Absorption and reflection infrared spectra of MgO and other diatomic compounds

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Accepted 2003 June 9. Received 2002 December 19; in original form 2002 March 19

ABSTRACT
Oxide and sulphide minerals are expected to occur in diverse astronomical environments. However, optical constants for such minerals are either lacking or poorly characterized. Minimizing errors in laboratory data, while extrapolating over wide frequency ranges, is the focus of this report. We present reflection and absorption spectra of single-crystal MgO from about ∼100 to 18 000 cm−1 (∼100 to 0.5 µm), and derive emissivity, dielectric and optical functions (n and k) using classical dispersion analysis and supplementary data to ensure that the reflectivity values are correct at the low- and high-frequency limits. Absorbance spectra of thin films of oxides (MgO, CaO, FeO and ZnO) and sulphides (MgS, CaS and FeS) are in good agreement with available reflectivity measurements, and provide information on the various effects of chemical composition, structure and optical depth. The greatest mismatch occurs for MgO, connected with this compound having the broadest peak in reflectance. The ferrous compounds (FeO and FeS) have relatively weak infrared features and may be difficult to detect in astronomical environments. Previous optical data based on transmission spectra of dispersions have underestimated the strength of the main infrared features because this approach includes spectral artefacts that arise from the presence of opaque particulates, or from non-uniform optical depth. We show that areal coverage, not grain size, is the key factor in altering absorption spectra from the intrinsic values, and discuss how to account for ‘light leakage’ in interpreting astronomical data. Previous reflectivity data on polycrystals differ from intrinsic values because of the presence of additional, internal reflections, creating errors in the derived optical functions. We use classical dispersion analysis and supplemental data from optical microscopy to provide correct n- and k-values for FeO from the far-infrared to the visible, which can then be used in radiative transfer models. Thin-film absorption data are also affected by internal reflections in the transparent regions: we show how to recognize these features and how to obtain the absorption coefficient, n, and k from thin-film infrared data on CaO, CaS and MgS using the damped harmonic oscillator model.

Key words: line: identification – methods: laboratory – techniques: spectroscopic – infrared: general.

1 INTRODUCTION
Dust particles occur in a wide range of astronomical environments (e.g. circumstellar shells around evolved stars, pre-planetary systems around young stars, and the interstellar medium). Identification is made through comparison with infrared (IR) laboratory data. Mostly, the high-frequency lattice modes have been studied, because of the ease and availability of laboratory equipment, coupled with collection of observational data also at frequencies above 400 cm−1 (wavelengths λ < 25 µm), the so-called mid-IR region. However, modes in crystalline solids from about ∼50 to 400 cm−1 (the far-IR region, ∼25 < λ < 200 µm) show a greater variety of intensities, widths and positions, and are thus better suited for identification. Only recently have direct astronomical observations at comparable frequencies become available, through the Infrared Space Observatory (ISO: Kessler 1996). Hence the existing mineralogical data are insufficient for the simple task of identifying substances in interstellar and circumstellar dust. In addition, absorption spectra are usually obtained from a powdered sample dispersed in a medium. However, variations in particle thickness and areal coverage within a
dispersion provide spectral artefacts (Horak & Vitek 1978; Hofmeister 1995). To address these problems, we are compiling a data base of IR spectra of minerals and other inorganic solids that may exist in space. Both reflection and absorption techniques are utilized, as advantages and disadvantages exist for each approach, and because the optical functions obtained from reflectivity are used as inputs to radiative transfer models in astronomy, whereas absorption measurements are directly compared with spectral patterns for the purpose of identification and for estimates of concentration.

This paper is the first of a series, and therefore focuses on the methodology. Our plan is to present the data base in segments, each of which covers structurally and/or chemically related minerals. Diatomic oxides and sulphides are examined here, with the focus being on MgO. This choice is motivated by astronomy, as well as pragmatics. Foremost, ISO has provided unprecedented high-resolution mid- and far-IR spectra of a variety of astronomical environments (see e.g. Waters et al. 2000), and references therein). One of the major new results from ISO data was the discovery of absorption features indicative of crystalline silicates in the spectra of evolved stars. However, reliable optical constants for such solid-state species are lacking. Numerous other unidentified dust features have also been observed, e.g. the ‘30-µm’ feature in evolved star spectra (e.g. Hony, Waters & Tielens 2001) or the ‘23-µm’ feature in the spectra of Herbig Ae/Be stars (Malfait, Bogaert & Vaneldken 1998). These quality astronomical spectra exemplify the need for new laboratory data with which to compare. Secondly, the structural and chemical simplicity of diatomic compounds makes these an ideal starting point for a such a database. The IR spectra are simple as a consequence, and spectral artefacts are relatively easy to recognize. However, artefacts are also easily engendered as a result of the extreme variation in optical functions between frequency regions where the intense, broad bands are active and where they are not. Thus, in comparing this class of substances with astronomical data, one must be aware how laboratory data are affected by the particulars of the experiment.

Our general approach is to obtain reflectivity data from suitably large crystals of good optical quality from the far-IR to the visible. A Kramers–Kronig analysis of the reflectivity data provides the optical and dielectric functions as well as the absorption coefficients. Classical dispersion analysis, which is also known as the damped harmonic oscillator model (Spitzer et al. 1962), additional single-crystal absorption data for the transparent regions, i.e. frequencies above 1000 cm$^{-1}$ ($\lambda < 10 \mu$m), and previous, independent measurements of the low-frequency dielectric constant ($\epsilon_\infty$) and the high-frequency index of refraction ($n = \epsilon_\infty^{1/2}$) are used to verify the absolute values of the reflectivity, and to extrapolate the data into the visible region. The Lydanne–Sachs–Teller relationship provides a cross-check between IR peak positions and dielectric data. Classical dispersion analysis can be used to obtain $n$ and $k$ from absorption data if the thickness is known. Emissivity is obtained from the optical functions using Kirchhoff’s law. For the lattice modes below 1000 cm$^{-1}$, we obtain absorption spectra from films of various thicknesses formed by compression in a diamond anvil cell. This technique provides spectra consistent with Kramers–Kronig analysis of reflectivity data of complex silicates (McAloone & Hofmeister 1993; Hofmeister 1995), thereby allowing expansion of the data base to substances for which sufficiently large and clear crystals for reflection measurements are not available. Films with a thickness of 6 µm have been made using a spacer. We focus on the far-IR, owing to the paucity of laboratory data, on recognizing and compensating for spectral artefacts, and on problems and limitations in comparing observational with laboratory data.

