1. INTRODUCTION

There are a number of ways in which light interacts with condensed matter. In most cases, these are associated with the electric field of an incident photon interacting with the vibrational or electronic states of materials. The presence and strength of these interactions are principally dependent on bonding properties, the configurations of electronic states, and local symmetry of ions, molecules or crystals. Here, three separate types of light-mediated spectroscopies of interest to geophysics and mineral sciences are examined: 1) infrared spectroscopy; 2) Raman spectroscopy; and 3) optical absorption spectroscopy.

Each of these techniques provides complementary information on the vibrational and electronic properties of Earth materials. The bonding properties which produce infrared and Raman-active vibrational bands provide not only a useful fingerprinting technique for determining the presence or abundance of different functional groups, such as hydroxyl or carbonate units, but also (in a bulk sense) fundamentally control a variety of thermochemical properties of materials, including their heat capacity. Moreover, the vibrational spectrum provides basic information on the bond strengths present within a material. Electronic transitions may occur in the infrared, visible or ultraviolet region of the spectrum, and commonly produce the colors of many minerals: these are dictated by the local bonding environments and electronic configurations of different elements in crystals or molecules. The role of electronic transitions in controlling the electrical conductivity and in reducing the radiative thermal conductivity of minerals at high temperatures is briefly reviewed, and their relation to spectroscopic observations summarized. Additionally, observations of optical transitions may be used to constrain the energetic effects of different electronic configurations on element partitioning between sites of different symmetries and distortions.

2. VIBRATIONAL SPECTROSCOPY: INFRARED AND RAMAN TECHNIQUES

The primary feature of importance in vibrational spectroscopy is the interaction between the electric field associated with a photon and changes induced by vibrational motions in the electronic charge distribution within a material. The most common unit utilized to describe the frequency of these vibrational motions (as well as, in many cases, electronic transitions) is inverse centimeters, or wavenumbers (cm⁻¹); these may be readily converted to Hertz by multiplying by the speed of light, c (2.998 x 10¹⁰ cm/sec), to the wavelength of light (in cm) by taking its inverse, and to energy by multiplying by c and Planck’s constant, h (6.626 x 10⁻³⁴ J·sec).

Here, we focus on infrared and Raman spectroscopic characterization of vibrational states: in this discussion, we explicitly treat only normal Raman scattering and disregard non-vibrational effects such as Raman electronic and magnon scattering and non-linear effects such as the hyper-Raman and resonance Raman effects, none of which have had significant impact to date in the Earth sciences.
(see [10] for discussion of these effects).

In the case of infrared spectroscopy, a photon of energy below ~14000 cm\(^{-1}\) (and most often below 5000 cm\(^{-1}\)) is either absorbed or reflected from a material through interaction with interatomic vibrations. The primary measurement is thus of the intensity of transmitted or reflected infrared light as a function of frequency. With Raman spectroscopy, a photon of light interacts inelastically with an optic vibrational mode and is either red-shifted towards lower frequency (Stokes lines) or blue-shifted to higher frequency (anti-Stokes lines) by an amount corresponding to the energy of the vibrational mode. When such an interaction occurs with an acoustic mode (or sound wave), the effect is called Brillouin spectroscopy (see the section on elastic constants in this volume). Notably, Raman measurements rely on monochromatic light sources (which, since the 1960's, have almost always been lasers) to provide a discrete frequency from which the offset vibrational modes may be measured. Furthermore, the Raman effect is rather weak: only about 1 in \(10^5\) to \(10^6\) incident photons are Raman scattered, necessitating relatively high powered monochromatic sources, sensitive detection techniques, or both.

