K) to date is that of DURBEN and WOLF (1992), who observed eleven peaks between 249 and 666 cm^{-1} (Fig. 2). In neither the IR nor the Raman spectra have all the expected modes been observed, nor their symmetries reliably assigned experimentally (DURBEN and WOLF, 1992; LU *et al.,* 1994). This should be pursued in further studies, for the following reasons.

First, the vibrational data have proved useful in calculations of the specific heat and vibrational entropy of this phase (NAVROTSKY, 1989; AKAOGI and ITO, 1993b; GILLET *et al.,* 1993a; LU *et al.,* 1994). These calculated properties have helped to determine and rationalize the negative *P-T* slopes of reactions forming perovskite from lower pressure phases (NAVROTSKY, 1980; AKAOGI and ITO, 1993a). Of critical importance in determining the heat capacity and entropy are the positions of the lowest frequency vibrations of this phase. The lowest frequency Raman mode found by DURBEN and WOLF (1992) occurred at 249 cm^{-1}, and no obvious additional modes were found down to 30 cm^{-1} in the study by WILLIAMS *et al.* (1987) (Fig. 2). LU *et al.* (1994) found the lowest lying IR mode to occur at 180 cm^{-1}, although their data do not absolutely rule out the possibility of features at lower wavenumber. Further careful IR and Raman spectroscopy in the region below 200 cm^{-1} will be required to fully resolve this question.

Information on the low-lying vibrational modes, along with their dispersion across the Brillouin zone, is readily obtained from lattice dynamics calculations. HEMLEY *et al.* (1989) used a first principles method based on the modified electron gas approach, allowing for charge relaxation via spherical breathing of the O^{2-} anions (COHEN *et al.,* 1987), to calculate the structure and vibrational properties of $MgSiO_3$ perovskite. There was good agreement between some of the calculated mode frequencies and experimental values, but in general such approximate calculations are not expected to be able to reproduce the measured frequencies. For example, because such ionic model calculations underestimated the degree of distortion from the high-symmetry cubic structure, the frequencies of the lower octahedral librational modes were underestimated. Likewise, the frequencies of some of the higher modes are overestimated. The occurrence of the first-order Raman spectrum results from the descent in symmetry associated with the Brillouin zone folding arising from *R*- and *M*-point instabilities within the cubic aristotype, so that the Raman frequencies are particularly sensitive to details of the calculation (HEMLEY and COHEN, 1992; CHIZMESHYA *et al.,* 1994; BUKOWINSKI *et al.,* 1996). These modes are also particularly sensitive to potential symmetry changes in the perovskite structure with pressure and temperature (HEMLEY *et al.,* 1987b; MCMILLAN and ROSS, 1988; WOLF and BUKOWINSKI, 1987). In contrast to the approximate ionic model calculations, vibrational frequencies predicted from full electronic structure methods (*e.g.,* linearized augmented plane wave) give much better agreement with experiment as demonstrated for stishovite, as discussed below (KINGMA *et al.,* 1995). Although calculations at this level have been performed for $MgSiO_3$ perovskite (STIXRUDE and COHEN, 1993; WENTZCOVITCH *et al.,* 1993), the vibrational frequencies have not been reported.

The lowest lying modes in the Raman spectrum are associated with coupled rotations of the linked SiO_6 octrahedra, and these are expected to be extremely sensitive to the degree of orthorhombic distortion of the perovskite structure; in particular, they should soften if $MgSiO_3$ perovskite undergoes a displacive phase transition to tetragonal or cubic structures at high temperature (WOLF and JEANLOZ, 1985; WOLF and BUKOWINSKI, 1987; BUKOWINSKI and WOLF, 1988; HEMLEY *et al.,* 1989; SALJE, 1989). Accurate calculations indicate a wide stability field for the orthorhombic form, at least for the $MgSiO_3$ endmember (HEMLEY *et al.,* 1987b; D'ARCO *et al.,* 1993; STIXRUDE and COHEN, 1993; WENTZCOVITCH *et al.,* 1993; BUKOWINSKI *et al.,* 1996). *In situ* X-ray diffraction measurements show that the orthorhombic form remains stable over the *P-T* range of the lower mantle explored so far experimentally (MAO *et al.,* 1989; FUNAMORI and YAGI, 1993; WANG *et al.,* 1994; YAGI *et al.,* to be published). The possibility of such critical transitions still exists (WANG *et al.,* 1992; MEADE *et al.,* 1995; BUKOWINSKI *et al.,* 1996), because the entire *P-T* range of the lower mantle has not been explored experimentally with *in situ* techniques, nor have detailed experiments been carried out for Fe-bearing perovskite. This could be tested by carrying out Raman spectroscopy *in situ* under simultaneous high *P-T* conditions, via laser heating in the diamond anvil cell (GILLET *et al.,* 1993b).

In the IR spectrum, the bands between 770 and 950 cm^{-1} observed by LU *et al.* (1994) could be assigned to the ν_3 asymmetric stretching vibration of the SiO_6 octahedra ($B_{1u} + 2B_{2u} + 2B_{3u}$ symmetries) from lattice dynamics calculations (HEMLEY *et al.*, 1989), and bands in the 600–725 cm^{-1} and 380–540 cm^{-1} regions to the ν_4 and ν_6 deformation vibrations (B_{1u} + $2B_{2u}$ + B_{3u}, and $2B_{1u}$ + B_{2u} + B_{3u}, respectively) (Fig. 2). Five modes (B_{1u} + $2B_{2u}$ + $2B_{3u}$) are expected in the low frequency region (~250–350 cm^{-1}) due to Mg^{2+} translation, and additional low frequency modes will arise from acoustic lattice modes, through folding of the Brillouin zone from the ideal cubic structure ($2B_{1u}$ + $2B_{2u}$ + $2B_{3u}$) (WILLIAMS *et al.*, 1987; WOLF and BUKOWINSKI, 1987; HEMLEY *et al.*, 1989). The behavior of these low frequency translational modes is of interest, because they determine the ferroic character of many perovskite materials (SCOTT, 1974). In their calculation of $CaSiO_3$ perovskite during decompression, HEMMATI *et al.* (1995) showed that a low frequency mode associated with off-centre Si^{4+} displacements within the SiO_6 octahedra became unstable, contributing to the amorphization phenomenon observed in this phase at or near ambient pressure. This type of low frequency mode would result in an increased far-IR reflectivity due to the large static dielectric constant, ϵ_o (SPITZER *et al.*, 1962; GRZECHNIK *et al.*, 1996). No such behaviour is indicated for $MgSiO_3$ perovskite: the far-IR reflectivity at low frequency is quite "normal" (~0.35; Fig. 2) (LU *et al.*, 1994). However, this should be investigated more fully in further experiments. In a recent theoretical study, BUKOWINSKI *et al.* (1996) have found that the lowest lying ferroic mode frequency for $MgSiO_3$ perovskite lies above 300 cm^{-1} at 50 GPa, and only softens near 3500 K, above the predicted instability temperatures for the soft modes associated with octahedral rotational motions.

Vibrational spectroscopy at high pressure and ambient temperature has been used to determine vibrational mode Grüneisen parameters ($\gamma_i = -d \ln \nu_i / d \ln V$), for comparison with the thermodynamic Grüneisen parameter γ_{th} ($=\alpha K_T V/C_v$). WILLIAMS *et al.* (1987) found frequency shifts ($d\nu_i/dP$) of 2.6 cm^{-1}/GPa for four IR-active modes between 500 and 850 cm^{-1} measured to 27 GPa, giving γ_i in the range 1.15–1.45. Using assumptions for non-observed vibrational modes, they estimated an average value of $\gamma \sim 1.9 \pm 0.2$, close to the experimental value $\gamma_{th} = 1.77$ obtained from the results of KNITTLE *et al.* (1986). Recent "best" estimates for this parameter at ambient density include $\gamma_{th} = 1.7$–1.9 (HEMLEY and COHEN, 1992); 1.3 ± 0.2 (WANG *et al.*, 1994), and 1.5 ± 0.2 (ANDERSON *et al.*, 1995). In the theoretical study by HEMLEY *et al.*, (1989), the value of γ_{th} was estimated to be 2.0 at ambient temperature, decreasing to 1.59 in the high temperature limit, by summing over all zone center vibrational modes ($\langle\gamma\rangle = \Sigma C_{vi}\gamma_i/\Sigma C_{vi}$, where C_{vi} is the contribution of each mode to C_v). Experimentally, HEMLEY *et al.* (1989) found frequency shifts ranging from 1.7 to 4.2 cm^{-1}/GPa, for seven Raman active modes measured to 26 GPa. CHOPELAS and BOEHLER (1992) found slightly smaller shifts (1.37–3.28 cm^{-1}/GPa) for the same modes observed over a greater pressure range (to 47 GPa). These values correspond to high mode Grüneisen parameters (HEMLEY and COHEN, 1992). Measurements of the anharmonicity of the material under lower mantle conditions could be obtained from analysis of the Raman linewidths and infrared reflectivity spectra under high pressure and high temperature conditions (GERVAIS, 1983; GILLET *et al.*, 1993c). *In situ* high *P-T* vibrational spectroscopic experiments could also yield information on melting (and possible pre-melting) behaviour of silicate perovskite (MATSUI and PRICE, 1991; WINKLER and DOVE, 1992; WASSERMAN *et al.*, 1993; BELONOSHKO, 1994; RICHET *et al.*, 1994), of considerable importance for mantle dynamics (VAN KEKEN *et al.*, 1994).

The temperature dependence of the Raman spectrum has been investigated at ambient pressure by DURBEN and WOLF (1992) (Fig. 3). These authors found no observable shift in the lowest frequency modes (the 249–254 cm^{-1} doublet), which might be expected to be extremely sensitive to changes in orthorhombic distortion, and only a small temperature dependence (~ −0.001 cm^{-1}/K) for the other modes. An obvious conclusion is that any critical behaviour in perovskite must lie at very high temperature, especially at high pressure (DURBEN *et al.*, 1991; STIXRUDE and COHEN, 1993; BUKOWINSKI *et al.*, 1996). DURBEN and WOLF (1992) also observed that the metastable perovskite phase transformed irreversibly to an amorphous material above approximately 300°C. During the transformation, the Raman peaks of the remaining perovskite material were found to be shifted irreversibly to higher wavenumber, as if the crystal had been placed under compression by the presence of the glass (DURBEN and WOLF, 1992). This illustrates the problems inherent in studying the material outside its stability field (HEMLEY and COHEN, 1992). The behavior of the vibrational spectra of silicate perovskites during amorphization has been examined theoretically (HEMMATI *et al.*, 1995; see also HEMLEY and COHEN, 1992).

To date, most vibrational studies have been focused on end-member $MgSiO_3$ perovskite. LU *et al.* (1994) and WANG *et al.* (1994) obtained the infrared and Raman spectra of $(Mg,Fe)SiO_3$ perovskites, and found little change in the spectra with

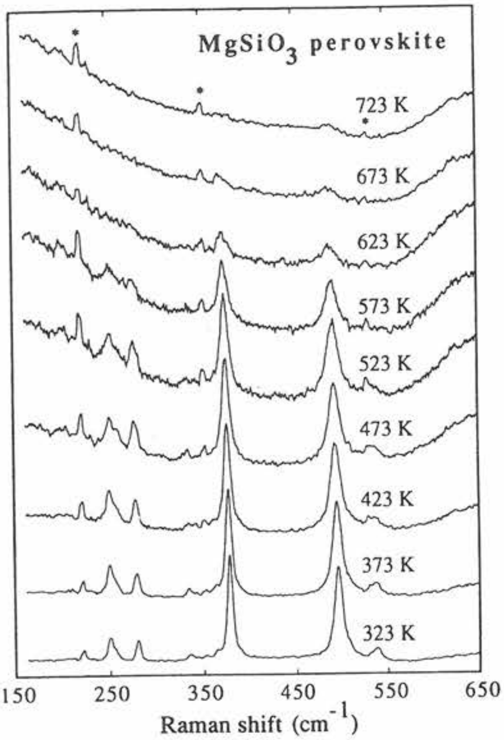


FIG. 3. Raman spectrum of $MgSiO_3$ perovskite as a function of temperature at ambient pressure, taken from DURBEN and WOLF (1992; Fig. 1, p. 891). At high temperature, the perovskite bands begin to weaken, and are replaced by broad bands due to $MgSiO_3$ glass (causing the rise in intensity to high and low frequencies), as the metastable perovskite reverts to an amorphous phase.

Fe^{2+}/Mg^{2+} substitution, except that the Raman peaks were broadened, indicating some structural disorder. Additionally, the Raman frequencies were shifted slightly to lower wavenumber, consistent with the small lattice expansion (KUDOH *et al.*, 1990; MAO *et al.*, 1991; WANG *et al.*, 1994).