The methods used here are not new, as each component exists in various scientific literatures. However, to our knowledge the cross-checks have not been used in astronomical studies, and have not been taken full advantage of elsewhere. For the most part, in mineralogical studies large crystals are used in reflectivity measurements to avoid potential problems, and the focus has largely been on frequencies of the peaks, which are less prone to artefacts than peak profiles, band strengths and widths. Because all peak parameters are important in astronomical applications of the data, however, multiple measurements and cross-checks are necessary.

2 EXPERIMENTAL METHODS

Three single crystals of synthetic, pure MgO were purchased from Atomergic Chemetals Corporation. The large faces are perpendicular to a crystallographic axis and 10 $\times$ 10 mm$^2$. Thicknesses were initially 0.5, 1.0 and 1.0 mm. Spectra were collected on freshly polished or cleaved surfaces to minimize surface hydration. In some cases, however, the surface hydrated rapidly.

Powdered MgO was prepared by dehydrating pure Mg(OH)$_2$ at 600 K in air for 2 d. A sample of Mg$^{18}$O was prepared by reacting Mg metal with enriched water in a sealed Pt tube at $\sim$1100 K and 0.6 GPa with a gas-media apparatus. This starting product was dehydrated and recrystallized at 1700 K for 16 h. Pure (better than 99.5 per cent) CaO, FeO, MgS, CaS and FeS were purchased from Alfa/Aesar. The vials, packed in argon, were opened and immediately measured in the lowest frequency region where their fundamental modes exist. Samples were subsequently stored in an evacuated desiccator. Higher frequency data (if needed) were collected months to a year later. CaO showed evidence of hydration, which was almost entirely removed by heating in N$_2$ at 800 K for 4 d. An additional sample of FeS is as synthesized and described by Laurent, Kremser & Fegley (1996). Naturally occurring magnetite (Fe$_3$O$_4$) from Magnet Cove, Arkansas is essentially chemically pure. Natural pyrrhotite from E1 mine, Vershire, Vermont and pyrite, locality unknown, were also studied. These minerals tend to have few impurities (Arnold 1967; Deer et al. 1992).

IR reflectivity spectra of MgO were acquired at near-normal incidence using a SpectraTech Fourier transform IR spectrometer (FTIR$^3$) microscope and using an evacuated Bomem DA 3.02 Fourier transform spectrometer$^4$ at 1 cm$^{-1}$ resolution. The accuracy of the instrument is $\sim$0.01 cm$^{-1}$. An Si-bolometer and a coated mylar beamsplitter were used for the far-IR range from $\sim$50 to 650 cm$^{-1}$ ($\sim$200–15 µm). An HgCdTe detector with a KBr beamsplitter covered the mid-IR from $\sim$450 to 4000 cm$^{-1}$ ($\sim$23–2.5 µm). A CaF$_2$ beamsplitter and an InSb detector were used for the near-IR from $\sim$1800 to 8500 cm$^{-1}$ ($\sim$6–1.2 µm). An SiC source was used for these IR regions. A quartz source, an Si avalanche detector and a quartz beamsplitter probed the visible region of $\sim$8500 to 20 000 cm$^{-1}$ ($\sim$1.2–0.45 µm). A gold mirror was used as the reference for the far- and mid-IR, and silver for the near-IR and visible regions. The number of scans ranged from 800 to 2000.

Optically thin ($<1$ µm) films were made by crushing particles in a diamond anvil cell (DAC). The films were thinned until the absorbance was near or below unity, or until the profile of the main peak was unchanged by further thinning. Thicker films were used to probe the less absorbing regions. Spectra were acquired using the DAC as a holder in a beam condenser using one of the source.$^1$

$^1$ Brighton, MA, USA.
$^2$ Ward Hill, MA, USA.
$^3$ Spectra-Tech Inc., Stamford, CT, USA.
$^4$ Bomem Inc., Quebec, Canada.
detector and beamsplitter combinations as above. Very thick films were made by placing a small amount of powder in the centre of a 25 cm diameter disc of BaF₂ or of KBr. A thin gasket with a thickness of 6 μm (NSG Precision Cells, Inc., Farmingdale, NY, USA) was placed at the edge of the disc. The sample was compressed to the same thickness as the gasket by a second BaF₂ (or KBr) disc using a commercial holder (Spectratech, Inc.). To attain the same thickness for sample and gasket we made sure that the powder did not extend to the edge of the disc, but that the area covered by powder occluded the entire IR beam, and was without visible cracks and was even in appearance upon examination under a binocular microscope. These measurements provide useful information on the overtones and O–H modes at frequencies above ∼500 cm⁻¹. Use of BaF₂ limits transmission to above 690 cm⁻¹ (<14.5 μm). Absorption spectra were also collected from single crystals of MgO placed on an aperture directly in the beam, or in a Spectratech IR microscope. For the latter approach, the image was masked. To avoid errors and non-linear response as transmission becomes small, thicknesses yielding absorbance below unity were sought for the frequency region of interest. The thicknesses of the films made without a spacer can be determined by comparing peak heights of features that are common and trustworthy in the various spectra, but such features do not always exist, and slopes and shoulders sometimes need to be used.

Procedural details regarding reflectivity measurements or use of the DAC were given previously (e.g. Hofmeister 1997; Hofmeister & Mao 2001).

3 DATA ANALYSIS

In any reflectivity study, some uncertainty exists in the absolute value of the reflectivity because the reference mirror and sample may not be precisely aligned in the same position in the beam or may differ slightly in the surface polish, or the sample may provide additional secondary reflections from fractures, grain boundaries, or the back surface. The reflectivity in the far-IR region is cross-checked as follows against independent measurements of the low-frequency dielectric constant ɛ₀. The reflectivity is

\[ R = \frac{(n - n_{med})^2 + k^2}{(n + n_{med})^2 + k^2}, \]

where \( n \) and \( k \) are the real and imaginary components of the complex index of refraction (the optical functions) and \( n_{med} \) is the index of refraction of the medium (\( n_{med} = \) unity for air or vacuum). The complex dielectric function \( \epsilon = \epsilon_2 + i\epsilon_1 \) is related to the complex optical function \( (n + i k) \) through

\[ \epsilon_1(v) = n^2 - k^2, \quad \epsilon_2(v) = 2nk. \]

For dielectric materials at frequencies near 0, \( k \) is negligible, so

\[ R_0 = (\epsilon_1^0 - 1)^2/(\epsilon_1^0 + 1)^2. \]