The vibrational modes measured in infrared and Raman spectroscopy may be described as a function of the force constant of the vibration or deformation and the mass of the participating atoms. For the simplest case of a vibrating diatomic species, this relation may be described using Hooke's Law, in which

\[
v_{\text{vib}} = (1/2\pi)\sqrt{(K/\mu)},
\]

(1)

where \(K\) is the force constant associated with stretching of the diatomic bond, and \(\mu\) is the reduced mass of the vibrating atoms. Clearly, a range of different force constants are required to treat more complex molecules, which have more possible vibrational modes beyond simple stretching motions (see Figure 1): because of the more complex interatomic interactions, different stretching and bending force constants are necessitated. Approximate equations relating these force constants to the frequencies of vibration for different polyatomic molecules have been reviewed and developed by Herzberg [12], while a detailed review of the frequencies of vibrations of different molecules is given by Nakamoto [18]. Figure 1 shows the vibrational modes expected for an isolated silicate tetrahedra, which comprise symmetric and antisymmetric stretching and bending vibrations. That different force constants are required to describe these vibrations is apparent from the atomic displacements illustrated: for example, the symmetric stretch of the tetrahedron depends predominately on the strength of the Si-O bond. For comparison, the symmetric bending vibration is controlled principally by the O-Si-O angle bending force constant, the magnitude of which is dictated in turn largely by repulsive interactions between the oxygen anions.

Considerable insight in distinguishing vibrations such as those shown in Figure 1 from one another has been derived from isotopic substitution experiments, which effectively alter the masses involved in the vibration without significantly affecting the force constants.

Within crystalline solids, the number of vibrations potentially accessible through either infrared or Raman spectroscopy in \(3n-3\), where \(n\) is the number of atoms in the unit cell of the material. This simply results from the \(n\) atoms in the unit cell having 3 dimensional degrees of freedom during displacements, with three degrees of translational freedom of the entire unit cell being associated with acoustic (Brillouin) vibrations. These \(3n-3\) vibrations represent the maximum number of observable vibrational modes of a crystal, as some vibrations may be symmetrically equivalent (or energetically degenerate) with one another, and others may not be active in either the infrared or Raman spectra. Because the wavelength of even visible light is long relative to the size of crystallographic unit cells, both infrared and Raman spectroscopy primarily sample vibrations which are in-phase between different unit cells (at the center of the Brillouin zone). Characterizing vibrational modes that are out-of-phase to different degrees between neighboring unit cells requires shorter wavelength probes, such as neutron scattering techniques. These shorter wavelength probes are used to characterize the dispersion (or change in energy) of vibrations as the periodicity of vibrations becomes longer than the unit cell length-scale (that is, vibrations occurring away from the center of the Brillouin zone). Such dispersion is characterized by vibrations of adjacent unit cells being out-of-phase with one another [6].

For crystals, a range of bonding interactions (and thus force constants), the crystal symmetry (or atomic locations), and the masses of atoms within the unit cell are generally required to solve for the different vibrational frequencies occurring in the unit cell. Broadly, the calculation of the vibrational frequencies of a lattice entails examining the interchange between the kinetic energies of the atomic displacements and the potential energy induced by the bonding interactions present in the crystal. The primary difficulties with such calculations lie in determining adequate potential interactions, and in the number of different interatomic interactions included in these calculations. Such computations of lattice dynamics
Fig. 1. The normal modes of vibration of an SiO₄-tetrahedron. Within isolated tetrahedra, all vibrations are Raman-active, while only the v₃ and v₄ vibrations are active in the infrared. However, environments with non-tetrahedral symmetries frequently produce infrared activity of the v₁ and v₂ vibrations in silicate minerals [modified from [12] and [18]].

The physical origin of Raman scattering may be viewed from a simple classical perspective in which the electric field associated with the incident light interacts with the vibrating crystal. In particular, this interaction occurs through the polarizability of the material: that is, its ability to produce an induced dipole in an electric field. It is the oscillations in the polarizability produced by vibrations which cause Raman scattering: if a vibrational motion produces a change in the polarizability of a material, then the vibration is Raman active. Notably, while the induced dipole is a vector, the polarizability is a second rank tensor, and it is the symmetric properties of this tensor which allow the prediction of which families of modes will be active when observed along different crystallographic directions. Thus, both Raman and infrared activities are governed by interactions of the electric field of the incoming light with vibrationally produced changes in the charge distribution of the molecule or unit cell. Yet, despite Raman active vibrations depending on changes in the polarizability tensor and infrared active vibrations being generated by changes in the dipole moment, the two sets of vibrations are not always mutually exclusive: for non-centrosymmetric molecules (or unit cells), some vibrations can be both Raman and infrared active. Finally, the intensities of different vibrations in the two different types of spectroscopy may be related to the magnitude of the changes produced in the dipole moment or polarizability tensor in a given vibration.