$CaSiO_3$ perovskite

Phase equilibrium studies, together with constraints from cosmochemical constraints, indicate that $CaSiO_3$ perovskite is the next most abundant silicate in the lower mantle (HEMLEY and COHEN, 1992; IRIFUNE, 1994). It was first synthesized by LIU and RINGWOOD (1975). Unlike $(Mg,Fe)SiO_3$ perovskite, this phase appears to remain cubic over the entire *P-T* range of the lower mantle (MAO *et al.*, 1989; HEMLEY and COHEN, 1992; BUKOWINSKI *et al.*, 1996). To date, there has been no experimental study of the vibrational properties of $CaSiO_3$ perovskite, in part because this phase tends to amorphize upon decompression. *In situ* IR would be of particular interest to observe the behaviour of the far-IR reflectivity as a function of pressure, to give information on the low-lying ferroic mode as the sample is decompressed (HEMMATI *et al.*, 1995; BUKOWINSKI *et al.*, 1996). HEMMATI *et al.* (1995) have proposed that this vibration, which involves off-centre motions of the Si^{4+} ions within their octahedral sites, plays a role in the amorphization process. It is possible to recover at ambient pressure perovskites synthesized under pressure along the $CaSiO_3$-$CaTiO_3$ join (RINGWOOD and MAJOR, 1967, 1971). LEINENWEBER *et al.* (1994, 1996) have recently obtained Raman and infrared spectra for $CaSiO_3$—$CaTiO_3$ perovskites synthesized at high pressure. This system forms an orthorhombic or tetragonal solid solution between $CaSiO_3$ and 50 mol% $CaTiO_3$, and a new ordered compound at the Ca_2SiTiO_6 composition. Strong Raman bands appear near 750 and 450 cm^{-1} as the silicate content is increased, which can be assigned to Si—O stretching and OSiO bending vibrations associated with the SiO_6 octahedral groups.

(Mg,Fe)O magnesiowüstite

MgO and FeO have the cubic NaCl (B1) structure, which has no first order Raman spectrum. The zone centre optic mode has symmetry

$$\Gamma_{vib} = F_{1u}(IR) \tag{3}$$

This triply degenerate vibration is actually split into transverse (2 TO) and longitudinal (LO) components by the macroscopic electric field associated with the vibration (FERRARO, 1984; MCMILLAN, 1985; MCMILLAN and HOFMEISTER, 1988). The infrared reflectance spectrum under ambient conditions shows a broad reflectance band extending from $\sim 350\ cm^{-1}$ to $\sim 750\ cm^{-1}$ with low- and high frequency limits determined by the TO and LO frequencies (PIRIOU, 1964, 1974; PIRIOU and CABANNES, 1968). The pure absorption frequency, which would be visible in thin film measurements, would give rise to a single peak near 380 cm^{-1}. However, additional features are often observed in powder measurements in the 550–650 cm^{-1} region, due to vibrational mode coupling, and particle size effects (LUXON *et al.*, 1969; PIRIOU, 1974; MCMILLAN, 1985).

The characterization of the thermophysical properties of (Mg,Fe)O solid solutions is crucial for understanding the lower mantle (ANDERSON *et al.*, 1992, 1993). There has been a large number of theoretical studies of the lattice dynamics of MgO under lower mantle conditions (Cohen *et al.*, 1987; Agnon and Bukowinski, 1990; Burnham, 1990; Bukowinski, 1994; Chizmeshya *et al.*, 1994; Bukowinski *et al.*, 1996): however, the frequency of the LO modes is typically overestimated in these studies because of constraints imposed on the electronic relaxation associated with the vibration. The zone centre frequency fixes the upper limit of the vibrational spectrum. The IR spectra at ambient conditions are well understood (Piriou, 1964; Brehat *et al.*, 1966; Farmer, 1974; Ferraro, 1984). The infrared reflectance spectrum of MgO has been studied at high temperature, giving information on the anharmonicities of the lattice modes (Piriou, 1964, 1974; Piriou and Cabannes, 1968). To date, there has been no direct study of the IR spectrum at high pressure. The far IR spectra of several halides with the B1 and B2 structures have been studied at high pressure in the diamond anvil cell (Ferraro, 1984), and this type of study could be extended to magnesiowüstite in future studies. Chopelas and Nicol (1982) noted that the side bands present on the V^{2+} or Cr^{3+} luminescence for these ions doped in MgO contained information on the vibrational density of states of the host oxide crystal, due to vibronic coupling between the electronic excitation of the transition metal ion and the lattice vibrations of MgO. They used these data to construct a density of states function $g(\omega)$ for MgO, and to calculate thermodynamic properties of this phase within the quasiharmonic approximation, up to 10 GPa. Chopelas (1990a, 1992) has revised and extended these studies to over 20 GPa.

Stishovite

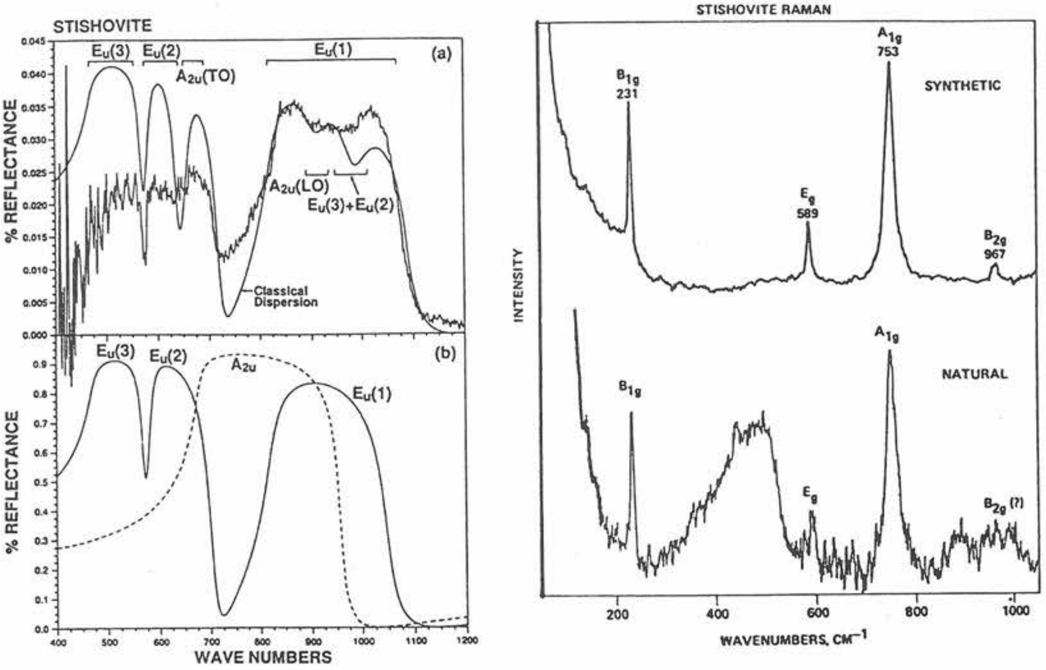
Stishovite with the rutile structure is the high pressure phase of SiO_2, stable above 9 GPa (Stishov and Popova, 1961). The natural occurrence of this mineral was first described as a product of impact metamorphism of quartz in sandstone (Chao *et al.*, 1962). However, its high pressure stability means that it could be present throughout the mantle, being formed in disproportionation reactions between silicate minerals and oxides (Hemley *et al.*, 1994; Kingma *et al.*, 1995). The expected vibrational modes for the stishovite structure are:

$$\Gamma_{vib} = A_{1g}(R) + A_{2g}(inactive) + B_{1g}(R) + B_{2g} + E_g(R) + 2B_{1u}(IR) + 2E_u(IR) \quad (4)$$

A powder transmission spectrum of stishovite separated from a natural sample was first recorded by (Lyon, 1962). This spectrum showed many more peaks than expected from the symmetry analysis. However, the powder spectrum closely resembles the polycrystalline IR reflectance spectrum obtained by Hofmeister *et al.* (1990) (Fig. 4). Analysis of the reflectivity data gave the zone centre TO modes at $\sim$650 cm^{-1} (A_{2u}), and 470, 580 and 820 cm^{-1} (E_u). These frequencies do not correspond simply to the positions of transmission minima in the powder spectrum, because of the variation in optical constants due to overlapping modes of different symmetry with large TO-LO splitting (Hofmeister *et al.*, 1990). The reflectivity data are noisy in the low-frequency region, and do not constrain the IR spectrum well in the region below 700 cm^{-1}.

Williams *et al.* (1993) measured the pressure dependence of peaks in the powder IR transmission spectrum of stishovite. Two bands were followed to approximately 36 GPa, with pressure shifts of 2.4 and 3.3 cm^{-1}/GPa, respectively. The two bands followed have absorbance maxima at 611 and 861 cm^{-1} at room pressure, and were assigned to two of the E_u modes observed by Hofmeister *et al.* (1990). As noted by Williams *et al.* (1993), these frequencies do lie close to (within 40 cm^{-1}) of the TO frequencies determined in the reflectivity study: however, this region of the stishovite spectrum is considerably complicated by overlap between E_u and the A_{2u} modes, and resulting interference effects (Hofmeister *et al.*, 1990) (Fig. 4). Based on the resemblance between the powder reflectance and the transmission data (Hofmeister *et al.*, 1990; Williams *et al.*, 1993), it is most likely that the transmission minima (inverted to give absorbance maxima, via $A(\nu) = -\log_{10} T(\nu)$) contain contributions from both TO and LO components, of both E_u and A_{2u} modes in the case of the lower frequency bands. However, the pressure shifts measured by Williams *et al.* (1993) give information on the average Grüneisen parameter for these modes. The high pressure behaviour of the IR spectrum should be subjected to further analysis, especially because of the impending transition to the $CaCl_2$-structured phase at $\sim$50 GPa, as discussed below.

The Raman spectra of natural and synthetic stishovite have been reported by Hemley *et al.* (1986a) and Hemley (1987) (Fig. 4). The results of earlier studies were complicated by the introduction of impurities due to the extraction process of stishovite from natural samples and the presence of glassy material: this only became apparent once the spectrum of synthetic samples had been recorded (Hemley *et al.*, 1986a; Hemley, 1987). The Raman spectrum shows all four expected modes: A_{1g} at 753 cm^{-1}, B_{2g} at 967 cm^{-1}, E_g at 589 cm^{-1}, and B_{1g} at 231 cm^{-1}. Hemley (1987) measured the pressure



(a) **(b)**

FIG. 4. (a) Infrared and (b) Raman spectra of SiO_2 stishovite. The infrared reflectance spectrum is taken from HOFMEISTER *et al.* (1990; Fig. 1, p. 952). The experimental (unpolarized) polycrystalline spectrum is shown at top, along with the TO and LO mode frequencies obtained from analysis of the reflectivity data. The synthetic spectrum at bottom was reconstructed using these parameters, for both mode symmetries (A_{2u} and E_u). The Raman spectrum at right is from HEMLEY *et al.* (1986a). The four expected modes are clearly visible in the spectrum of the synthetic sample at top. The natural sample (bottom) shows broad bands corresponding to amorphous SiO_2.

shifts of these Raman active vibrations. The behavior of the low-lying B_{1g} mode is particularly interesting, because its frequency decreases with increasing pressure (Fig. 5). The atomic displacements associated with this mode correspond to those required to transform stishovite from the rutile into the calcium chloride structure (HEMLEY, 1987; NAGEL and O'KEEFFE, 1971). Recent theoretical (COHEN, 1992; LACKS and GORDON, 1993; MATSUI and TSUNEYUKI, 1992) and experimental (TSUCHIDA and YAGI, 1989, 1990; KINGMA *et al.*, 1995, 1996) work has shown that the rutile structure transforms to a phase with the calcium chloride structure. From theoretical calculations of the vibrational mode frequency with increasing pressure, this transition was predicted to occur near 50 GPa (COHEN, 1992), in remarkable agreement with the recent experimental result of KINGMA *et al.* (1995) (Fig. 5). This work indicates that free SiO_2 would exist in the $CaCl_2$ structure below 1200–1500 km within the lower mantle (depending on the *P-T* slope of the transition, which has not yet been determined experimentally). A further transition to a modified fluorite or *Pa3* phase is predicted to occur at Earth core pressures, above ~150 GPa (COHEN, 1994; HAINES *et al.*, 1996).