The most accurate type of electrical measurements provides \( \epsilon_0 = 9.83 \) for MgO (Fontanella, Andeen & Schuele 1974), which is within the 1 per cent uncertainty of recent measurements of 9.9 derived from a less accurate technique (Subramanian et al. 1989). Both values are in excellent agreement with the raw far-IR data. We therefore scaled the mid-IR spectra to match and performed a Kramers–Kronig analysis on the merged file (Spitzer et al. 1962; Andermann, Caron & Dons 1965). The reflectivity above and below the range of measured frequencies was assumed to be a constant in the presented results. This approach is used because the presence of reflections from the back surfaces (see below) induces some errors in the near-IR reflectivity, and assuming constant \( R \) creates the fewest artefacts for this case. Wooten’s approximation, wherein the high-frequency reflectivity is assumed to go as frequency to the fourth power (Wooten 1972), was used as a cross-check. This approach provides the trend expected for damped harmonic oscillators, but can create artefacts if errors exist in the measured high-frequency reflectivity. Another cross-check exists against \( n_{\infty} \), measured in the visible as 1.736 by minimizing the relief in liquids of known \( n \) in an optical microscope (Deer et al. 1992).

Obtaining accurate values of the optical functions at high frequency requires that the sample be large enough to avoid back reflections for the transparent spectral regions. Our sample of MgO has back reflections (Fig. 1) above ∼1200 cm⁻¹ (<8.25 μm). For this case, classical dispersion analysis and measured absorption spectra from crystal fragments are used to constrain the high-frequency results, discussed below.

IR modes are split by the interaction with light into transverse optic (TO) and longitudinal optic (LO) components. The \( n \)th TO frequency (\( \nu \)) occurs at maxima in \( \epsilon_2(v) \) and the LO frequency is determined from minima in \( \epsilon_2(v) \). The damping coefficient \( \Gamma = 2\pi \text{FWHM} \), where FWHM is the full width at half-maximum of each peak in \( \epsilon_2(v) \) in frequency \( v \) units. The oscillator strength \( f_i = 2\pi \text{FWHM} \sigma_{\max}/v^2 \) where the conductivity \( \sigma(v) = v\epsilon_2(v)/2 \) [see Spitzer et al. (1962) or Wooten (1972)]. The absorption coefficient \( A \) is calculated from

\[ A(v) = \frac{2\pi v \epsilon_2(v)}{n(v)} = 4\pi v k(v). \]

The reflectance was fitted using classical dispersion analysis (e.g. Spitzer et al. 1962). This method treats the vibrations as damped harmonic oscillators, and as a result the peaks in \( \epsilon_2 \) and \( \text{Im}(1/\epsilon) \) have Lorentzian shapes. A perfect harmonic oscillation would produce a delta function shape in the dielectric functions, and reflectivity that is shaped like a square wave. The widths of the peaks in \( \epsilon_2 \) and \( k \) in the spectral measurements are due to phonon–phonon scattering, which damps the vibrations. This method represents IR spectra well because the classical and quantum mechanical analyses of damped harmonic oscillations provide essentially the same formulae. For further discussions, see Mitra (1969) and Hofmeister (2001). We use a three-parameter description of the peaks, wherein the \( n \)th LO frequency
is a function of the TO peak parameters: \( v_i, \Gamma_i \) and \( f_i \). The equations for \( m \) oscillators using the circular frequency \( (\omega = 2\pi v) \) are

\[
\epsilon_1 = \epsilon_\infty + \sum_{j=1}^m \frac{f_j \omega_j^2}{\omega_j^2 - \omega^2 + \Gamma_j \omega^2},
\]

(4)

where \( \epsilon_\infty \) is obtained from measurements of \( n^2 \) in the visible, and

\[
\epsilon_2 = \sum_{j=1}^m \frac{f_j \omega_j^2 \Gamma_j / \omega}{(\omega_j^2 - \omega^2)^2 + \Gamma_j^2 \omega^2}.
\]

(5)

This approach allows extrapolation of the data to frequencies above and below the range of measurements, and aids in deciphering artefacts from overtones-combination bands which are present as weak shoulders or structure on the main peaks. Generally, the Kramers–Kronig parameters are considered as the rough description of the IR spectrum of a solid, and the classical dispersion parameters as the preferred representation (Wooten 1972). We used the Kramers–Kronig parameters as the starting point for the initial fit to the dielectric functions, and made the final fit to the raw reflectivity data. Thin film data were also fitted.

Wave propagation is described by \( E = E_0 \exp[(\mathbf{q} \cdot \mathbf{r} - \omega t)] \), where \( E \) is the electric field strength, \( \mathbf{q} \) is the wavevector, \( \mathbf{r} \) is the space coordinate and \( t \) is time. Physical properties such as the dielectric functions and optical functions are derived from wave propagation data using this form and Maxwell’s equations (e.g. Wooten 1972). This representation of wave propagation requires exponential attenuation of the intensity \( I \), which is proportional to \( E \), with thickness. Consequently, the true absorbance \( (a) \) and absorption coefficients \( (A) \) are related to light transmission through

\[
a = Ad = -\ln(\frac{I_T}{I_0}) = -\ln[1 - I_{abs}/I_0],
\]

(6)

where \( I_T \) is the transmitted intensity, \( I_0 \) is the incident intensity and \( d \) is the sample thickness (Brewster 1992).

From Kirchoff’s law, emissivity \( (\xi = I_{\text{em}}/I_0) \) equals absorptivity \( (\Omega = I_{\text{abs}}/I_0) \). From equations (3) and (6), \( \xi \) depends on frequency and thickness:

\[
\xi(v, d) = 1 - \exp[-dA(v)].
\]

(7)

The emission spectrum is

\[
\Sigma(T, v) = \xi(T, v)\mathcal{B}(T, v),
\]

(8)

where \( \mathcal{B} \) is the blackbody curve of Planck. The temperature dependence of \( \xi \) is derived from measurements of \( A \) at \( T \). The intensity, width and position of the peaks depend on \( T \) and \( \Sigma \) is truncated at a high frequency when \( \mathcal{B} \) becomes negligible: this truncation frequency depends strongly on \( T \).