It is the relation of the change in the polarizability tensor and shifts in the dipole moment to the symmetry of the lattice which enables different vibrations to be associated with different symmetry species, as well as with possible crystallographic directionality for the infrared and Raman modes. The way in which this characterization of vibrational mode symmetries is conducted is through an application of group theory called
factor group analysis. This is a means of utilizing the site symmetries of atoms in the primitive unit cell of a crystal (as given, for example, in The International Tables of X-ray Crystallography), coupled with character tables of the site symmetry and crystal symmetry group, and correlation tables between different symmetry groups to determine the number, activity, and symmetry of infrared and Raman vibrations of a crystal. Character tables for different symmetries are given in many texts (for example, 5), and correlation tables are given in [7] and [8]: the latter text provides a number of worked examples of factor group analysis applied to minerals and inorganic crystals.

Infrared spectra may be presented from two different experimental configurations: absorption (or transmission), or reflection. Sample absorbance is dimensionless, and is defined as

\[ A = -\log(I/I_0), \tag{2} \]

where \( I \) is the intensity of light transmitted through the sample, and \( I_0 \) is the intensity of light transmitted through a non-absorbing reference material. Frequently, such data are reported as per cent transmittance, which is simply the ratio \( I/I_0 \) multiplied by 100 (note that vibrational peaks are negative features in transmittance plots and positive features in absorbance). Because of the intensity of many of the absorptions in rock-forming minerals (greater than \( \sim 2 \mu m \) thicknesses in the mid-infrared (\( \sim 400 \text{ cm}^{-1} \) often render samples effectively opaque), such absorbance or transmission data are often generated from suspensions of powdered minerals or glasses within matrices with indices of refraction which compromise and orientation information is lost.

A second means by which infrared spectra are measured is through measurement of reflection spectra. Reflection spectra of crystals sample two components of each vibrational modes: transverse optic and longitudinal optic modes, while absorption spectroscopy ideally samples only the transverse modes. That there are two types of modes in reflection is because each vibrational motion may be described either with atomic displacements oriented parallel (longitudinal modes) and perpendicular (transverse modes) to the wavevector of the incoming light. Those with their atomic displacements oriented parallel to the wavevector of the incoming light can be subject to an additional electrostatic restoring force produced by the differing displacements of planes of ions relative to one another, an effect not generated by shear. Such transverse and longitudinal modes are thus separated from one another by long-range Coulombic interactions in the crystal [3, 6].

In practice, reflection spectra generally have broad flattened peaks, with the lowest frequency onset of high reflectivity of a peak corresponding approximately to the transverse optic frequency, while the higher frequency drop in reflectivity of a peak is near the frequency of the longitudinal optic vibration. These data are generally inverted for TO and LO frequencies and oscillator strengths (a measure of the intensity of the reflection of the band) using one of two types of analyses: Kramers-Kronig, or an iterative classical dispersion analysis. Such analyses, described in [17] and elsewhere, are designed to model the extreme changes in the optical constants (expressed as the frequency dependent and complex index of refraction or dielectric constant) occurring over the frequency range of an optically active vibration.

For many minerals, the types of vibrational modes may be divided into two loose categories: internal and lattice modes. Internal modes are vibrations which can be associated with those of a molecular unit, shifted (and possibly split) by interaction with the crystalline environment in which the molecular unit is bonded: the vibrations of the silica tetrahedra shown in Figure 1 are typical examples of the types of motions which give rise to internal modes. Such internal modes are typically associated with the most strongly bonded units in a crystal, and thus with the highest frequency vibrations of a given material. We note also that even the simple picture of molecular vibrations is often complicated by the presence of interacting molecular units within a crystal. For example, it is difficult to associate different bands in feldspars with stretching vibrations of distinct AlO4 or SiO4 tetrahedra: because of the interlinking tetrahedra, a silica symmetric stretching vibration such as is shown in Figure 1 will involve a stretching motion of the adjoining AlO4 tetrahedra, and vibrations of these two species must be viewed as coupled within such structures.