GILLET *et al.* (1990) measured the temperature dependence of the Raman active modes of stishovite at ambient pressure, and calculated the heat capacity and entropy of this phase via vibrational modeling. In this study, the pressure- and temperature derivatives of the Raman peaks were used to estimate the intrinsic anharmonicity of the vibrational modes, and to obtain a high temperature heat capacity corrected for anharmonicity, beyond the quasiharmonic approximation. In the high-temperature study, broad bands were observed to appear due to back-transformation of the high pressure phase into glass dominated by tetrahedrally coordinated silicate groups (GILLET *et al.*, 1990; GRIMSDITCH *et al.*, 1994). These broad glass bands are also present in the Raman spectrum of natural

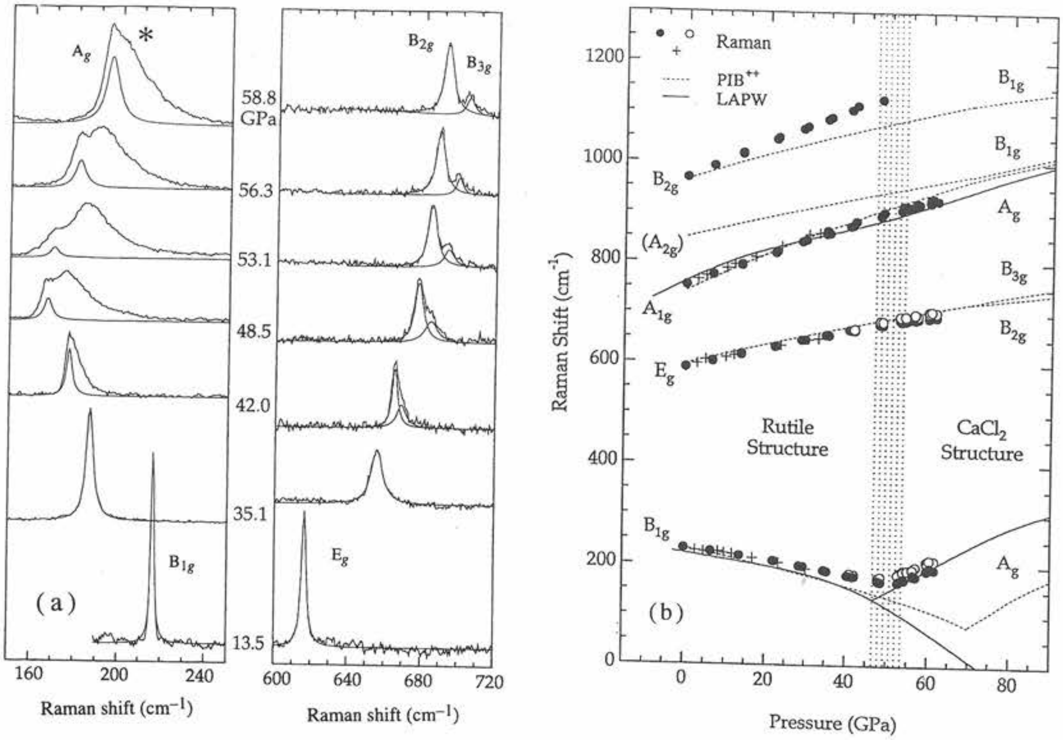


FIG. 5. (a) Raman spectra from KINGMA *et al.* (1995) showing evidence for the rutile-CaCl$_2$ transition in SiO$_2$ at high pressure. The smooth lines under the observed bands are Lorentzian fits for the expected fundamentals of both phases (KINGMA *et al.*, 1995). The broad band marked * is not predicted by theory, and is dependent upon the stress state of the sample. The low frequency B$_{1g}$ peak for the rutile form softens with increasing pressure. Above the transition pressure (~50 GPa), this becomes the A$_g$ mode of the CaCl$_2$ structure, and its frequency begins to increase with further compression. (b) Frequency shifts of Raman bands of stishovite and CaCl$_2$-structured SiO$_2$ with pressure at ambient temperature, during compression (filled circles) and decompression (open circles). The experimental data are compared with results of theoretical calculations, using first-principles LAPW (COHEN, 1992: full line) and parametrized PIB (potential induced breathing: dashed line) methods.

stishovite (HEMLEY *et al.*, 1986a). The phenomenon of pressure- and temperature-induced amorphization of SiO$_2$ phases has been studied extensively using vibrational spectroscopy (HEMLEY, 1987; GILLET *et al.*, 1990; WOLF *et al.*, 1992; WILLIAMS *et al.*, 1993; GRIMSDITCH *et al.*, 1994).

TRANSITION ZONE MINERALS

β- $(Mg,Fe)_2SiO_4$

Along with the spinel (γ) polymorph discussed below, a (Mg,Fe)$_2$SiO$_4$ polymorph with the wadsleyite, or "modified spinel", (β) structure is likely to form one of the dominant constituents of the mantle transition zone. The transition from the low pressure olivine (α-(Mg,Fe)$_2$SiO$_4$) to the β-phase occurs at approximately 13 GPa at ~1700 K, and marks the 410 km seismic discontinuity (BINA and WOOD, 1987; AKAOGI *et al.*, 1989; KATSURA and ITO, 1989; MENG *et al.*, 1993; MORISHIMA *et al.*, 1994). The Raman and infrared spectra of the β- and γ-polymorphs of Mg$_2$SiO$_4$ were first reported by AKAOGI *et al.* (1984), who used the vibrational data to construct model density of states functions g(ω) for specific heat and entropy calculations. This information was then combined with calorimetric data to establish a *P-T* phase diagram for the Mg$_2$SiO$_4$ polymorphs (AKAOGI *et al.*, 1984). This study has been superseded by more recent work (AKAOGI *et al.*, 1989; GASPARIK, 1990; CHOPELAS, 1991b), but it represented the first application of KIEFFER's (1979a,b,c) approach to mantle mineralogy.

The powder IR spectrum of β-Co$_2$SiO$_4$ was obtained by JEANLOZ (1980). Unlike the α-(olivine) and γ-(spinel) polymorphs of M_2SiO_4 phases, this spectrum showed a peak at 686 cm^{-1}, associated with a bending vibration of the SiOSi linkage between tetrahedral groups. Similar features at 700 and 675 cm^{-1} appear in the IR spectrum of β-Mg_2SiO_4 (AKAOGI *et al.*, 1984; WILLIAMS *et al.*, 1986; CYNN and HOFMEISTER, 1994) (Fig. 6). These weak but characteristic bands reveal the presence of the unusual Si_2O_7 units in the structure (JEANLOZ, 1980; HORIUCHI and SAWAMOTO, 1981), which require the presence of oxygen bound only to Mg atoms in the β-polymorph. This structural feature is important for the ability of this nominally anhydrous phase to accept large quantities of H into its structure (SMYTH, 1987; DOWNS, 1989), discussed further below.

The expected vibrational modes for β-Mg_2SiO_4 are:

$$\Gamma_{vib} = 11A_g(R) + 7B_{1g}(R) + 9B_{2g}(R) + 12B_{3g}(R) + 7A_u(inactive) + 14B_{1u}(IR) + 13B_{2u}(IR) + 11B_{3u}(IR) \quad (5)$$

The Raman spectrum of β-Mg_2SiO_4 originally reported by AKAOGI *et al.* (1984) was incorrect, because the sample partly back-transformed during heating by the laser in the Raman experiment. The Raman spectrum for this phase was later obtained by MCMILLAN and AKAOGI (1987) and by CHOPELAS (1991b). In both of these studies, a strong peak (most likely of A_g symmetry) was observed at 723 cm^{-1}, due to the SiOSi linkage vibrations, (Fig. 6). REYNARD *et al.* (1996) have recently found some differences with the previous spectra. They did not reproduce a peak found at 86 cm^{-1} by CHOPELAS (1991b), which is important for defining the low frequency limit of the density of states function for heat capacity and entropy calculations (AKAOGI *et al.*, 1984; CHOPELAS, 1991b), and they did not observe the weak peaks in the 1000–1100 cm^{-1} region reported by MCMILLAN and AKAOGI (1987). REYNARD *et al.* (1996) have suggested that these peaks could be due to Si_3O_{10} units, created locally within the structure associated with the presence of stacking faults in the structure (BREARLEY *et al.*, 1992). If this assignment is correct, Raman spectroscopy could provide a powerful *in situ* method for characterizing the defect structure in β-Mg_2SiO_4 at high pressure and temperature (*e.g.*, with a diamond-anvil cell).

The kinetics and mechanism of transformations between α-, β- and γ-polymorphs of $(Mg,Fe)_2SiO_4$ are important for understanding the seismicity

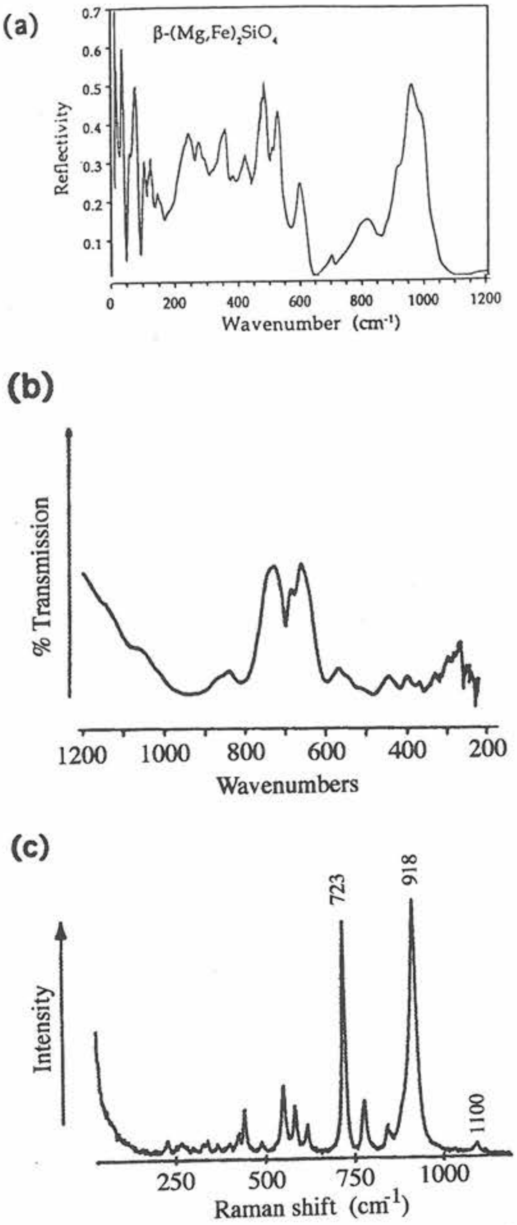


FIG. 6. Infrared (a,b) and Raman (c) spectra of β-$(Mg,Fe)_2SiO_4$. The infrared reflectance spectrum (a) is redrawn from CYNN and HOFMEISTER (1994; Fig. 1, p. 17,718). The weak peaks associated with the SiOSi linkages in the structure are more easily distinguished in the powder transmission spectrum, from AKAOGI *et al.* (1984) (b). The Raman spectrum (c) was obtained by MCMILLAN and AKAOGI (1987). The weak peak at 1100 cm^{-1} was not observed in the recent study by REYNARD *et al.* (1996), and may correspond to a structural defect in the sample (see text).

within subducting slabs (SUNG and BURNS, 1976; WU *et al.,* 1993; BREARLEY *et al.,* 1992; RUBIE and BREARLEY, 1994; REYNARD *et al.,* 1996). Raman spectroscopy provides a useful technique for characterizing these structural changes (CHOPELAS, 1991b; DURBEN *et al.,* 1993; REYNARD *et al.,* 1996). The accidentally back-transformed spectrum of AKAOGI *et al.* (1984) resembled that of Mg_2SiO_4 olivine, but with considerably broadened bands. In a high temperature single crystal X-ray diffraction study of β-Mg_2SiO_4 at ambient pressure, TSUKIMURA *et al.* (1988) had observed anomalous changes in the lattice parameters above 580°C which might be associated with a structural transformation. MCMILLAN *et al.* (1991) obtained a Raman spectrum for a sample that had been heated to 585°C at ambient pressure. This spectrum showed the broadened bands corresponding to a disordered olivine-like material found by AKAOGI *et al.* (1984), along with weak broad bands in the 650–700 cm^{-1} region. These suggested the presence of SiOSi linkages persisting within the structure, presumably as the β-Mg_2SiO_4 back-transformed to olivine via a series of spinelloid intermediate structures (HYDE *et al.,* 1982; MADON and POIRIER, 1983). REYNARD *et al.* (1996) have recently carried out a detailed kinetic study of this transformation at ambient pressure via Raman spectroscopy. DURBEN *et al.* (1993) have used Raman spectroscopy to investigate the compression mechanism in olivine (α-Mg_2SiO_4) at room temperature, and observed changes which might be associated with formation of SiOSi linkages within the structure, perhaps accompanied by Si coordination changes (GUYOT and REYNARD, 1992). Further compression of the olivine end-members at room temperature leads to amorphization, as shown by WILLIAMS *et al.* (1990) and RICHARD and RICHET (1990) for Fe_2SiO_4 and by ANDRAULT *et al.* (1995) for $(Mg,Fe)_2SiO_4$. Further experiments using both Raman and infrared spectroscopy under mantle *P-T* conditions are likely to yield new information on the nature of the forward- and back-transformations between the α-, β- and γ-phases of $(Mg,Fe)_2SiO_4$.

WILLIAMS *et al.* (1986) measured the powder IR spectrum of β-Mg_2SiO_4 to 27 GPa at room temperature, and CYNN and HOFMEISTER (1994) have obtained the mid- and far-IR spectrum of a sample with composition $(Mg_{1.80}Fe_{0.15})SiO_4$, to ~23 GPa. The spectrum of the Fe-containing sample is less well-resolved, presumably due to Fe/Mg disorder. The peaks in the powder absorption spectrum correspond quite closely with the TO modes determined from the IR reflectivity (CYNN and HOFMEISTER, 1994), in contrast to the case for stishovite mentioned above. It has been noted that, as the complexity of the mineral phase increases and more peaks are present in the IR spectrum, the powder transmission spectrum gives a better representation of the true TO mode frequencies, at least for modes which are not strongly polar (such as the Si—O stretching vibrations) (MCMILLAN and HOFMEISTER, 1988). The average mode Grüneisen parameter was determined to be $\langle\gamma\rangle = 1.28 \pm 0.02$, in good agreement with the thermodynamic value $\gamma_{th} = 1.05 \pm 0.2$ (WILLIAMS *et al.,* 1986). REYNARD *et al.* (1996) measured the temperature shifts of the Raman peaks of β-Mg_2SiO_4 up to 800–900 K (the back-transformation temperature), and combined the data with pressure shifts to determine intrinsic mode anharmonicity parameters (GILLET *et al.,* 1991). In her study of the Raman spectrum at high pressure, CHOPELAS (1991b) observed changes in the pressure shifts at 9.2 GPa and perhaps also at 17 GPa, which might indicate some structural transformation in β-Mg_2SiO_4. Similar changes in slope are apparent in the IR data taken at high pressure (CYNN and HOFMEISTER, 1994). Although the possibility of weak structural distortions deserves further study, no anomalies have been noted in X-ray diffraction measurements of β-$(Mg,Fe)_2SiO_4$ to 26 GPa and 900 K (FEI *et al.,* 1992). LIU *et al.* (1994) has also investigated the Raman spectrum of this phase to 18 GPa at ambient temperature.