Comparing the ideal absorbance calculated from Kramers–Kronig or classical dispersion analysis of reflectivity data to measured absorption spectra requires two adjustments. In most spectroscopic, chemical and mineralogical literature, the following convention is used: absorbance \( (a_{\text{cm}}) \) and the absorption coefficient \( (A_{\text{cm}}) \) are defined by common, not natural logarithms:

\[
a_{\text{cm}} = A_{\text{cm}}d = -\log(I_{\text{max}}/I_0).
\]

(9)

This convention is pervasive to the extent that equation (9) is incorporated in the software for commercial IR spectrometers and in spectral analysis packages. From Fig. 1, the measured amount of light transmitted \( (I_{\text{cm}}) \) is affected by reflections at the front and back interfaces. Combining Fig. 1 with equations (6) and (9) gives

\[
a_{\text{cm}} = \frac{Ad}{\sum_{3026}} - 2 \log(1 - R)
\]

(10)

(Shankland, Nitsen & Duba 1979). For small \( R \), the last term is close to \( \log(1 - 2R) \). This formula assumes parallel, smooth surfaces in a non-converging beam. If the reflectance is unknown, then the measured absorbance is obtained relative to a baseline. This approach is valid for weak peaks, and is necessary if the surface is rough or if additional internal reflections are present (e.g. from fractures or grain boundaries) or when the beam converges strongly.

Parallel surfaces can create interference fringes if the spacing \( (b) \) is related to an integer multiple of the wavelength. The relationship is

\[
b = \frac{1}{2n\Delta v}.
\]

(11)

where \( \Delta v \) is the fringe spacing. In this study, the spacing is probably the gap between the diamonds or between the KBr or BaF2 discs. Fringes can also be correlated with the size of the aperture (e.g. the 500-\( \mu \)m diameter of the diamond tip or of any masking aperture).

### 4 SYMMETRY ANALYSIS

The number of fundamental IR modes expected for a compound depends on its crystallographic structure. The number, type and polarizations of the modes can be predicted from applying group theory to the symmetry elements for the atoms in the structure (e.g. Cotton 1971). Most of the diatomic compounds examined here (MgO, CaO, FeO, MgS and CaS) crystallize in the cubic NaCl (rocksalt or B1) structure. The rocksalt structure, with both types of atom in octahedral sites, has few expected modes. One strong IR band is predicted from symmetry (Fateley et al. 1972) which consists of a doubly degenerate TO component and one LO component. Transverse acoustic (TA) and longitudinal acoustic (LA) modes also exist, but symmetry considerations suggest that these should not be detected by IR spectroscopy. However, IR spectra of compounds with the rocksalt structure often have weak IR modes superimposed on the one strong IR band (Kachare, Andermann & Brantley 1972). Such resonances are generally attributed to acoustic modes (Mitra 1969). Resonances or combination/overtone modes cannot be predicted by symmetry analysis because these types of vibrations are due to interactions among the fundamental modes (Mitra 1969). The presence of phonon interactions is implicit in the measurable widths of the peaks, whereas non-interacting vibrational modes would be manifest as delta functions in the dielectric constants (e.g. Hofmeister 2001).

FeO is the nominal composition for wüsite, but this mineral is neither purely ferrous (Fe\(^{2+}\)), nor perfectly cubic. The structure and physical properties of wüsite are reviewed by Hazen & Jeanloz (1984). In summary, the real mineral contains a small portion of ferric (Fe\(^{3+}\)) iron, and a sufficient number of octahedral cation vacancies \((\square)\) to balance charge, i.e. 2Fe\(^{3+}\) + \(\square\) = 3Fe\(^{2+}\). However, the situation is even more complicated because Fe\(^{3+}\) ions not only occupy the octahedral sites expected for the rocksalt structure, but also occur in tetrahedral interstices that are normally not filled in the rocksalt structure. Therefore the fraction of octahedral vacancies is larger than the chemical formula (Fe\(_1\)\(_{\square}\)\(_{\square}\)O). Thus the vacancy content is usually not explicitly stated, and compositions are indicated as Fe\(_x\)O. The distribution of vacancies and of the cations is not random, but occurs as defect clusters, leading to variable amounts of short- and long-range order within the basically cubic structure. Also, synthesis tends to produce compositions near Fe\(_{0.93}\)O, by exsolution either of Fe metal or of magnetite (Fe\(_2\)O\(_4\)). The above complications can potentially alter the IR spectrum from that intrinsic to pure Fe\(_x\)O which has the rocksalt structure, and which could form in a highly reducing environment possible in space.
ZnO has the hexagonal wurtzite structure, in which both atoms occupy tetrahedral sites. This structure is identical with the simplest 2H polytype of hexagonal α-SiC (Wyckoff 1963). From symmetry analysis (Fateley et al. 1972), one band is expected in each of the polarizations along and perpendicular to the e-axis, such that the latter mode is degenerate. These modes are also Raman-active. Symmetry predicts two additional acoustic, two Raman and two inactive modes. Although two IR bands exist for this structure, it is unlikely that these can be distinguished for ZnO by thin-film or dispersive methods, as these methods revealed only one strong band in the IR spectrum of α-SiC (e.g. Speck, Hofmeister & Barlow 1999). The underlying reasons for the equivalence of the IR modes from the two polarizations are that (1) the two cation–anion bond lengths in the wurtzite structure are similar, and (2) the motion of the atoms involved in producing the TO mode of $E_2^1$ is related to the motion producing the LO mode of $E_2^1$, and vice versa. Raman data on wurtzite-type compounds (Arguello, Rousseau & Porto 1969) are consistent with this analysis. Furthermore, the stacking disorder that forms the additional hexagonal or rhombohedral polytypes of SiC results in additional weak modes being superimposed on the strong modes in the IR spectra (Choyke & Patrick 1962). Such a stacking disorder has not been reported for ZnO, but exists for ZnS.

FeS is the nominal composition for a family of structurally and chemically complex minerals (see e.g. Vaughan & Craig 1978; Deer et al. 1992; Gaines et al. 1997). As occurs in wüstite, some of the Fe is ferric, and charge balance is attained through cation vacancies. Chemical compositions are reported as Fe$_{1-x}$S to indicate the minimum degree of defects. Compositions near Fe$_{0.05}$S (ferric troilite) crystallize in the NiAs parent structure (Deer et al. 1992) which has anions in hexagonal close-packing, whereas the cations are octahedrally coordinated. Symmetry analysis of NiAs gives mode types that are identical to those found in the wurtzite structure, suggesting only one IR mode would be observed for such ferric troilites. The troilite structure, which is formed with lower ferric contents, $x < 0.06$, is described as a superlattice of the NiAs structure which contains 12 FeS molecules in the crystallographic unit cell (Wyckoff 1963). Using symmetry analysis, we predict two IR modes for troilite when $E$ is polarized along the e-axis and six IR modes perpendicular to e (acoustic modes are not included). Because the modes polarized perpendicular to e are doubly degenerate, these are more intense, and six bands should be seen in unpolarized measurements. However, the relationship of the troilite structure to the NiAs parent structure through multiple stackings of the small NiAs unit cell parallels the polytypism of SiC, suggesting that many modes are weak. It is possible that troilite could have fewer IR bands, or one strong peak and several weak ones.