Lattice modes comprise both a range of (often comparatively low-frequency) vibrations not readily describable in terms of molecular units, and so-called external modes. External modes are those which involve motions of a molecular unit against its surrounding lattice: for example, displacements of the SiO4 tetrahedra against their surrounding magnesium polyhedra in forsterite would constitute an external motion of the
tetrahedral unit. Typically, such lattice modes are of critical importance in controlling the heat capacity of minerals at moderate temperatures (of order less than ~1000 K). As it is the thermal excitation of vibrational modes which produces the temperature dependence of the lattice heat capacity, considerable effort has been devoted to designing methods to extract thermochemical parameters such as the heat capacity and the Gruneisen parameter (the ratio of thermal pressure to thermal energy per unit volume) from vibrational spectra at ambient and high pressures [13]. A fundamental limitation on such techniques lies in that infrared and Raman spectra access only vibrations which have the periodicity of the unit cell (that is, effects of dispersion are ignored).

Representative Raman spectra of quartz and calcite are shown in Figure 2, along with a powder infrared absorption spectrum of quartz and an unpolarized infrared reflectance spectra of calcite. The factor group analysis of quartz predicts 16 total optically active vibrations, with four being Raman-active (A1 symmetry type), four being infrared-active (A2 symmetry), and eight being both Raman and infrared-active (E symmetry: doubly degenerate). For calcite, such an analysis predicts five Raman active vibrations (3A2u and four doubly degenerate E2g symmetry modes) and eight infrared-active vibrations (3A2u and 5 doubly degenerate E2u). Two features are immediately apparent from these spectra: first, the differences between the vibrations of the silicate group and those of the carbonate group are immediately apparent: in the infrared, the asymmetric stretching and out-of-plane bending vibrations of the carbonate group are present near 1410 and 870 cm⁻¹, while the strongest high frequency vibrations in quartz lie near 1100 cm⁻¹ (the asymmetric stretches of the silica tetrahedra) and 680-820 cm⁻¹ (corresponding to Si-O-Si bending vibrations). Moreover, the LO-TO splitting of the asymmetric stretching vibration of the carbonate group is clearly visible in the reflectance spectrum. Within the Raman spectrum, the most intense vibration of calcite is the symmetric stretching vibration of the carbonate group at ~1080 cm⁻¹, while that within quartz is predominantly a displacement of the bridging oxygens between tetrahedra at 464 cm⁻¹. At lower frequency (below 400 cm⁻¹), the spectrum of the carbonate has Raman bands associated with external vibrations of the carbonate group relative to stationary calcium ions. At lower frequencies than are shown in Figure 2 in the infrared spectrum, both lattice-type vibrations of the calcium ions relative to the carbonate groups and displacements of the carbonate groups and the calcium ions both against and parallel to one another occur.

Figure 3 shows representative vibrational frequencies of different functional, or molecular like groupings, in mineral spectra. In the case of many minerals with complex structures, normal modes involving motions of the entire lattice, or coupled vibrations of different functional groups may occur, and these are not included in Figure 3. As expected from Equation 1, there is a general decrease in frequency with decreases in bond strength for different isoelectronic and isostructural groupings, such as occurs in the PO₄-SiO₄-AlO₄ sequence of tetrahedral anions.