Because the composition of β-Mg_2SiO_4 is that of an orthosilicate, formation of the SiOSi linkage in the high pressure phase results in one oxygen per asymmetric unit being bound to only Mg atoms, in an irregular five-fold coordinated site (HORIUCHI and SAMAMOTO, 1981; SAWAMOTO and HORIUCHI, 1990). SMYTH (1987) and DOWNS (1989) suggested that this might provide a potential site for protonation of the nominally anhydrous mineral, so that β-Mg_2SiO_4 could act as an important source or sink for water in the mantle (DOWNS, 1989; SMYTH, 1987). MCMILLAN *et al.* (1991) examined a synthetic sample of β-Mg_2SiO_4 using micro-Raman spectroscopy, and found that an asymmetric band was present at 3322 cm^{-1}, due to OH groups within the structure (Fig. 7). Measurement of the absorbance via micro-infrared spectroscopy allowed an estimate of the OH content as approximately 0.06 % by weight (as g OH per 100 g Mg_2SiO_4: this corresponds to ~10,300 H/10^6 Si) (MCMILLAN *et al.,* 1991). These authors considered that this value represented a maximum degree of hydration for the β-Mg_2SiO_4 phase, because other stable hydrous magnesium silicates were known to be pres-

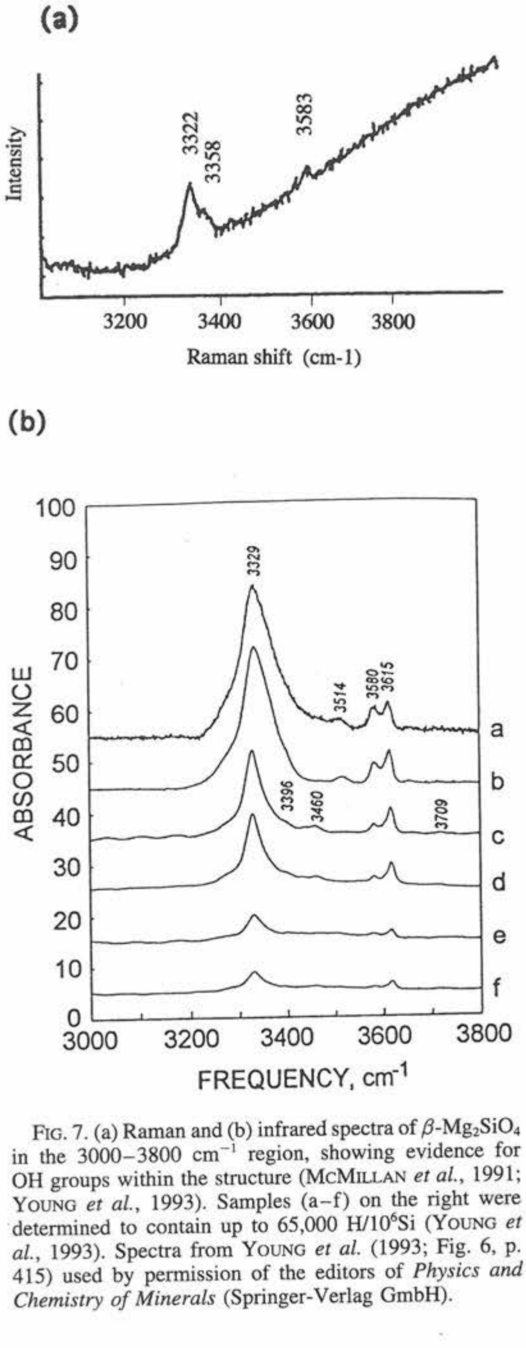


FIG. 7. (a) Raman and (b) infrared spectra of β-Mg_2SiO_4 in the 3000–3800 cm^{-1} region, showing evidence for OH groups within the structure (McMILLAN *et al.*, 1991; YOUNG *et al.*, 1993). Samples (a–f) on the right were determined to contain up to 65,000 $H/10^6Si$ (YOUNG *et al.*, 1993). Spectra from YOUNG *et al.* (1993; Fig. 6, p. 415) used by permission of the editors of *Physics and Chemistry of Minerals* (Springer-Verlag GmbH).

ent. From quantitative IR absorption spectra on single crystal samples of $(Mg_{0.92},Fe_{0.08})_2SiO_4$, prepared at 14 GPa and 1550–1650 K, YOUNG *et al.* (1993) determined much higher OH concentrations, between 10,000 and 65,000 $H/10^6$ Si. It was suggested that these higher values could be due to the presence of Fe in the sample (YOUNG *et al.*, 1993).

KOHLSTEDT *et al.* (1996) have recently prepared a suite of $(Fe,Mg)_2SiO_4$ samples from natural olivine at pressures and temperatures up to 15 GPa and 1100°C, and have found water contents ranging up to ~2.4 wt% (400,000 $H/10^6$ Si) via quantitative IR absorbance spectroscopy (Fig. 7). This is consistent with the recent determination of OH in β-Mg_2SiO_4 (to give an actual composition close to $Mg_{1.75}H_{0.5}SiO_4$) via SIMS (INOU *et al.*, 1995). KOHLSTEDT *et al.* (1996) also documented a similar quantity of hydrous component dissolved in γ-$(Fe,Mg)_2SiO_4$, prepared at 19.5 GPa and 1100°C. These results are extremely important for the mineralogy of the transition zone, and water storage within the Earth. CYNN and HOFMEISTER (1994) have investigated the behaviour of the OH stretching vibrations in the $(Mg,Fe)_2SiO_4$ sample prepared by YOUNG *et al.* (1993), and have documented an increase in hydrogen bonding in this phase with increasing pressure. Such behaviour could help in stabilizing hydrous phases at high pressure (WILLIAMS, 1992; KNITTLE *et al.*, 1992).

γ-$(Mg,Fe)_2SiO_4$

At pressures above 18–20 GPa for the temperature range encountered within the transition zone of the normal mantle, β-Mg_2SiO_4 transforms further into a phase with the spinel structure, γ-Mg_2SiO_4 (AKAOGI *et al.*, 1989; RIGDEN *et al.*, 1991). Unlike the magnesian end-member, Fe_2SiO_4 transforms directly from olivine into spinel at much lower pressure, ~6–7 GPa, over the same temperature range. For this reason, the Fe content of the $(Mg,Fe)_2SiO_4$ component is an important parameter in determining the depth and width of the α-(β)-γ transitions occurring within the mantle (AKAOGI *et al.*, 1989; BINA and WOOD, 1987; KATSURA and ITO, 1989; WU *et al.*, 1993; GILLET, 1995).

There have been several vibrational studies of the Mg_2SiO_4 and Fe_2SiO_4 spinel end-members, and their solid solutions (Fig. 8, 9). The expected vibrational modes for a cubic (*Fd3m*) spinel structure are:

$$\Gamma_{vib} = A_{1g}(R) + E_g(R) + T_{1g}(inactive) + 3T_{2g}(R) + 2A_{2u}(inactive) + 2E_u(inactive) + 4T_{1u}(IR) + 2T_{2u}(inactive) \quad (6)$$

JEANLOZ (1980) obtained a powder IR absorption spectrum of Fe_2SiO_4 spinel, and observed three infrared peaks at 848, 503 and 344 cm^{-1} (Fig. 8). The lower frequency peaks correspond quite well with the TO mode frequencies estimated from the reflectance spectrum obtained by HOFMEISTER (see

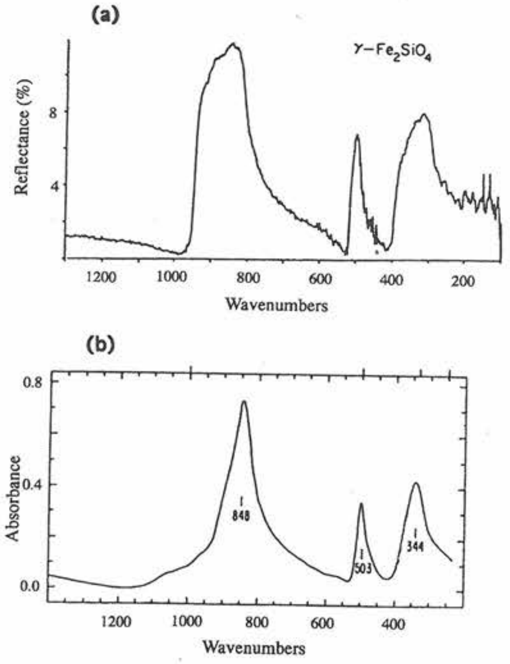


FIG. 8. (a) IR reflectance (obtained by A. Hofmeister, reported in McMillan and Hofmeister, 1988) and (b) powder transmission (Jeanloz, 1980) spectra for γ-Fe_2SiO_4. Three of the expected four resonances are clearly visible in these spectra. Spectra from Jeanloz (1980; Fig. 2, p. 331) used by permission of the editors of *Physics and Chemistry of Minerals* (Springer-Verlag GmbH).

McMillan and Hofmeister, 1988), and correspond to the deformation vibration (ν_4) of the SiO_4 tetrahedra, and an octahedral FeO_6 stretching mode, respectively. The highest frequency mode is attributed to the ν_3 asymmetric stretching vibration of the tetrahedral SiO_4 groups. This highly polar vibration is associated with a large TO—LO splitting, and gives rise to a broad reflectance band (Fig. 8). The upper limit of this band occurs near 960 cm^{-1}, which fixes the approximate upper limit in the density of states function, g(ω). The powder IR absorption frequency lies close to the inflexion on the low-frequency side of the reflectance band, which corresponds to the TO mode frequency (McMillan and Hofmeister, 1988). The fourth mode expected in the IR spectrum has not yet been observed.

Akaogi *et al.* (1984) observed broad bands at 830 and 445 cm^{-1} in their powder transmission IR spectrum for γ-Mg_2SiO_4 (Fig. 9). The remaining infrared modes for Mg_2SiO_4 have still not been characterized. There have been several lattice dynamical calculations for γ-Mg_2SiO_4 using empirical interatomic potentials, but the vibrational frequencies were not reported (Matsui and Busing, 1984; Price and Parker, 1984; Price *et al.*, 1987).

Akaogi *et al.* (1984) obtained a Raman spectrum for Mg_2SiO_4 spinel, which showed the strong peaks expected for the symmetric (ν_1) and asymmetric (ν_3) stretching vibrations of the SiO_4 tetrahedra, in the 780–900 cm^{-1} region. A similar spectrum was obtained by Guyot *et al.* (1986) for a natural sample of γ-$(Mg_{0.74}Fe_{0.26})_2SiO_4$, although an additional weak peak was observed in that study at 844 cm^{-1}, which has not been assigned (and could be due to coating from the microscope objective). The remaining weak peaks expected in the spinel spectrum were recorded by McMillan and Akaogi

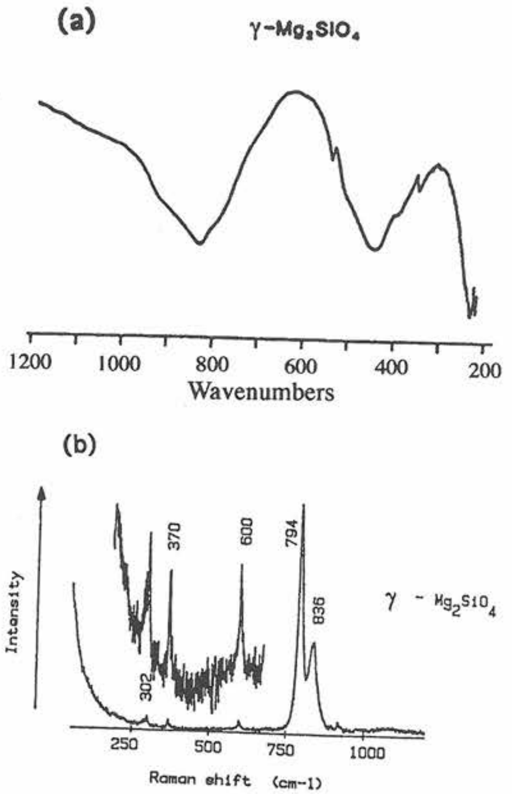


FIG. 9. (a) Infrared and (b) Raman spectra of γ-Mg_2SiO_4. The Raman spectrum shows all five peaks expected for the spinel structure. McMillan and Akaogi (1987) assigned the strong peak at 794 cm^{-1} to the A_g mode, and the 836 cm^{-1} peak to the T_{2g} mode, expected from the SiO_4 symmetric and asymmetric stretching vibrations. Based on results of a single crystal polarized study, Chopelas *et al.* (1994) have now reversed this assignment. The mid-IR transmission spectrum (a) was obtained by Akaogi *et al.* (1984). This shows only two bands, instead of the expected four. Further work is required to locate the additional resonances.