To complicate matters, other structures exist for Fe$_{1-x}$S. Stacking disorder analogous to that of hexagonal SiC exists as $x$ increases in the series Fe$_{1-x}$S, such that the various polytypes are associated with specific values of $x$. Pyrrhotite, with $x$ below or near 0.17, is common in terrestrial environments, whereas troilite is almost always meteoric in origin. Samples with $x$ near 0 can occur metastably in either a cubic form (isoostructural with β-SiC) or a tetragonal form (mackinawite, isostructural with PbO).

5 RESULTS

5.1 Single-crystal reflection spectra of MgO

A strong, broad band dominates the reflectivity spectrum of MgO (Fig. 2a), as expected from symmetry analysis. Superimposed on the intense band is a depression near 650 cm$^{-1}$. This feature, in

![Figure 2. Reflectivity at normal incidence of MgO and derived functions. Asterisks mark weak peaks. (a) Raw reflectivity (thick solid line, left y-axis) was joined at 600 cm$^{-1}$ by dividing the mid-IR by 1.125. Data below 125 cm$^{-1}$ are approximated by constant $R_0 = 0.266$ from the dielectric measurements (Fontanella et al. 1974). For the Kramers–Kronig analysis, $R$ was assumed to be constant at and above that at 2690 cm$^{-1}$. Reflectivity calculated from the classical dispersion fitting parameters in Table 2 is shown as open circles. Absorption coefficients (right y-axis) are determined from Kramers–Kronig (light solid line) and classical dispersion (dotted line, almost hidden by solid line). (b) Dielectric functions determined from Kramers–Kronig (solid lines) and classical dispersion (dotted and dashed lines). Heavier lines indicate $\varepsilon_2$. One main peak is seen in $\varepsilon_2$, but the shape indicates that it is a composite of three unresolved components. (c) Optical functions determined from Kramers–Kronig (solid lines) and classical dispersion (broken lines). Heavier lines indicate n. Although the mode at 650 cm$^{-1}$ is prominent in reflectivity and $n$, it is subtle in $A$, $k$ and $\varepsilon_2$.](https://example.com/figure2.png)
violation of symmetry analysis, has been previously observed in MgO and isostructural LiF (Piriou 1964; Andermann & Duesler 1970). Although our spectrum repeats the essential features of the earlier measurements, our profile differs near 400 cm\(^{-1}\), and in the absolute values. The present reflectivity values appear to be correct, as these agree with independent dielectric measurements (Fontanella et al. 1974). The previous, more squared profiles were duplicated in our instrument by slightly mis-aligning the sample or the spectrometer (not shown). These differences may also be related to the lower, and frequency-dependent, resolution used in the previous studies involving scanning instruments. A detailed analysis will be given in a companion paper that focuses on peak widths, overtones, and the effect of high temperature (Hofmeister, in preparation). The purpose of the current paper is to describe the major IR bands, which could potentially be present in astronomical observations (cf. Figs 2 to 3) because these are located on a flat region of the dielectric function. Similarly, a weak mode at 283 cm\(^{-1}\) appears to be resolved in \(\Delta\epsilon\) and \(\cot\) because this spectral region is relatively flat. We assign this mode as a TA component, but it is possible that this is an artefact arising in a relatively noisy section of the spectrum.

Parameters from Kramers–Kronig analysis (Table 1) should be accurate because the resulting dielectric functions are classical in appearance: nearly Lorentzian shapes exist for the imaginary part of the dielectric function, \(\epsilon_2\), and the imaginary part of the inverse of the dielectric function, \(\Delta\epsilon\) (Fig. 2b), and a derivative shape is seen for the real part of the dielectric function, \(\epsilon_1\) (not shown). The derived absorption coefficient (Fig. 2a) is asymmetric with more intensity towards the LO position, as expected (see Wooten 1972). The overall appearance of all functions obtained from Kramers–Kronig analysis (Fig. 2) suggests that the functions and parameters are reliable. Using Wooten’s approximation for the high-frequency extrapolation gives more asymmetry to the peak than that shown in Fig. 2, which was obtained by assuming that \(R\) is constant for frequencies above the range measured here. Appearance of asymmetry in the derived dielectric peak, regardless of the approximation used to extrapolate the results to high frequency, points to the main IR peak being a multiplet. More problems arise with Wooten’s approximation because the measured \(R\) in the transparent regions is higher than the true value, because of back reflections (discussed below). Back reflections do not occur in the absorbing parts of the spectrum because the strong attenuation of the light does not allow measurable intensity to reach the back side of the sample or the internal cracks.

Table 1. Kramers–Kronig analysis for MgO using \(\epsilon = 9.83\) (Fontanella et al. 1974) to constrain the data below 125 cm\(^{-1}\). Frequencies and FWHM are in cm\(^{-1}\). The weakest peaks appear as shoulders and reliable parameters could not be derived. Instead these were determined by classical dispersion analysis near 400 cm\(^{-1}\), which could potentially be present in astronomical observations (cf. Figs 2 to 3) because these are located on a flat region of the dielectric function. Similarly, a weak mode at 283 cm\(^{-1}\) appears to be resolved in \(\Delta\epsilon\) and \(\cot\) because this spectral region is relatively flat. We assign this mode as a TA component, but it is possible that this is an artefact arising in a relatively noisy section of the spectrum.

The LO component at 737 cm\(^{-1}\) arises from a singlet, as it is reproduced by one Lorentzian oscillator. The LO positions of the two weak components (Table 1) are revealed by expanding the field of view (cf. Figs 2b to 3) because these are located on a flat region of the dielectric function. Similarly, a weak mode at 283 cm\(^{-1}\) appears to be resolved in \(\Delta\epsilon\) and \(\cot\) because this spectral region is relatively flat. We assign this mode as a TA component, but it is possible that this is an artefact arising in a relatively noisy section of the spectrum.