While both infrared and Raman spectroscopy represent useful techniques for characterizing bonding environments, vibrational mode frequencies and the molecular species present within minerals, infrared spectroscopy has been extensively utilized as a quantitative technique for determining the concentration and speciation of volatile components within samples. Specific examples include the determination of the dissolved molecular water and hydroxyl content of glasses and crystals, the amount of dissolved CO₂ relative to CO₃²⁻ groups, and the amount of impurities within crystals such as diamond and a range of semiconductors. Such determinations depend on an application of the Beer-Lambert Law, in which the amount of absorption is assumed to be proportional to the number of absorbing species present in the sampled region. This may be expressed as

\[ c = (M \cdot A)(p \cdot d \cdot \varepsilon), \]  

in which \( c \) is the weight fraction of a dissolved species, \( M \) is the molecular weight of the dissolved material, \( A \) is the absorbance of a diagnostic band of the dissolved species, \( p \) is the density of the matrix in which the species is suspended, \( d \) is the path length through the sample, and \( \varepsilon \) is the molar absorption coefficient of the suspended species, with units of length²/mole. It is the determination of this last parameter on which the quantitative application of Equation 3 depends: typically, a non-vibrational means of analysis is used to quantify the amount of dissolved species within a sequence of samples in order to calibrate the value of \( \varepsilon \). Several complications exist in the straightforward application of Equation 3: first, the extinction coefficient can be frequency-dependent, in that the amount of absorption can depend on the structural environment in which a given species occurs. Second, for some applications a more appropriate measure of the number of species present is not the amplitude of absorption, but rather the integrated intensity underneath an absorption band (see [21] for a mineralogically-oriented discussion of each of these effects in hydrated species).
Fig. 2. Infrared and Raman spectra of SiO₂-quartz and CaCO₃-calcite. The infrared spectrum of quartz is an absorption spectrum from powdered material, while that of calcite is an unpolarized reflectance spectrum from a single crystal. Both Raman spectra are from single crystal samples using 514.5 nm excitation.
The application of Raman spectroscopy to quantitative measurement of molecular species is complicated by practical difficulties in determining the absolute Raman scattering cross-section of different species, and in maintaining a constant volume of Raman excitation from which scattered light is collected. Its utility has thus been principally in determining what species are present in a sample, as opposed to their quantitative abundance. Yet, for analysis of samples whose sizes are of the order of the wavelength of infrared light (such as some fluid inclusions), diffraction of incident infrared light limits the usefulness of infrared techniques. Considerable effort has thus been devoted to characterizing Raman scattering cross-sections of gas-bearing mixtures, with the motivation of establishing Raman spectroscopy as a quantitative, non-destructive compositional probe of fluid inclusion compositions [e.g., 20].

3. OPTICAL SPECTROSCOPY

There are a number of different processes which may generate optical absorption (see [19] for a discussion of different causes of color) in the visible and ultraviolet wavelength range. The three processes of primary importance for minerals are: 1) crystal-field absorptions; 2) intervalence transitions; and 3) charge transfer or absorption into the conduction band (4, 15, and Burns in [2]). The first of these processes involves an ion with a partially filled d- (or in some cases f-) electron shell being incorporated into a crystalline environment whose symmetry produces a difference in energy between the different orbitals. A representative example of this phenomenon is shown in Figure 4: when the five atomic d-orbitals are octahedrally coordinated by anions, the \( d_x^2 \), \( y^2 \) and \( d_z^2 \) orbitals, which have lobes of electron density...
Fig. 4. The effect of octahedral coordination on the different d-orbitals of a transition metal cation (labelled M). The surfaces of the d-orbitals represent contours of constant probability that an electron lies within the boundaries. The repulsive effect produced by close proximity of the negatively charged oxygen cations to the \( d_{x^2-y^2} \) and \( d_{z^2} \) orbitals separates these in energy from the \( d_{xy}, d_{yz} \) and \( d_{xz} \) orbitals by an amount referred to as the crystal field splitting energy (also as \( 10D_q \) or \( \Delta_0 \)). Oriented towards the anions, lie at higher energy than the remaining three orbitals because of the larger repulsive interactions between the \( d_{x^2-y^2} \) and \( d_{z^2} \) orbitals and their neighboring anions. Thus, optical absorption may be produced by excitation of electrons into and between these separated, or crystal-field split, energy levels, the energetic separation between which is often referred to as \( 10D_q \) or \( \Delta_0 \). Such crystal-field effects are observed within compounds containing such transition metal ions as Fe\(^{2+}\), Fe\(^{3+}\), Mn\(^{2+}\), Ti\(^{3+}\), Cr\(^{3+}\), and is associated with both the colors and fluorescent properties of a range of minerals, gems and laser crystals, including forsteritic olivines (peridot: Mg\(_2\)SiO\(_4\) with Fe\(^{2+}\)), ruby (Al\(_2\)O\(_3\) with Cr\(^{3+}\)) and both silicate and aluminate garnets (which may contain a range of transition elements). The preferential occupation of the lower energy levels produces a net crystal field stabilization energy (CFSE) which contributes to the thermochemical energetics of transition metal-bearing crystals. The characteristic magnitude of the CFSE for Fe\(^{2+}\) (d\(^6\) configuration) in octahedral coordination in minerals is between about 40 and 60 kJ/mole; that for octahedral Cr\(^{3+}\) (d\(^3\)) is generally between 200 and 275 kJ/mole. Characteristic octahedral CFSE values for other transition metal cations with unpaired d-electrons generally lie in between these extremes; tetrahedrally coordinated cations typically have CFSE energies between ~30 and ~70% that of octahedrally coordinated cations, thus producing a net preference of many transition metal ions for octahedral sites. For comparison, characteristic cohesive energies of divalent transition metal ions octahedrally coordinated by oxygen are on the order of 3000-4000 kJ/mole \([4, 15, 16]\).