(1987). In their unpolarized powder spectrum, these authors assigned the strong peak at 794 cm^{-1} peak to the ν_1 symmetric stretching vibration of the SiO_4 groups (A_{1g} symmetry), and the 836 cm−1 band to the ν_3 asymmetric stretch with T_{2g} symmetry, based on their relative intensities (Fig. 9). Based on oriented spectra of single crystals, CHOPELAS *et al.* (1994) re-assigned these peaks, suggesting that the symmetric stretching vibration corresponded to the *higher* frequency component (Fig. 10) (this has consequences for the Si—O stretch-stretch interaction force constant of the SiO_4 tetrahedron: MCMILLAN and HESS, 1990). These authors used the Raman data to determine a model vibrational density of states for quasiharmonic calculations of heat capacity and entropy. It is interesting to note that, although the calculated entropy differs by ~10% from the earlier model of AKAOGI *et al.* (1984) for the value calculated at room temperature, the difference at 1000 K is only ~2%. This serves to illustrate the relative insensitivity of the calculated high temperature heat capacity and entropy to details of the vibrational modeling. The pressure shifts in the Raman spectrum of γ-Mg_2SiO_4 were measured in the study by CHOPELAS *et al.* (1994) to 20 GPa.

$MgSiO_3$ ilmenite

The ilmenite phase of $MgSiO_3$ would be stable in a narrow *P-T* range within cold subducted regions at approximately 600–700 km depth (ITO and YAMADA, 1982). It enters into solid solution with Al_2O_3 component (LIU, 1977). There have been several studies of this phase by Raman and infrared spectroscopy, and by computer simulation

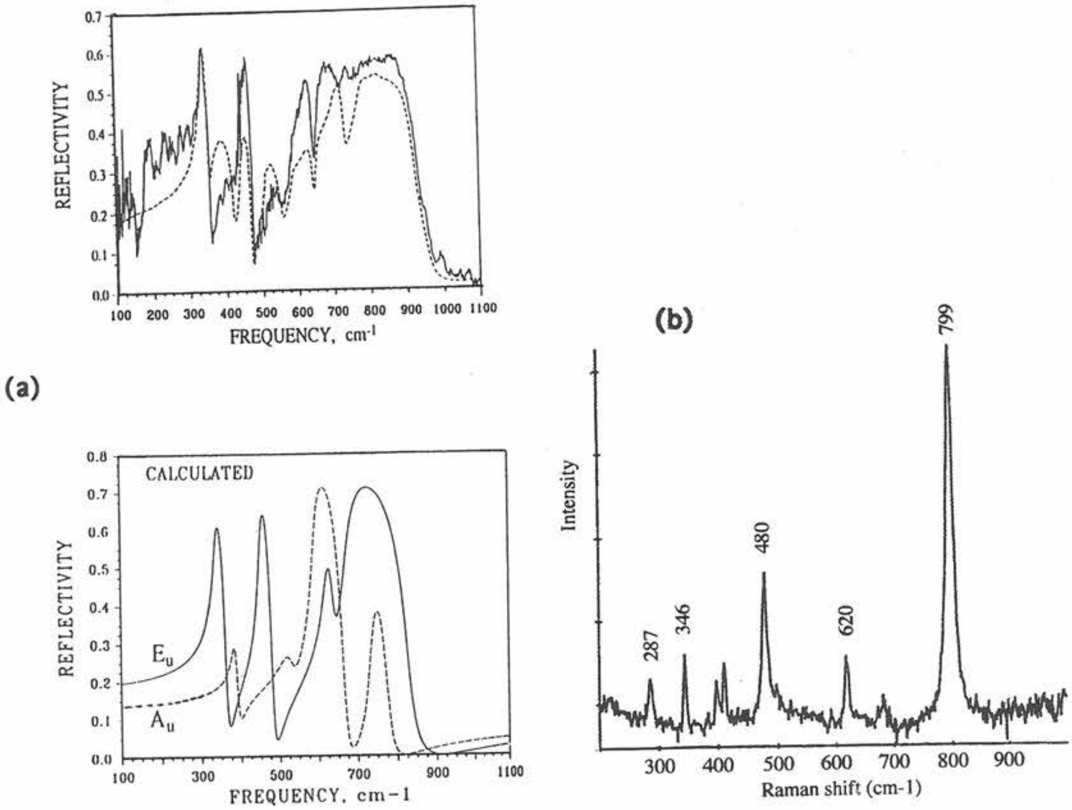


FIG. 10. (a) Infrared and (b) Raman spectra of $MgSiO_3$ ilmenite. The infrared reflectance spectrum is redrawn from HOFMEISTER and ITO (1992; Figs. 1 and 2, p. 426. Used by permission of the editors of *Physics and Chemistry of Minerals,* Springer-Verlag GmbH). The unpolarized experimental spectrum is shown at top. The synthetic spectrum at bottom was reconstructed for both mode symmetries (A_u and E_u). All expected modes are observed. The Raman spectrum at right is from MCMILLAN and ROSS (1987). Recent careful measurements (REYNARD and RUBIE, 1995) indicate that all indicated modes are real, including the weak shoulder at 499 cm^{-1}.

of its lattice dynamics. The expected vibrational mode symmetries are:

$$\Gamma_{vib} = 5A_g(R) + 5E_g(R) + 4A_u(IR) + 4E_u(IR) \quad (7)$$

The Raman spectrum of $MgSiO_3$ ilmenite was first recorded by Ross and McMillan (1984), who observed seven of the expected ten modes. A better quality spectrum was obtained by McMillan and Ross (1987), in which eight peaks were clearly resolved, and a further mode was apparent as a shoulder on the band at 480 cm^{-1} (Fig. 10). The spectrum is dominated by an intense peak at 799 cm^{-1}, assigned to an A_g mode associated with symmetric Si—O stretching of the SiO_6 groups (McMillan and Ross, 1987; Hofmeister and Ito, 1992). Wall and Price (1988) carried out a theoretical calculation of the lattice dynamics of $MgSiO_3$ ilmenite using a polarizable ion (shell) model with empirical potentials. These workers used their results to predict the positions of the missing Raman peaks not observed by McMillan and Ross (1987), and to reassign the suggested mode symmetries. However, Hofmeister and Ito (1992) noted that all of the calculated vibrational frequencies were overestimated, and they made a further re-assignment of the observed infrared and Raman active modes. They suggested that the "missing" Raman mode corresponded to an unresolved pair of peaks at 620 cm^{-1}, with A_g and E_g symmetry. However, Reynard and Rubie (1996) have recently obtained a high quality Raman spectrum for this phase, and find no evidence for splitting in the 620 cm^{-1} peak.

Madon and Price (1989) first obtained a powder IR transmission spectrum for $MgSiO_3$ ilmenite. Unfortunately, these authors observed *nine* peaks between 282 and 825 cm^{-1}, compared with the eight IR-active modes expected for the ilmenite structure. Hofmeister and Ito (1992) carried out infrared reflectance measurements for both polycrystalline and single samples of $MgSiO_3$ ilmenite, and observed all of the expected modes, although there may be some remaining uncertainty in the detailed analysis of the reflectance spectrum, because of noise in the data below 300 cm^{-1}, the occurrence of overlapping peaks, and the presence of weak additional oscillators, presumably due to combination bands (Hofmeister and Ito, 1992) (Fig. 10). There is generally good agreement between the spectra of Madon and Price (1989) and the reflectance data of Hofmeister and Ito (1992), except that the lowest frequency peak observed by Madon and Price (282 cm^{-1}) is not reproduced, and the transmission minima ("absorption" maxima) of the broad high frequency bands occur at considerably higher wavenumber than the true TO mode frequencies, as expected (McMillan and Hofmeister, 1988; Hofmeister and Ito, 1992).

Liu *et al.* (1994) recorded the principal Raman peaks of $MgSiO_3$-ilmenite to 30 GPa. A more complete study has recently been carried out by Reynard and Rubie (1996), in which accurate pressure shifts were obtained for nine Raman modes, with $(\partial\nu_i/\partial P)_T$ ranging from 1.7–3.7 cm^{-1}/GPa. These investigators also measured the temperature shifts of the Raman peaks $(\partial\nu_i/\partial T)_{P,298} = -0.0148$ to -0.0285 cm^{-1}/K), which permitted evaluation of the intrinsic mode anharmonicity parameters. These are all very small, indicating that $MgSiO_3$-ilmenite behaves nearly quasiharmonically over the temperature range studied. Because the anharmonicity parameters for garnets are much larger (Gillet *et al.*, 1992), it has been proposed that intrinsic mode anharmonicity corrections might play a role in determining the slope of garnet-ilmenite phase boundaries (Reynard and Guyot, 1994; Reynard and Rubie, 1996). From their data, Reynard and Rubie (1996) calculated an average value of the Grüneisen parameter (defined as $\langle\gamma\rangle = \Sigma C_{vi}\gamma_{iT}/\Sigma C_{\nu i}$, where $\gamma_{iT} = K_T(\partial \ln \nu_i/\partial P)_T$) of 1.38 at room temperature, and 1.24 in the high temperature limit, compared with the value of $\gamma_{th} = 1.74$ (ambient P,T) which can be estimated from the available thermodynamic parameters (Ashida *et al.*, 1988; Hofmeister and Ito, 1992).

McMillan and Ross (1987) used the structural analogy between $MgSiO_3$ ilmenite and Al_2O_3 corundum, for which the full vibrational spectrum across the Brillouin zone was known from inelastic neutron scattering measurements, to construct a model vibrational density of states $g(\omega)$ for the high pressure silicate phase, and calculated its vibrational heat capacity and entropy within the quasiharmonic approximation. The calculated entropy was combined with calorimetric data by Ashida *et al.* (1988) to obtain phase boundaries between $MgSiO_3$ ilmenite, pyroxene, β-Mg_2SiO_4 + stishovite, and γ-Mg_2SiO_4 + stishovite in a P-T range appropriate for the transition zone. Hofmeister and Ito (1992) have constructed an alternative model for $g(\omega)$ based on their infrared spectra and the Raman data of McMillan and Ross (1987), combined with the lattice dynamics calculation of Wall and Price (1988). The calculated specific heat was in better agreement with the experimental data of Ashida *et al.* (1988).

Reynard and Rubie (1996) have recently obtained the Raman spectrum for a rhombohedral phase with composition $Mg_3Al_2Si_3O_{12}$ (corresponding to pyrope). This showed eight distinct peaks which matched up well with those observed for $MgSiO_3$ ilmenite, indicating that the $3MgSiO_3$-Al_2O_3 phase has an ilmenite structure, rather than the corundum structure expected for a fully-disordered material. A disordering transition between the ilmenite and averaged corundum structures might be expected at high temperature, as discussed below for $(Mg,Fe)SiO_3$ garnet (majorite), and this could be studied most easily by vibrational spectroscopy. However, the importance of such an ordering transition on phase relations or mineral properties in the transition zone has yet to be demonstrated.

$MgSiO_3$ garnet

Garnets in the $(Ca,Fe,Mg)_3(Al,Fe)_2Si_3O_{12}$ (pyrope-grossular-almandine-spessartine) system are important phases in the lower crust and upper mantle. In addition, a majorite garnet phase, containing octahedrally coordinated silicon, with composition in the system $(Mg,Fe,Ca)_3(Si,Al,Fe)_2Si_3O_{12}$, is likely to be present within the transition zone (Akaogi and Akimoto, 1977; Kato and Kumazawa, 1985; Akaogi *et al.,* 1987; Gasparik, 1990; Yusa *et al.,* 1993). A majorite garnet with composition close to $(Mg,Fe)SiO_3$ was first identified in natural samples from the Coorara and Tenham meteorites (Smith and Mason, 1970), following a laboratory synthesis from pyroxene (Ringwood, 1967). X-ray diffraction and vibrational spectroscopic studies of pure $MgSiO_3$ garnet indicate that this phase has a slight tetragonal distortion from cubic symmetry (Kato and Kumazawa, 1985; Akaogi *et al.,* 1987; McMillan et al., 1989). At high temperatures and pressures, there is extensive solid solution in a cubic garnet phase between pyrope ($Mg_3Al_2Si_3O_{12}$) and the majorite end member, extending to approximately 80 mol% $MgSiO_3$ component at 1000°C and 16 GPa (Akaogi *et al.,* 1987; Kanzaki, 1987).