In contrast, the TO components of the threefold multiplet could not be completely resolved because these are shoulders on the steeply rising main peak: expanding the axis smears the features. The spectra show weak manifestations of these extra modes: a shoulder occurs in reflectivity from about 385 to 410 cm\(^{-1}\) (Fig. 2a) and excess intensity is seen in \(\epsilon_1\) on the high-frequency side compared with a single-oscillator fit (not shown). Similarly, an additional very weak feature is seen near 590 cm\(^{-1}\). The visibility of the weaker features strongly depends on their position in the spectrum, relative to that of the strong mode, and the same feature can be resolved to varying degrees in the raw data and functions derived by Kramers–Kronig analysis. This observation is clarified by comparing the expression of the 650 cm\(^{-1}\) peak with that of the 285 cm\(^{-1}\) peak in Figs 2 and 3. The weak peaks listed in Table 1 were derived by examining both the raw data and the derived functions. Their existence is confirmed by classical dispersion analysis, in that the measured reflectivity could not be fitted with fewer than three peaks near 400 cm\(^{-1}\) (Table 2). The fit to the region near 590 cm\(^{-1}\) could be further improved by the addition of another oscillator. However, because this is near the join of the far-IR and mid-IR frequency regions, and because the existing fit is reasonable (Figs 2 and 3), we did not complicate the analysis with this additional peak. For similar reasons, the peak at 285 cm\(^{-1}\), which could be the TA mode, was not included in the fitting.

Considerably weaker features (barely above the noise level) exist at 380, 440 and 505 cm\(^{-1}\). These features coincide with absorption

![Dielectric Functions](image)
peaks in the coated mylar beamsplitter, and appear to be artefacts of less than perfect alignment of the spectrometer and its accessories, or of the sample with respect to the reference. (Slight motions of the thin, mylar beamsplitter are also a likely cause.) The features are resolved because of the high signal-to-noise ratio. We therefore omitted these probable artefacts from the classical dispersion analysis. Weak peaks exist near 850 cm$^{-1}$, but were not included in the analysis, because this transparent spectral region is affected by a secondary reflection (as sketched in Fig. 1) and because the absorption measurements provide better constraints (see below).

Roughly 300 synthetic spectra with differing numbers of modes and mode parameters were calculated to probe the limitations and trade-offs in fitting, particularly regarding the thousand multiplet. There is little leeway in the fitting because the steep reflectivity edge at high frequency and the gradual slope in reflectivity at low frequency provide opposing constraints (Fig. 2a). This steep slope constrains the FWHM as 18 to 20 cm$^{-1}$ for all components of the multiplet, the maximum reflectivity constrains the oscillator strength $f_1$ of the strongest peak, and the gradual slope from 300 to 400 cm$^{-1}$ constrains $f_2$ of the weaker peaks (Table 2). The asymmetry of the main peak requires that the component near 405 cm$^{-1}$ be more intense than the high-frequency component at 429 cm$^{-1}$. The position of the main LO band also constrains $f_3$ of the main TO peak.

The existence of the thousand multiplet is corroborated by the positions and numbers of IR overtone and combination bands (Hofmeister, in preparation; see Section 5.2) and of second-order Raman peaks (Manson, der Ohe & Chodos 1971). Although the Raman spectra are adequately described in terms of combinations of the IR and acoustic fundamentals, the IR overtones are too numerous (see next section) to have originated from only one strong IR fundamental. The multiplet exists because the resonances occur between the TO, LO and LA modes at various places in the Brillouin zone (which is the reciprocal of the primitive cell, and is used to describe scattering of X-rays and particles from the crystal lattice). As shown by inelastic neutron scattering (Peckham, Saunderson & Sharpe 1967; Sangster, Peckham & Saunderson 1970), for a large portion of the Brillouin zone, the LA mode is situated between the TO and LO modes. The TO and LO modes are described as components, but in actuality these are the same vibration. IR and Raman methods excite modes at the centre of the Brillouin zone only; however, these modes interact with all vibrational modes in the crystal to various degrees, as indicated by finite peak widths (Hofmeister 2001). The IR modes are mixed through phonon–phonon scattering. A detailed discussion of the known dependence of vibrational frequencies on position in the Brillouin zone, the IR resonances, and the overtone–combination bands in MgO is in preparation.

### Table 2. Classical dispersion fitting parameters using $\epsilon_\infty = n^2 = 3.0176$

(Fromantella et al. 1974). For MgO, the fit was made to the reflectivity data. Frequencies and FWHM are in cm$^{-1}$.

<table>
<thead>
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<th>Phase</th>
<th>Assign.</th>
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<th>FWHM</th>
<th>$f$</th>
<th>$\nu_{LO}$</th>
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<tr>
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<td>22</td>
<td>9.5</td>
<td>417</td>
<td>14.6</td>
</tr>
</tbody>
</table>

*Resonances involving edges of the first Brillouin zone. The TO, LO and LA branches cross and resonate within the Brillouin zone so the assignments are intended to indicate the dominant character of modes. For CaO and CaS, $n = 1.84$ and 2.14, respectively (Gaines et al. 1997). For MgS, $n = 2.19$ (Boswarva 1970). Although resonances for these substances occur within the main IR mode, these are neglected in fitting the thin-film data.
(Hofmeister, in preparation). Similar behaviour was seen in the IR spectra of Mg$_2$SiO$_4$ and Fe$_2$SiO$_4$ with the spinel structure, which also have simple IR spectra (Hofmeister & Mao 2001). For the current paper, it suffices that the measured reflectivity is reproduced with a threefold multiplet (Fig. 2a), and the dielectric and optical functions from the Kramers–Kronig and classical dispersion analyses (Figs 2b, c and 3) are in excellent agreement over the fundamental region.