Furthermore, as each orbital can contain two electrons of opposite spins, two possible configurations are possible for octahedrally coordinated cations containing between three and eight d-electrons: high spin configurations, in which the energy required to pair two electrons within an orbital is greater than the crystal field splitting energy, and electrons enter into the higher energy unoccupied \( d_{x^2-y^2} \) and \( d_{z^2} \) orbitals (\( \text{eg states} \)) rather than pairing in the lower energy three-fold \( t_{2g} \) states. For comparison, electrons in low spin configurations fully occupy the \( t_{2g} \) states before entering the \( \text{eg} \) levels. Among major transition elements, iron essentially always occurs in the high spin configuration in minerals: this is simply a consequence of the energy required to pair spins in divalent iron being larger than the crystal field stabilization energy. Estimates of the spin-pairing energy in iron-bearing minerals are poorly constrained, but representative values for this quantity are generally greater than 100 kJ/mole at ambient pressure. Historically, the high spin to low spin transition of iron in crystalline silicates has been frequently invoked as a possible high pressure phenomena. Essentially no experimental evidence
exists, however, that indicates that such an electronic transition occurs over the pressure and compositional range of the Earth's mantle.

The values of the crystal-field splitting, discussed in detail elsewhere [4, 15, 16], clearly depend on the valence of the cation (as this controls the amount of occupancy in the d-orbitals, as well as contributing to the amount of cation-anion interaction, through the cation-anion bond strength), the anion present (as the charge and radius of the anion will also control the amount of crystal field splitting which takes place), and the type and symmetry of the site in which the ion sits. Such effects of symmetry are demonstrated by a comparison between octahedral and tetrahedral sites: in tetrahedral sites, the $d_{x^2-y^2}$ and $d_{z^2}$ orbitals lie at lower energy than the three remaining $d$-orbitals. In more complex environments, such as distorted octahedral or dodecahedral sites, a larger number of crystal field bands may be observed because of further splitting of the $d$-levels. An example of spectra produced by different polarizations of light incident on Fe$_2$SiO$_4$-fayalite, a material with distorted octahedral sites, is shown in Figure 5, combined with an interpretation of the different crystal field transitions present in this material [4]. The lower than octahedral symmetry of the M1 and M2 sites produces more extensive splitting of the energy levels than occurs in sites of ideal octahedral symmetry.