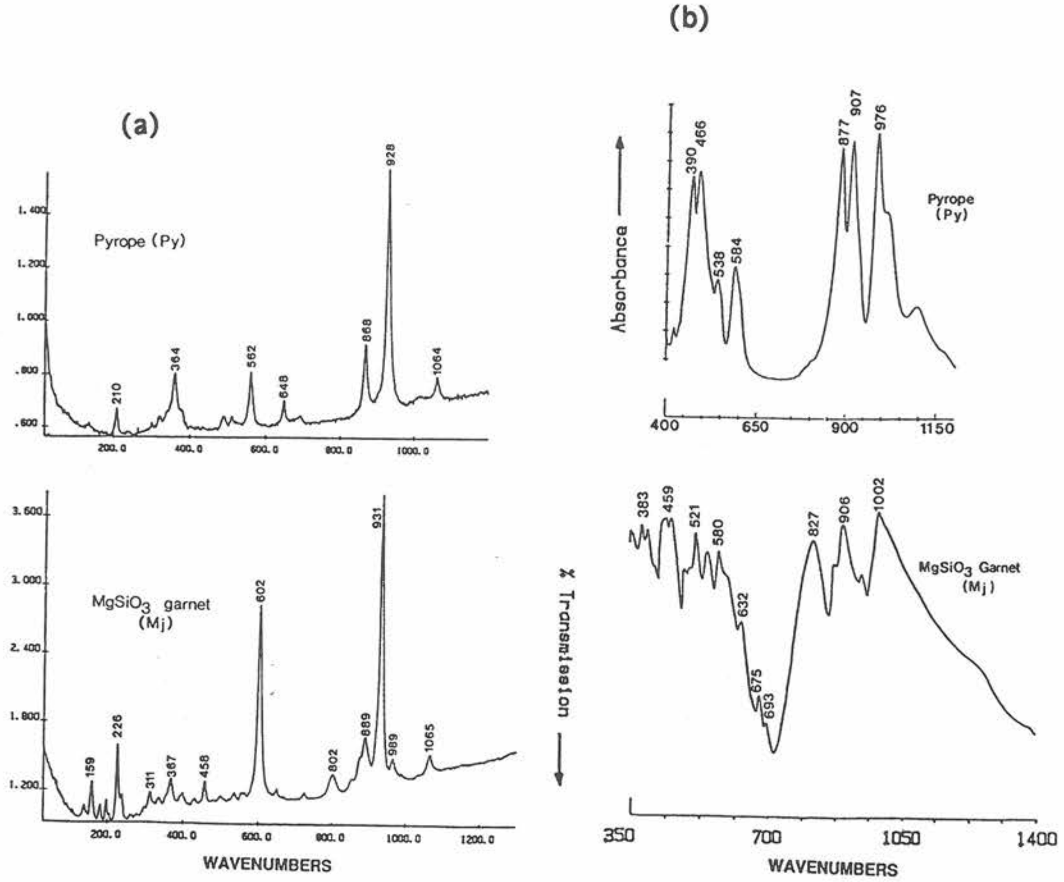
The expected vibrational spectrum for an ideal cubic garnet structure, such as pyrope, almandine, grossular and the $Mg_3Al_2Si_3O_{12}$-$Mg_4Si_4O_{12}$ solid solutions, is already quite complex due to the large number of atoms in the unit cell:

$$\begin{aligned}\Gamma_{vib} = {} & 3A_{1g}(R) + 5A_{2g}(inactive) + 8E_g(R) \\ & + 14T_{1g}(inactive) + 14T_{2g}(R) + 5A_{1u}(inactive) \\ & + 5A_{2u}(inactive) + 10E_u(inactive) + 17T_{1u}(IR) \\ & + 16T_{2u}(inactive) \qquad (8)\end{aligned}$$

There have been several systematic infrared and Raman spectra of garnet minerals (Moore *et al.,* 1971; Omori, 1971; Tarte and Deliens, 1973; Delany, 1981; Suwa and Naka, 1975; Kieffer, 1979b; Dietrich and Arndt, 1982; Geiger *et al.,* 1989; McMillan *et al.,* 1989; Hofmeister and Chopelas, 1991a; Pinet and Smith, 1993). In particular, Hofmeister and Chopelas (1991a) have assigned the symmetries for the expected Raman and infrared active modes for the principal garnet end members, through detailed polarized single crystal measurements (Fig. 11).

Hofmeister and Chopelas (1991b) used the vibrational spectra of pyrope and grossular to construct model density of states functions, $g(\omega)$, for calculation of the specific heat and entropy of these phases. The relative heat capacities of these garnets has been of some interest. From crystal chemical and mineral thermodynamics systematics, it was expected that the standard entropy for pyrope should be smaller than that for grossular, but instead, the reverse is observed (Kieffer, 1980; Hofmeister and Chopelas, 1991b). Kieffer (1979a, 1980) suggested that the "excess entropy" of pyrope could be attributed to low frequency vibrations of the small Mg^{2+} ion "rattling" in the large dodecahedral site in the garnet (Delany, 1981; Hofmeister and Chopelas, 1991a,b). Hofmeister and Chopelas (1991a) do find the lowest frequency (IR-active) vibrations of pyrope (140 cm^{-1}) to lie at lower wavenumber than the lowest frequency mode in grossular (159 cm^{-1}). However, they assign the low frequency mode of pyrope to a translation of the SiO_4 group, and that of grossular to a Ca^{2+} vibration, based on the relative cation masses. It seems that the alternative assignment proposed by Kieffer (1979a, 1980) could still hold, if the effect of the lengthened bond in pyrope on the Mg-O force constant were taken into account. This question seems to be an obvious candidate for study by $^{24}Mg/^{26}Mg$ isotopic substitution (Pâques-Ledent and Tarte, 1973), particularly since the result might have implications for the low temperature heat capacity and hence entropy of majorite ($(Mg,Fe)SiO_3$ garnet), which have not yet been determined (Yusa *et al.,* 1993).

Raman spectra for cubic garnets have been measured at high pressure and high temperature by several authors (Dietrich and Arndt, 1982; Mernagh and Liu, 1990; Gillet *et al.,* 1992; Liu *et al.,* 1995). Gillet *et al.* (1992) combined the high P and high T data for pyrope, grossular and almandine to calculate intrinsic mode anharmonicity parameters, showing that a relatively large (~3%) anharmonic correction to the heat capacity would be necessary. As already noted, this could affect the slope of the garnet-ilmenite phase boundary, in



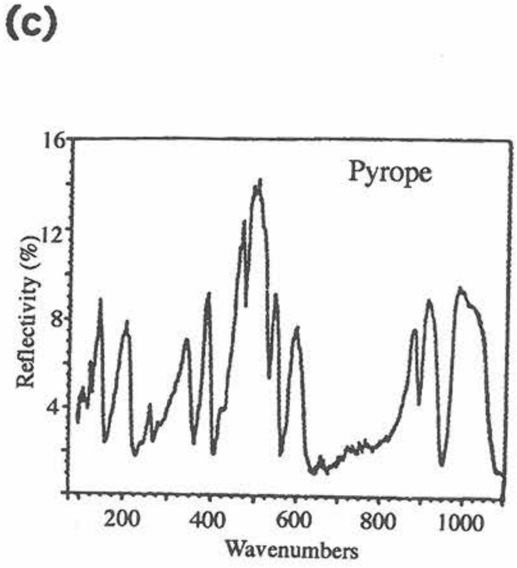


FIG. 11. Infrared and Raman spectra of pyrope and $MgSiO_3$ garnets. The Raman (a) and powder transmission IR data (b) are from MCMILLAN *et al.* (1989), and show the additional peaks which appear due to the tetragonal distortion of $MgSiO_3$ garnet compared with cubic pyrope. The single crystal IR reflectance spectrum of pyrope (c) is taken from HOFMEISTER and CHOPELAS (1991a). Peaks are assigned to internal vibrations of the SiO_4 tetrahedra (ν_3 asymmetric stretching, ν_4 and ν_2 deformation) and external modes associated with the Mg and Al sites. Spectra from HOFMEISTER and CHOPELAS (1991a; Fig. 1, p. 507) used by permission of the editors of *Physics and Chemistry of Minerals* (Springer-Verlag GmbH).

hot regions of the transition zone (REYNARD and RUBIE, 1996). LIU *et al.* (1995) have recently recorded the high frequency (>800 cm^{-1}) Raman spectrum of a garnet with composition 0.9 $MgSiO_3$:0.1 Al_2O_3, to 13.6 GPa at room temperature, and 875 K at room pressure.

The pure $MgSiO_3$ end member garnet exhibits a small tetragonal distortion from cubic symmetry (KATO and KUMAZAWA, 1985; AKAOGI *et al.*, 1987; YAGI *et al.*, 1992), probably resulting from ordering Mg and Si atoms on the [6]-coordinated sites (HATCH and GHOSE, 1989). This ordering and tetragonal distortion causes the appearance of weak additional peaks and splittings in its infrared and Raman spectra, when compared with pyrope (KATO and KUMAZAWA, 1985; MCMILLAN *et al.*, 1989) (Fig. 11). It has already been noted that $Mg_3Al_2Si_3O_{12}$-$Mg_4Si_4O_{12}$ garnet solid solutions are cubic, as are high pressure $Fe_3Al_2Si_3O_{12}$-$Fe_4Si_4O_{12}$ garnets (AKAOGI and AKIMOTO, 1977). The X-ray, IR and Raman spectra of a natural majorite garnet ($(Mg_{0.79}Fe_{0.21})_4Si_4O_{12}$) from the Catherwood meteorite indicated that it was cubic also, consistent with some samples studied by KATO (1986). However, (Mg,Fe)SiO_3 majorites with Fe/(Fe+Mg) up to $\sim$0.24 have been reported to exhibit a tetragonal distortion (KATO, 1986; MATSUBARA *et al.*, 1990; OHTANI *et al.*, 1991). It appears that the presence or absence of complete solid solution between tetragonal (Mg,Fe)SiO_3 and cubic majorite garnets may be associated with the energetics of cation ordering on the octahedral sites (AKAOGI *et al.*, 1987; MCMILLAN *et al.*, 1989; ANGEL *et al.*, 1989; HATCH and GHOSE, 1989; PHILLIPS *et al.*, 1992). On the basis of modulated microstructures observed by transmission electron microscopy, WANG *et al.* (1993) have suggested that a tetragonal-cubic transition associated with octahedral cation disordering occurs near 2400°C for pure $MgSiO_3$ garnet (HATCH and GHOSE, 1989), and that the transition temperature drops rapidly with increasing Fe content. This transition would have implications for garnet elastic properties within the transition zone (WANG *et al.*, 1993). The existence and nature of this possible phase transformation in (Mg,Fe,Al)-SiO_3 majorites merits further investigation, by *in situ* studies at combined high *P-T* conditions, and studies on phases equilibrated at high *P-T* and quenched to ambient. Although X-ray diffraction is probably a first choice for these studies, IR (or perhaps even Raman scattering, but cubic and tetragonal structures might be less easy to distinguish: see Fig. 11) spectroscopy combined with laser heating techniques in the diamond anvil cell (GILLET *et al.*, 1993b) might be useful in determining small deviations from local cubic symmetry, during development of the ordered domains (see, for example, analogous work on cordierite: MCMILLAN *et al.*, 1984).

UPPER MANTLE

(Mg,Fe)$_2$SiO$_4$ olivine

This phase, along with (Mg,Fe)SiO_3 pyroxenes and (Mg,Fe,Ca)$_3Al_2Si_3O_{12}$ garnets, dominates the mineralogy of the upper mantle (LIU and BASSETT, 1986). The garnet phases have been discussed in the previous section, and the chain silicates are described below. The lattice dynamics of synthetic and natural olivines have been thoroughly investigated, both experimentally and by theoretical calculation. The zone centre vibrational modes for the orthorhombic (*Pbnm*) structure are:

$$\Gamma_{vib} = 11A_g(R) + 11B_{1g}(R) + 7B_{2g}(R) + 7B_{3g}(R) + 10A_u(inactive) + 9B_{1u}(IR) + 13B_{2u}(IR) + 13B_{3u}(IR) \quad (9)$$

All of the infrared and Raman-active modes have been assigned via polarized measurements on single crystals (SERVOIN and PIRIOU, 1973; IISHI, 1978; PIRIOU and MCMILLAN, 1983; HOFMEISTER, 1987; CHOPELAS, 1991a; REYNARD, 1992). The lattice dynamics of forsterite have been investigated by single crystal and powder inelastic neutron scattering spectroscopy, coupled with lattice dynamical calculations within the rigid ion approximation (RAO *et al.*, 1988). The experimental data and the theoretical modeling have been used to construct vibrational density of states functions, for calculation of the specific heat, entropy, and other thermodynamic properties within the quasiharmonic approximation (AKAOGI *et al.*, 1984; CHOPELAS, 1990b; CHOUDHURY *et al.*, 1989; HOFMEISTER, 1987; HOFMEISITER *et al.*, 1989; PRICE *et al.*, 1987; RAO *et al.*, 1988). The pressure and temperature dependence of infrared and Raman modes in forsterite and fayalite has been measured in several studies (BESSON *et al.*, 1982; DIETRICH and ARNDT, 1982; XU *et al.*, 1983; GILLET *et al.*, 1988, 1991; HOFMEISTER *et al.*, 1989; CHOPELAS, 1990b; GILLET *et al.*, 1991; LIU and MERNAGH, 1992; SHARMA *et al.*, 1992; WANG *et al.*, 1993; DURBEN *et al.*, 1993). ANDERSON and SUZUKI (1983) have discussed the effects of anharmonicity on the thermodynamic properties of olivines at mantle temperatures, and GILLET *et al.* (1991) and REYNARD *et al.* (1992) have shown the importance of taking anharmonic effects into account for calculations of the vibrational heat capacity. More recently, GUYOT *et al.* (1996) have used available high-pressure and high-temperature IR and Raman data to calculate the equations of state of olivines at various *P-T* conditions. The agreement with experiment is excellent.