Reflectivity data from 1000 to 4000 cm$^{-1}$ (10–2.5 µm) contain some additional weak and broad peaks (Fig. 4). Their poor resolution, along with intensities <1/100th of the fundamentals, and broad widths, suggests an origin as overtones. The spectrum above ∼1200 cm$^{-1}$ is affected by a back reflection, and thus the peak parameters are not trustworthy, nor are the values of $R$ (note expanded y-axis in Fig. 4). The back reflection exists to various degrees in all measurements, regardless of whether a cleaved or polished sample was used, or whether the sample was doubly or singly polished. The back reflection should double the light received, less a contribution for transmissivity departing from unity (Fig. 1). Reflectivity in excess of the classical dispersion calculation is seen for the cleaved crystal and the three polished crystals of different thicknesses (Fig. 4). The differences between the spectra are attributed to some surface hydration on the two polished samples, and its greater thickness for the polished sample in Fig. 4(a), leading to more absorption. Multiple reflections existed for the cleaved crystal because of the internal cracks developed during cleaving. The intensities of the absorption features are exaggerated because of the path, and corrupted because both reflectivity and absorption are superimposed. Fig. 4 shows, however, that even the exaggerated overtones at $\nu > 1200$ cm$^{-1}$ have sufficiently low intensity that these are unlikely to appear in astronomical observations for dust of µm sizes. Owing to the excess reflectivity and exaggerated absorptions, the absorption coefficient from the Kramers–Kronig analysis first goes negative, and then steeply rises with increasing $\nu$ (Fig. 4a). The problems exist into the visible region (Fig. 4b). The absolute values are generally larger than that predicted from independent measurements of $n$, consistent with back reflections. The one exception is the visible range. The lowered $R$-values in the visible may be connected with surface hydration, which increased over the course of the measurements, as this effectively reduces the polish. It is difficult to obtain accurate visible spectra with a Fourier transform instrument, and the low $R$ may be due to baseline drift. Because of the combination of reflectation and absorption existing at normal incidence for such weakly reflecting and absorbing samples (Fig. 1), the spectra of MgO with thickness $\lesssim$1 mm are not reliable in the transparent region. For extrapolation to high frequency, the classical dispersion results should be used for $A$, $n$ and $k$ above ∼1000 cm$^{-1}$. From Fig. 4, the calculated reflectivity gradually increases with $\nu$ above about 2000 cm$^{-1}$ to $R = 0.0724$ for yellow light (∼18 000 cm$^{-1}$). This extrapolation should be valid until the metal–oxygen charge transfer bands in the ultraviolet are encountered (see e.g. Blazey 1977).

5.2 Single-crystal and thick-film absorption spectra of MgO

The prominent fundamental bands in the IR spectra are accompanied by overtones and combinations occurring at higher frequency. Absorption spectra were obtained to constrain better the optical functions where the crystals are largely transparent, and to try to determine the thicknesses of the films from which the IR fundamentals were studied, which could not be accurately measured in a binocular microscope.

![Figure 5. Single-crystal absorption spectra of MgO and comparison with films. (a) High-frequency spectral range. The doubly polished samples (solid lines) were placed on an aperture. The large baseline absorbance of the thicker sample is due to an imperfect surface polish. Peaks near 2900 cm$^{-1}$ are organic residues from polishing. The thinner piece was also viewed in a microscope (dotted line). Despite the fact that the area viewed was at the centre of the sample and was about half of the total sample area, stray light and scattered light were received by the detector, providing both incorrect relative intensities and spurious peaks. For high absorbance ($a_{\text{abs}}$ > 2.5), the values cannot be trusted, even for samples sitting on an aperture because of detector limitations. Both types of errors underestimate the true values of $a$. Dashed line = spectrum of a 6-µm film. The rise towards high $\nu$ is due to scattering for this incompressible substance. Peaks due to sorbed water are labelled. (b) Far-IR spectral range. Heavy line = spectra from a 0.10-mm crystal on an aperture. Because a room-temperature detector (deuterated triglycerine sulphate) was used, resolution was limited to 4 cm$^{-1}$. Dotted line = cleaved wedge of about 15-µm thickness. Thin line = spectra from a wedge with $t = 15$ µm, corrected for surface reflections (equation 10). Grey line = $a_{\text{abs}}$ (equation 9) obtained from the Kramers–Kronig analysis. Dashed line = thin film of MgO with $t$ near 1 µm. A shoulder at 285 cm$^{-1}$ is assigned to the TA peak.](image-url)
Direct observation of overtones and combinations features at \( \nu > 1000 \text{ cm}^{-1} \) requires thicknesses of \( \sim 0.1 \) to 0.3 mm (Fig. 5a). Thicker (0.5 to 1 mm) crystals were studied at frequencies up to 8500 \text{ cm}^{-1}, and indicated sorbed H\(_2\)O, but were otherwise featureless (Fig. 4b). MgO is hygroscopic and polished surfaces become dull (foggy) after exposure to air over hours to days. Fine powders also accumulate surface hydration on a similar time-scale, as indicated by features near 1500 and 3400 \text{ cm}^{-1} in the thick-film spectrum (Fig. 5a). At low frequencies, the thick-film spectrum compares reasonably well with the single-crystal results, considering the differences in optical path. Towards high \( \nu \), the absorbance of the film strongly increases (Fig. 5a). This behaviour is due to scattering. Because MgO is hard and incompressible, the grain boundaries were not eliminated by pressing between KBr discs.

The overtone features are weak but are in good agreement with absorption coefficients calculated from Kramers–Kronig analysis for the sample with the least back reflections. The thinnest crystal has a feature at 850 \text{ cm}^{-1} with an absorbance of 0.0168 \text{ } \mu \text{m}^{-1}, which is within the uncertainty of a noisy feature (Fig. 2a) at 847 \text{ cm}^{-1} with \( A = 0.0155 \text{ } \mu \text{m}^{-1} \). The 6-\text{um} film has a stronger absorbance of 0.035 \text{ } \mu \text{m}^{-1} but this value is affected by interference fringes.

Absorption spectra were acquired at low frequencies (Fig. 5b) to probe the possible feature at 290 \text{ cm}^{-1} in the reflectance (Fig. 2). The feature is of comparable strength to the noise for the thicknesses examined (Fig. 5b), whereas for thicker samples the steep rise in absorbance as frequency increased towards the main peak obscures this feature (not shown). The feature is too weak to be seen in the thinner films (Fig. 5b). Although it appears that this TA mode is real as all data are consistent (Table 1), it is not sufficiently resolved over the noise level of the spectra to be used to determine film thickness accurately. It can serve as a rough check on Kramers–Kronig analysis. From Fig. 5(b), the true absorption coefficient (peak minus sloping baseline) is \( \sim 0.12 \times 2.3/0.1 \text{ mm} = 3 \text{ mm}^{-1} \). The calculated absorption coefficient of \( \sim 15 \text{ mm}^{-1} \) (Fig. 2a) is larger, but may be enhanced (i.e. roughly doubled in strength) by a back reflection, as were the weak modes at high frequency (Fig. 4). To a good extent, these values differ simply as a result of the low signal-to-noise ratio and the weakness of the feature. We also compared the measured absorbances in the far-IR with values calculated from the Kramers–Kronig relationships, after subtracting the contribution for the reflections (equation 10). The wedge absorbs more light than expected between 100 and 330 cm\(^{-1}\) (Fig. 5b). Probably this is due to internal scattering, as the comparison for the thick crystal showed a larger discrepancy. Once the absorbance is moderate (>0.4), calculations and measurements are in good agreement, and for strong absorbances (>1.5) the reflectivity correction has little impact (Fig. 5b). Absorption measurements of even single crystals are therefore an approximation of the ideal absorption coefficient, with some problems occurring in the more transparent regions.