The intensities of crystal-field absorption bands can vary over four orders of magnitude: these are governed both by the abundance of the absorbing cation, in a manner directly analogous to Equation 3, and by a combination of the symmetry of the cation environment and quantum mechanical selection rules. For example, non-centrosymmetric environments (e.g., tetrahedrally coordinated cations) generally produce more intense absorptions. The primary selection rules are related to spin multiplicity (involving conservation of the number of unpaired electrons between the ground and excited state) and to conservation of parity (or, transitions being only allowed between orbitals which differ in the symmetry of their wavefunction: the Laporte selection rule). These selection rules may be relaxed through a range of effects which include orbital interactions, vibrational and magnetic perturbations, and lack of a centrosymmetric ion site, producing both weak spin-forbidden and Laporte-forbidden transitions. Indeed, such crystal field bands are frequently orders of magnitude less intense than the vibrational bands discussed above.

Inter-valence, charge transfer, and valence to conduction band transitions are all terms used to describe absorption mechanisms of similar origins: the transfer of electrons between ions in non-metals via an input of energy in the

---

![Figure 5](https://example.com/fig5.png)

**Fig. 5.** Polarized crystal field absorption spectra of Fe$_2$SiO$_4$-fayalite in three different crystallographic orientations, combined with an interpretation of the observed transitions in terms of the M1 and M2 cation sites of Fe$^{2+}$ in olivine [from 4]. The dotted spectrum is taken parallel to the $b$-axis of this phase, the dashed line parallel to $c$, and the solid line parallel to $a$. As the M1 and M2 sites are each distorted from perfect octahedral symmetry, additional splitting beyond that shown in Figure 4 occurs for the $d$-orbitals of iron ions within fayalite: this is shown in the insets. Short arrows in insets represent electrons occupying each $d$-orbital (Fe$^{2+}$ has six $d$-electrons). The sharp bands above 20,000 cm$^{-1}$ are generated by spin-forbidden transitions.
form of a photon. The term inter-valence transition is generally used to describe processes associated with the transfer of an electron between transition metal ions, especially those which are able to adopt multiple valence states in minerals, such as Fe (+2,+3) and Ti (+3,+4). Characteristically, these bands occur in the visible region of the spectrum, and are most intense in those minerals which have large quantities of transition metals, and relatively short metal-metal distances. As such, these transitions produce the coloration of many iron and iron/titanium-rich oxides and hydroxides.

Charge transfer transitions not only occur between transition metal ions, but also occur in excitation of electrons between cations and anions. Within oxides, such oxygen-to-metal charge transfer absorption bands typically occur at high energies in the ultraviolet, and are extremely intense: often three to four orders of magnitude more intense than crystal field transitions. Effectively, such charge transfer between anions and cations is often associated with delocalization of an electron, or photo-excitation of an electron into the conduction band of a material: the separation in energy between the valence and conduction band of materials is commonly referred to as the band gap. Within many materials, such charge transfer bands appear as an absorption edge, rather than a discrete band: this edge is simply generated because all photons with an energy above that of the edge will produce electron delocalization. This edge may be accompanied by discrete bands at slightly lower energy than the edge: such bands are often associated with a binding, or attractive force between the photo-excited electron and its ion of origin. These bound electron states are referred to as excitons, and are discussed in greater detail in solid state physics texts [e.g., 1]. There is an intimate association between such processes of electron delocalization and the high- and moderate-temperature electrical conductivity of insulators and semiconductors: in materials in which the electrical conductivity is not dominated by defect-related processes, the thermal excitation of electrons into the conduction band represents the primary means by which charge carriers are generated. This relationship is expressed through

\[ \sigma = \sigma_0 \exp(-E_g/2kT), \]

in which \( \sigma \) is the electrical conductivity of the material, \( E_g \) is the energy of the band gap, \( k \) is Boltzmann's constant (1.381 x 10^-23 J/K), and \( T \) is temperature [e.g., 22]. The pre-exponential factor, \( \sigma_0 \), is generally treated as a constant (although both it and the band gap may be temperature dependent: these dependences are, however, frequently small), and represents the intercept of a plot of the log of the conductivity and the inverse of temperature.