In a high-pressure Raman study of forsterite at room temperature, CHOPELAS (1990b) noted breaks in slope of the pressure shifts in several modes at 9.2 GPa, which was thought to be associated with a high order phase transformation occurring in olivine at high pressure and ambient temperature. WANG *et al.* (1993) noted similar breaks in slope, but concluded that no phase transition occurs, simply a change in the compression mechanism with pressure. Moreover, DOWNS *et al.* (1996) found no evidence for structural changes at these pressures in a single-crystal x-ray diffraction study to 17.2 GPa with a variety of pressure media. Such changes in the strength of pressure media used cause apparent changes in the slope of such frequency shifts with pressures. Compression of forsterite to higher pressure (50 GPa) at room temperature results in the appearance of new bands near 750 cm^{-1} and 960 cm^{-1} (DURBEN *et al.*, 1993). These are likely related to formation of SiOSi (dimer) linkages within the structure (perhaps related to the formation of spinelloid structures) or to the formation of high coordinate Si species (perhaps as a precursor to amorphization) (WILLIAMS *et al.*, 1990; GUYOT and REYNARD, 1992). In their infrared study of pressure-induced amorphization in fayalite, WILLIAMS *et al.* (1990) noted an increase in intensity of a band in the 600–800 cm^{-1} region above 35 GPa, which they attributed to the formation of six-coordinated silicon species. As already noted above, Raman and IR measurements *in situ* at high pressures and temperatures may be useful in phase identification and possibly for characterizing local and intermediate-range structures in kinetic studies of high-pressure transformations of olivine and other $(Mg,Fe)_2SiO_4$ polymorphs; such experiments are needed to further understand seismicity and rheology within the upper mantle and transition zone.

An area that deserves further attention is the exploration of pre-melting behavior of mantle minerals, through *in situ* high temperature vibrational spectroscopy, combined with diffraction and calorimetric experiments (RICHET *et al.*, 1994). The pre-melting regime is characterized by an anomalous rapid increase in heat capacity and entropy, below the thermodynamic melting point (RICHET and FIQUET, 1991). The origin of the phenomenon has been studied in detail using *in situ* Raman spectroscopy for $(Ca,Mg)GeO_4$ olivines, and has been related to M_1-M_2 disordering at high temperature, as well as to extreme anharmonicity (FIQUET *et al.*, 1992; RICHET *et al.*, 1994). This behavior has been observed to occur for silicate olivine, pyroxene and garnet, and has obvious implications for rheology of high temperature mineral assemblages in the mantle, as well as the kinetics of phase transformations. This phenomenon can now be studied with existing techniques by *in situ* high P-T IR and Raman spectroscopy to evaluate its importance in the mantle *P-T* regime.

Pyroxene

In comparison with the olivine group of minerals, there has been much less work done on the vibrational spectroscopy of pyroxenes, either at ambient or under mantle conditions (WHITE, 1975). The $(Mg,Fe)SiO_3$ rich enstatite phase shows complex polymorphism as a function of pressure and temperature (ANGEL *et al.*, 1992; LEE and HEUER, 1987; PREWITT, 1980; SCHRADER *et al.*, 1990; ANGEL and HUGH-JONES, 1994a,b). The orthorhombic phase (*Pbca*) is stable to approximately 8 GPa and 1300 K. Above this temperature, there is a displacive transformation to protoenstatite (*Pbcm*) at ambient pressure for pure $MgSiO_3$, but Fe-containing phases transform to *C2/c* structures (YANG and GHOSE, 1995). At pressures above 8 GPa, orthopyroxene transforms into a high density clinoenstatite structure (PACALO and GASPARIK, 1990; ANGEL *et al.*, 1992). CHOPELAS and BOEHLER (1992) prepared a sample of this phase by CO_2 laser heating single crystalline $MgSiO_3$ orthoenstatite in a diamond anvil cell, and investigated its Raman spectrum during decompression. The spectrum of the clinonenstatite polymorph is similar to that of diopside at the same pressure, consistent with the *C2/c* symmetry assigned by ANGEL *et al.* (1992), and it reverts to the orthorhombic polymorph on decompression below 5 GPa (CHOPELAS and BOEHLER, 1992). The pressure shifts of the Raman peaks in both phases are given by CHOPELAS and BOEHLER (1992). DIETRICH and ARNDT (1982) have investigated the infrared spectrum of natural orthopyroxene at lower pressures, to 5 GPa, at up to 250°C. SHARMA *et al.* (1987), SHARMA (1989, 1990) and GHOSE *et al.* (1994) have investigated the effect of temperature on the Raman spectra of $MgSiO_3$ pyroxene phases. In particular, GHOSE *et al.* (1994) have reported polarized single crystal Raman spectra of protoenstatite. The transitions between the ortho-, proto- and clino-enstatite phases are clearly observed by the appearance or disappearance of peaks in the spectra.

At lower pressures, a (Ca,Al)-rich pyroxene phase is found, forming a monoclinic (*C2/c*) solid solution in the system $CaMgSi_2O_6$ (diopside)-$NaAlSi_2O_6$ (jadeite) (GASPARIK, 1992). The Raman and infrared spectra of diopside have been characterized at ambient conditions via polarized single crystal measurements (ETCHEPARE, 1970, 1972; ZULUMYAN *et al.,* 1976), and an empirical lattice dynamics calculation has been carried out (TOMISAKA and IISHI, 1980). A Raman spectrum at 16 GPa is presented by CHOPELAS and BOEHLER (1992). SEKITA *et al.* (1988) have used Raman spectroscopy to study bands in the 600–700 cm^{-1} region of clinopyroxenes, and assigned peaks to SiOSi, SiOAl and AlOAl linkages. This type of calibration could prove useful in future high *P-T* studies of Ca-rich pyroxene phases. Raman and infrared studies of pyroxene phases, both at ambient conditions and *in situ* at high pressure and temperature, will be useful to complement diffraction studies in unraveling the detailed nature of the complex transformation mechanisms between the different polymorphs of $(Mg,Fe)SiO_3$ (YANG and GHOSE, 1994a,b; 1995; GHOSE *et al.,* 1994), as well as the onset of pre-melting behaviour as described above for olivine (RICHET *et al.,* 1994).

WATER AND CARBON IN THE MANTLE

Water in the mantle

The questions associated with "water" or the hydrogen content in the mantle (how much? where? in what form?) have been and still are a matter of intense interest and considerable debate. These are critical questions for mantle petrology, both to understand the volatile budget and recycling processes, and because of the large effects of even trace hydrous species on mineralogical phase relations, including melting, and rheology of mantle minerals and mineral assemblages (MACKWELL *et al.,* 1985; LIU, 1987; WYLLIE, 1988; MACKWELL and KOHLSTEDT, 1990; BELL and ROSSMAN, 1992a; THOMPSON, 1992; DUFFY and AHRENS, 1992; GASPARIK, 1993; GILLET, 1993a). Vibrational spectroscopy, particularly infrared absorbance measurements of natural mantle minerals and laboratory-synthesized samples, has played a role in helping establish our current estimates of the hydration state of the mantle.

It is well known that hydrous minerals such as phlogopitic mica and kaersutitic amphibole can be stable under the *P-T* conditions of the upper mantle. However, IR absorption studies of nominally anhydrous mineral phases have demonstrated that these can contain substantial amounts of OH in structural sites (BERAN and PUTNIS, 1983; AINES and ROSSMAN, 1984a; ROSSMAN, 1988; BELL and ROSSMAN, 1992a; BELL *et al.,* 1995). Measured OH contents for natural olivines, pyroxenes and garnets, which constitute >90% of peridotites sampled at the surface, range from 100–1500 $H/10^6$ Si (BERAN and PUTNIS, 1983; AINES and ROSSMAN, 1984b,c; MILLER *et al.,* 1987; BELL and ROSSMAN, 1992a,b, 1995; KUROSAWA *et al.,* 1992, 1993; BAI and KOHLSTEDT, 1993). Experiments are under way to determine the maximum OH concentration which can be incorporated in these phases (KOHLSTEDT *et al.,* 1996).

The case of garnet is particularly interesting, because grossular $(Ca_3Al_2Si_3O_{12})$ forms a solid solution with the hydrogarnet $(Ca_3Al_2(O_4H_4)_3)$, in which each Si^{4+} site is occupied by a distorted tetrahedron of OH groups (COHEN-ADDAD *et al.,* 1967; KOBAYASHI and SHOJI, 1983; LAGER *et al.,* 1987, 1989). This substitution permits the OH concentration of Ca-rich garnets to become very high. From vibrational spectroscopy, the structural arrangement of OH groups is determined by bifurcated hydrogen bonds to adjacent oxygens forming the tetrahedral site (HARMON *et al.,* 1982). In a high pressure study of hibschite $(Ca_3Al_2(SiO_4)_{1.5}(O_4H_4)_{1.5})$, KNITTLE *et al.* (1992) found both Raman-active O—H stretching vibrations and the higher frequency IR mode to decrease in frequency with increasing pressure, as expected for increased hydrogen bonding, but the lower frequency IR band increased in frequency. It was suggested that this could result from H...H or H...Ca^{2+} repulsive interactions (SHEU and MCMILLAN, 1988; WILLIAMS, 1992).

The *P-T* stability and breakdown behaviour of hydrous minerals such as amphibole or mica play a critical role in volatile recycling. A few studies of the vibrational properties of these minerals at ambient conditions have been reported (see MCMILLAN and HOFMEISTER, 1988), and some high pressure work is now beginning to appear (HOLTZ *et al.,* 1993). Raman and IR studies under high *P-T* conditions will be extremely important in helping determine the thermodynamic properties of these phases (GILLET *et al.,* 1989b; ROBIE *et al.,* 1991), and will shed light on their formation or dehydration mechanisms within the upper mantle. A related field which is only beginning to receive attention is the study of hydrous silicate melt phases, under mantle *P-T* conditions (WILLIAMS, 1990; FARBER and WILLIAMS, 1992; WILLIAMS, 1992; CLOSMANN and WILLIAMS, 1995). Vibrational spectroscopy is expected to play a critical role in these studies, which can not be easily addressed by diffraction methods.

Considerable interest has been stimulated by the possibility that large amounts of water could be stored in the transition zone, contained in structural sites in β-$(Mg,Fe)_2SiO_4$, as discussed above (Smyth, 1987; Downs, 1989; McMillan *et al.,* 1991; Young *et al.,* 1993; Kohlstedt *et al.,* 1996), or within high pressure hydrous minerals in the system $MgO—SiO_2—H_2O$ (Liu, 1987; Kanzaki, 1991; Prewitt and Finger, 1992). These phases (chondrodite, clinohumite, phases A, B, C, D, E, etc.) have been partly characterized by infrared and Raman spectroscopy (Akaogi and Akimoto, 1986; Finger *et al.* 1989; McMillan *et al.,* 1991), but much work remains to be done. This is an essential complement to X-ray diffraction, because it is much easier to study the H atom environment via vibrational spectroscopy. Williams (1992) has studied a natural chondrodite to ~9 GPa, showing the importance of H-bonding in one of the O—H stretching vibrations, and used IR spectroscopy to investigate phase changes following laser heating at pressures between 22 and 44 GPa.

Two other interesting cases of trace OH in nominally anhydrous mantle minerals have also recently been demonstrated by IR absorption spectroscopy. Pawley *et al.* (1993) have shown that stishovite, the high pressure phase of SiO_2, can accept hydrogen in defect sites within its structure, and the H content was shown to scale with Al substitution into the SiO_2 phase (Pawley *et al.,* 1993; Smyth *et al.,* 1995). This is consistent with the observed dissolution of H into TiO_2 rutile (Vlassopoulos *et al.,* 1993; Swope *et al.,* 1995). Lu *et al.* (1994) and Meade *et al.* (1994) have also shown by IR spectroscopy that $(Mg,Fe)SiO_3$ perovskite, the dominant phase in the lower mantle, can accept trace OH within its structures, with considerable potential implications for the water content of the deep Earth. The study of Meade *et al.* (1994) was carried out with the synchrotron infrared technique, a promising new method for micro-spectroscopy of materials at ambient and high-pressure conditions (Reffner *et al.,* 1994).

Carbonates

A second problem of intense interest is the carbon budget and oxidation state of the deep Earth (Kushiro *et al.,* 1975; Irving and Wyllie, 1975; Katsura and Ito, 1990; Blundy *et al.,* 1991; Gillet, 1993b; Gillet *et al.,* 1996a). Carbonate minerals are fundamental actors in the global carbon cycle because, on the one hand, they may store carbon, and on the other, they provide carriers for carbon when sediments are recycled in subduction zones. Experimental studies as well as observations of natural samples have shown that carbonates could provide major hosts for carbon in the Earth's upper and lower mantle. High-pressure experiments have shown that in the presence of pyroxene and olivine, or their high-pressure equivalents (β-$Mg,Fe)_2SiO_4$ and the assemblage $(Mg,Fe)SiO_3$ perovskite + (Mg,Fe)O magnesiowüstite), $MgCO_3$ is the stable carbonate phase (Brey *et al.,* 1983; Canil and Scarfe, 1990; Katsura and Ito, 1990; Biellmann *et al.,* 1993b). Vibrational spectroscopy has been used to demonstrate the stability of carbonates under pressure and temperature conditions relevant to the mantle (Gillet, 1993b; Gillet *et al.,* 1996b) (Fig. 12).

The expected vibrational modes of calcite and magnesite with space group $R\bar{3}c$ are:

$$\Gamma_{vib} = A_{1g}(R) + 3A_{2g}(inactive) + 4E_g(R) + 2A_{1u}(inactive) + 4A_{2u}(IR) + 5E_u(IR) \quad (10)$$

The vibrational modes of dolomite $(CaMg(CO_3)_2)$ are related by the disappearance of the c-glide (space group $R\bar{3}$).

$$\Gamma_{vib} = 4A_g(R) + 4E_g(R) + 5A_u(IR) + 5E_u(IR) \quad (11)$$

The infrared and Raman spectra of these phases are well known, through extensive single crystal spectroscopy (White, 1974; Gillet *et al.,* 1993a).

Several recent infrared and Raman studies of carbonate minerals have been carried out at ambient temperature, to pressures in excess of 30 GPa (Gillet *et al.,* 1988; 1993a; Liu and Mernagh, 1990; Kraft *et al.,* 1991; Biellmann and Gillet, 1992). Calcium carbonate has two stable polymorphs, calcite and aragonite, the high pressure form. Calcite also shows transitions to metastable forms of $CaCO_3$ (calcite-II and calcite-III) in the 1.4–2.0 GPa range (Fong and Nicol, 1971; Hess and Ghose, 1988; Gillet *et al.,* 1988; Liu and Mernagh, 1990; Collerson *et al.,* 1992; Biellmann and Gillet, 1992). Biellmann *et al.* (1993a) have shown that, after heating of calcite to 2000 K at 40 GPa, calcite II can be quenched to ambient conditions. In contrast to this behaviour, dolomite and magnesite show no evidence for any phase transitions to the highest pressures studied (34 GPa) (Fig. 12), nor does the stable high pressure aragonite phase of $CaCO_3$ (Kraft *et al.,* 1991; Collerson *et al.,* 1992; Biellmann and Gillet, 1992; Gillet, 1993b; Gillet *et al.,* 1993a; Gillet *et al.,* 1996a).

The effect of temperature on the room pressure

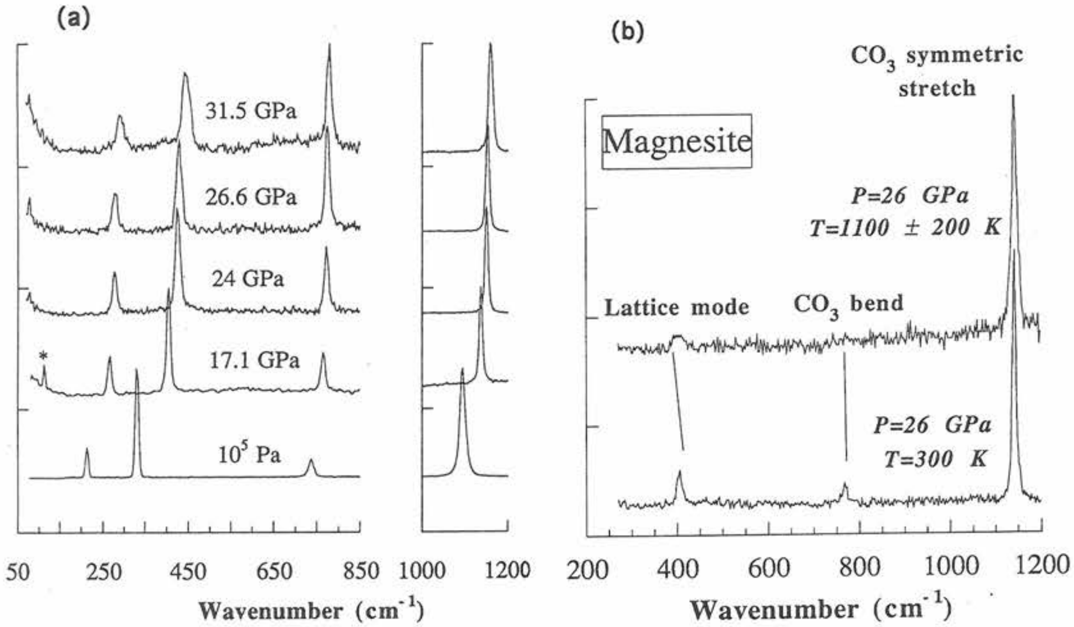


FIG. 12. (a) Effect of pressure on the Raman spectrum of magnesite, $MgCO_3$, to mantle pressures. (b) *In situ* high *P-T* spectrum of magnesite, at 26 GPa and 1100 K, showing the stability of this phase under mantle conditions (GILLET, 1993b).

infrared spectrum of calcite (SAKURAI and SATO, 1971), and the Raman spectra of calcite, dolomite and magnesite (GILLET *et al.,* 1993a), has been investigated up to 800–1200 K. The measured frequency shifts with temperature have been combined with the observed pressure-induced shifts to calculate mode anharmonic parameters (GILLET *et al.,* 1993a). These must be taken into account for a realistic calculation of $^{16}O/^{18}O$ isotopic fractionation factors at high pressure and temperature (GILLET *et al.,* 1996b). It is found that these anharmonic parameters are larger for the lattice modes than for the CO_3 internal modes. Moreover, they are larger in calcite than in dolomite and magnesite, consistent with increasing relaxational component to the libration of the CO_3 groups, premonitory to a rotational order-disorder phase transition in calcite at high temperatures (GILLET *et al.,* 1993a).

KRAFT *et al.* (1991) have investigated the vibrational spectrum of dolomite *in-situ* under high *P-T* conditions, at pressures up to 11.5 GPa and 550 K. The stability of magnesite ($MgCO_3$) has been studied by Raman spectroscopy at high pressure and high temperature, using a CO_2-laser-heated diamond anvil cell (GILLET, 1993b). Raman spectra recorded at simultaneous high pressure (26 GPa) and high-temperature (1200 K ± 200 K) show that under these conditions magnesite retains its ambient $R\bar{3}c$ structure (Fig. 12). Optical observations during heating as well as Raman spectra recorded at 30 GPa after laser heating up to 2000–2500 K showed that no decarbonation had occurred and that magnesite was stable. These results are in agreement with other experimental data that show that magnesite can act as a host for carbon storage down to at least 1000 km, and that this phase can also be the carrier for carbon in subducting plates (GILLET, 1993b; GILLET *et al.,* 1995).

The Raman data for magnesite, combined with compressibility measurements at high pressures and room temperature, have been used to compute the specific heat and vibrational entropy, and calculate the equation of state of magnesite up to 135 GPa and 3500 K (GILLET *et al.,* 1995), in good agreement with existing experimental data. The model was then used to calculate the decarbonation curve $MgCO_3 \Leftrightarrow MgO + CO_2$, under mantle conditions, which provides an upper limit for the stability of magnesite in the Earth's mantle.

Diamond

This high pressure form of carbon also provides an important source or sink for carbon in the mantle. Diamond is the window material of choice for *in situ* diffraction and spectroscopic experiments under high *P-T* conditions, in the diamond anvil cell, for mineral physics studies of the deep Earth. As discussed above, this same material also provides a "window" of a different type, acting as a host for mineral and fluid inclusions brought to the surface from great depths within the Earth (KESSON and FITZGERALD, 1992; HARTE and HARRIS, 1993; SAUTTER and GILLET, 1994). BELL (unpublished) has carried out measurements of the OH content in a suite of silicate inclusions in diamond with new synchrotron micro-IR techniques (REFFNER *et al.*, 1994). In contrast to studies on typical mantle minerals, OH was not detected in either olivines or orthopyroxene inclusions in diamonds, while its presence was clearly demonstrated in kyanite inclusions, with IR spectra similar to kyanites from mantle eclogite xenoliths. These results have important implications for the hydration history of the mantle and place constraints on processes of diamond formation. Notably, the measurements were not possible with conventional IR methods.

Vibrational studies of this phase have been carried out to help demonstrate the stability of diamond to high pressures and temperatures, and as a testing ground for first-principles theory. The vibrational spectrum of cubic diamond itself is very simple: the expected vibrational modes are

$$\Gamma_{vib} = T_{2g}(R) \tag{12}$$

which gives rise to a single first order peak in the Raman spectrum at 1332 cm^{-1}. Weak features due to second order Raman scattering are observed in the 2200–2600 cm^{-1} range. The Raman spectrum of diamond has been studied to ~40 GPa (BOPPART *et al.*, 1985; HANFLAND *et al.*, 1985; HANFLAND and SYASSEN, 1985; SHARMA *et al.*, 1985; ALEKSANDROV *et al.*, 1986). These studies confirm both the high-pressure stability and the singular high strength of this mineral over a pressure range extending well into the lower mantle. MAO and HEMLEY (1991) have carried out micro-Raman measurements on diamond anvils at sample pressures up to 300 GPa, and found some evidence for structural transformations driven by the large non-hydrostatic stresses of the anvils under these conditions. VOHRA (1992) has found evidence for a transition in highly stressed diamond anvils in studies to 420 GPa. ZOUBOULIS and GRIMSDITCH (1991) have investigated the Raman scattering in diamond at high temperatures, to 1900 K. Recently, FRANTZ and MYSEN (1996) have exploited the frequency shift of the T_{2g} mode in ^{13}C relative to ^{12}C and its weak temperature shift for pressure calibration in a diamond-anvil cell at high temperature. An exciting possibility for future work is the use of micro-IR and Raman spectroscopy of mineral and fluid inclusions in deep mantle diamonds, as well as defect species in the diamond matrix itself (NAVON *et al.*, 1988; FIELD, 1992), to better understand the volatile budget of the deep Earth.

CONCLUSIONS

Vibrational studies via infrared and Raman spectroscopy provide a set of powerful techniques for the characterization and structural study of mantle minerals. The vibrational spectra can reveal subtle structural distortions which are not immediately obvious in diffraction experiments, and are sensitive to the presence of hydrogen within the mineral, even as a defect species. It is usually quite simple to obtain spectra *in situ* at high pressure or at high temperature, and combined *in situ* high *P-T* studies are beginning to appear, allowing minerals to be examined directly under mantle conditions. The spectra can be used to obtain important thermodynamic information on the high-pressure phases, including heat capacity, vibrational entropy, and Grüneisen parameters, and detailed information on phase transformation mechanisms. These Raman and infrared studies are particularly fruitful when they are combined with theoretical calculations of the lattice dynamics, which give information on all vibrational modes throughout the Brillouin zone, and permit a structural interpretation of the observed spectra. Because the vibrational spectrum provides a fingerprint for a mineral, micro-Raman and IR measurements are proving very useful for phase identification of natural and experimental polyphase aggregates with spatial resolution close to the diffraction limit of the radiation used (*e.g.*, ~1 μm for visible-light Raman; ~10 μm at 1000 cm^{-1} for IR methods).

Most of the principal mantle mineral phases have been identified, and their infrared and Raman spectra assigned, but data on relevant solid solution series are often lacking. There are obvious gaps in the data base: for example, the far infrared spectra of γ-Mg_2SiO_4, and infrared and Raman data on the polymorphs of $(Mg,Fe)SiO_3$. In addition, further experimental and theoretical work on $MgSiO_3$ perovskite is required to fully characterize the low-frequency vibrational spectrum, and determine the presence or absence of soft modes at simultaneous high *P-T* conditions. In general, *in situ* studies under combined high *P-T* conditions will be useful to gain a better understanding of anharmonic behaviour, and to investigate phenomena such as pre-melting, which may play an important role in determining transport properties at high temperature. Vibrational spectroscopy has played a central role in the characterization of OH-containing phases likely to be stable within the mantle, and thus helping to constrain the sources and sinks for a hydrous component at depth. But more work is required under high pressure conditions, to help determine the role that hydrogen bonding may play in stabilizing these mineral phases, and also to investigate the dehydration mechanisms of hydrous phases during processes such as subduction.

This review has focused on vibrational spectroscopic studies of crystalline minerals within the mantle. Much is now known about the structure and properties of aluminosilicate melts which yield magmas observed at or near the surface, generated by partial melting events at relatively shallow depths within the lower crust and upper mantle (STEBBINS *et al.*, 1995). However, melting may also occur deeper in the mantle. Of paramount interest is the role of structural changes (*e.g.*, changes in coordination) in determining the density contrast between melt and crystalline phases, and also in determining the rates of chemical diffusion and viscous flow in the high pressure melt phase (MCMILLAN and WOLF, 1995). *In situ* vibrational spectroscopy has been instrumental in demonstrating that large structural changes take place in silicate glasses at high pressures [*e.g.*, HEMLEY *et al.*, 1986b; WILLIAMS and JEANLOZ, 1988]. More recently, IR and Raman studies have begun to shed light on the structural nature of ultrabasic melts likely to present in the deep mantle (MCMILLAN and WOLF, 1995). Vibrational spectroscopy will play a key part in investigating the structural behaviour and relaxation dynamics of melts under deep mantle conditions, through *in situ* experiments at combined high pressure and temperature (FARBER and WILLIAMS, 1992; GILLET *et al.*, 1993b).

Finally, future progress is likely to come from continued development of experimental techniques. Synchrotron IR techniques now permit vibrational spectra to be easily measured in both absorption and reflectivity on 10 μm samples to 200 GPa (HEMLEY *et al.*, 1996). The development of such synchrotron as well as IR laser techniques is expected to continue. An exciting prospect is the adaptation of micro-Raman and IR techniques to three-dimensional sample imaging. Such methods have been developed for Raman scattering and are being extended to IR absorption (LEWIS *et al.*, 1995). Another prospect is the continued development of IR lasers and detectors for Raman scattering in the IR, which can alleviate problems associated with laser-induced sample fluorescence and degradation at visible wavelengths (CHASE *et al.*, 1986). Also, there may be important applications of time-resolved and non-linear optical techniques (stimulated Raman scattering) (*e.g.*, SHARMA, 1989). Notably, although the *P-T* regime of the entire mantle of the Earth can now be created in the laboratory (MAO and HEMLEY, 1996), there have been few measurements of material properties under simultaneous high *P-T* conditions. It should be possible to combine each of these new spectroscopic methods with high *P-T* techniques for the next generation of *in situ* measurements on mantle minerals.

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