Absorptions generated by such cation-anion charge delocalization processes are common in ore minerals such as sulfides and arsenides, and produce the opacity or deep red color in the visible of many such minerals. Furthermore, they also induce effective opacity of most

![Fig. 6. The dependence of blackbody emission on wavelength at different temperatures, with the wavelength ranges of electronic and vibrational absorptions which inhibit radiative heat transport in mantle minerals illustrated. Vibrational absorptions (both single vibrational transitions and overtones) absorb strongly at wavelengths longer than about 5 \( \mu \text{m} \); if hydroxyl or carbonate units are present, then such vibrational absorptions may extend to 3 \( \mu \text{m} \). Crystal field absorptions of divalent iron in distorted octahedral sites, such as the M2 site in pyroxenes, can occur at wavelengths above 4 \( \mu \text{m} \); similarly, iron in the dodecahedral site of garnets can absorb at longer wavelengths than 2 \( \mu \text{m} \) (see Burns in [2]). Among the most intense crystal field absorptions of iron in minerals are those occurring near 1 \( \mu \text{m} \), such as are shown in Figure 5. Such crystal-field absorption bands tend to broaden markedly at high temperatures, increasing the efficiency with which they prevent radiative heat transport. The location of charge-transfer bands is known to be highly sensitive to pressure, with bands in relatively iron-rich phases (such as magnesiowüstite) shifting strongly to longer wavelength with increasing pressure. Such absorptions generate an effective means of impeding radiative conductivity under lower mantle pressure and temperature conditions.](image)
silicates in the far ultraviolet. The role of pressure (in most cases) is to decrease the energy at which such band-gap related absorptions occur (that is, it becomes easier to delocalize electrons as the distance between ions decreases). It is generally believed that among relevant deep Earth constituents only relatively iron-rich materials (such as FeO) will have absorption edges which decrease to zero energy and metallize over the pressure and temperature interval of the Earth's mantle. However, the effect of a lower energy absorption edge in compressed magnesiowüstite (Mg₂Fe₁₋₃O) may have a significant effect on the electrical conductivity of the deep mantle, in addition to producing an absolute impediment to radiative thermal conductivity at these depths.

This effect is illustrated in Figure 6; the intensity of radiative thermal emission is described by the Planck function,

\[ I(\nu) = \frac{2\nu^2e^{-\frac{h\nu}{kT}}}{\nu^5(\exp[h\nu/kT] - 1)} \]  \hspace{1cm} (5)

in which the emitted intensity, \( I \), is a function of frequency (\( \nu \)), \( e \) represents the emissivity of the material (assumed to be unity in the case of a blackbody, and to lie at a wavelength-independent value between zero and one for a greybody), and \( c, h, k \) and \( T \) are the speed of light, Planck's constant, Boltzmann's constant and temperature, respectively. Figure 6 shows representative values of emitted intensity for a range of temperatures, along with absorption mechanisms of minerals relevant to the Earth's upper and lower mantle. Among lower mantle minerals, no optical absorption data have been reported for silicate perovskite; however, the absorption of magnesiowüstite at both ambient and high pressures has been well-characterized [14]. Not shown in Figure 6 are the grain boundary scattering effects which may also act to reduce radiative conductivity over a broad frequency range. Clearly, given the wavelength ranges over which crystal-field absorptions (which broaden in width at high temperatures) and charge-transfer bands occur in transition-metal bearing minerals, radiative conductivity is unlikely to provide a rapid mechanism of heat transport within the deep Earth. Thus, the optical properties of mantle minerals play a passive but seminal role in the thermal and tectonic evolution of the planet: were radiative conductivity an efficient means of heat transport through the deep Earth, thermal convection (and its geochemical and geodynamic consequences) would not be necessitated.

Acknowledgments. I thank the NSF for support, and an anonymous reviewer, T.J. Ahrens and E. Knittle for helpful comments. This is contribution #207 of the Institute of Tectonics at UCSC.

REFERENCES

11. Hawthorne, F.C., (Ed.) Reviews in Mineralogy, Vol. 18, Spectroscopic methods in