The spectra collected from samples lying on an aperture show an increase in the intensity of the peak near 1000 \text{ cm}^{-1} that is proportional to thickness, as expected from the connection of peak area or height with concentration (Beer’s law). However, the intensity of the peak near 850 \text{ cm}^{-1} does not increase as much as the difference in thickness would suggest. Note also the high degree of noise for measured absorbance that is greater than 2. The loss of proportionality is a problem of sampling. Detectors are not noise-free, and, as the transmission decreases, it will lie within the uncertainty of ‘zero’ before the true absorbance value is infinite (see Fig. 6a: a small amount of noise in the transmission spectrum for the minimum near 425 \text{ cm}^{-1} strongly alters the maximum value of \( a \)). Thus, at some low value of transmission (high absorbance), the system response becomes non-linear. For this reason, commercial software often truncates absorbance (\( a_{\text{SCM}} \)) at values of 2, 3 or 4, at the discretion of the manufacturer. In our experience, absorbance near 1 minimizes artefacts of this nature. This observation is consistent with use of \( a > 2 \) to describe optically thick conditions (Siegel & Howell 1972).

A different type of non-linear response is seen in the spectrum obtained from a crystal using an IR microscope. In this case, light leaking around the edge of the sample reduces the absorbance from the actual values (Fig. 5a). As shown schematically in Fig. 6, the leakage of light reduces absorbance of the strong peaks more than the weak peaks (or shoulder), creating either rounded or flattened profiles. Placing apertures at the image points before and after the sample minimizes the light leakage, but not all IR microscope systems use the double-aperturing technique. Neither does the second aperture completely remove sampling artefacts.
Comparison of the overtone intensity indicates that the thin data from a crystal scaled to reference. At frequencies above 800 cm$^{-1}$, where the sample transmits to a greater degree, peaks are seen at the same positions as the sample of equal thickness that was masked by a physical aperture, but the relative intensities of the peaks, their components and shoulders are incorrect (Fig. 5a). For strong absorbers, the spectral profile is a predominantly determined by the amount of light leakage, as indicated by Fig. 6. Note that opaque regions of a sample with light leakage (i.e. a dispersion) provide finite absorbance, and that infinite absorbance cannot be distinguished from $a = 4$ at 50 per cent coverage. These conclusions are irrespective of the type of material sampled. Thus, for dispersions, the fraction of areal coverage is a primary factor in determining the appearance of the spectra.

5.3 Thin-film spectra of diatomic compounds

5.3.1 Oxides

Absorption spectra obtained from optically thin films of the simple oxides consist of a broad, asymmetric peak with superimposed structure (Fig. 7). For absorbances below 2, the spectra of MgO and CaO essentially scale as the sample is thinned, in accordance with Beer’s law. Multiple spectra were not acquired for ZnO. For the FeO sample, very low absorbance (the maximum below 0.2) is needed to obtain peak profiles that do not change upon further thinning. Because of this, and because of superimposed scattering (the rise to the visible, Fig. 7b), the width measured from the absorption spectra is large for FeO (Table 3). The width for FeO is difficult to determine as it depends on the baseline. The CaO and ZnO samples have smaller widths than that of MgO, and are more symmetric. Their longitudinal acoustic frequencies lie below that of the main band (Table 3), whereas in MgO the TO and LA frequencies are nearly equal. In FeO, the sum of the TA and LA frequencies is 382 cm$^{-1}$ which is close to the main peak position for the thicker samples (Fig. 7b). The combination of scattering and a multicomponent peak probably contributes to the dependence of spectral profile on thickness.

The peak for Mg$^{18}$O is shifted to 469 cm$^{-1}$ and is broader than that of MgO (Fig. 7a). The large breadth is probably due to the enriched sample containing a significant proportion of the normal isotope $^{16}$O. The normal sample would have levels below 0.2 atom per cent of the heavy isotope (Criss 1999). Isotopic exchange should affect the mass without altering the lattice constant, producing a decrease in frequency. Instead, an increase in $\nu$ is observed, and attributed to changes in the resonances between the IR and acoustic modes.

The superimposed structure on the high-frequency side of the peaks for MgO and CaO is mostly interference fringes (Fig. 7a). The fringes are related to the spacing between the diamond faces, which is larger than the sample thickness, and no simple method exists to remove them without affecting the spectra. The spacing of the fringes is broken by some weak combination peaks, and the LO modes. For MgO, its acoustic combination band at 645 cm$^{-1}$ and its strongest IR overtone near 850 cm$^{-1}$ are also present. The strength of the 850 cm$^{-1}$ band suggests a 2.3-µm film from comparison with the single-crystal data, whereas $t = 1$ µm is suggested from high $n$ is due to index of refraction mismatch. Arrows indicate approximate extrapolation between segments and to high $\nu$.
comparison with the thick film. The agreement is good, considering that the fringes interfere with determination of peak strengths. For the thinnest FeO film, a shoulder appears at 570 cm\textsuperscript{-1}. From comparison with previous reflectivity data, this is the LO mode. Similarly, for ZnO, a shoulder exists at 580 cm\textsuperscript{-1}, which is between the LO positions determined from Raman spectroscopy (Arguello et al. 1969). For MgO, the LO position is not revealed in the thin-film spectrum; instead, the resonance peak at 650 cm\textsuperscript{-1} is assigned as the LO component, because sums involving the acoustic modes do not match this position (Table 3). The resulting splitting between the LO and TO modes systematically decreases for the oxides (Table 3). This marker combines the effects of oscillator strength and damping coefficient.

Joining the two thin-film spectra results in an asymmetric peak for all of the oxides (ZnO data are not shown for clarity). The asymmetry increases from ZnO to CaO to MgO. For FeO, strong scattering makes it difficult to obtain data except for the thinnest films. For these low thicknesses, the LO mode becomes less important (the ideal is approached) and the peak appears symmetric. Magnette exhibits the same sort of scattering baseline as FeO (Fig. 7c). From comparing Fig. 7(a) with Figs 2(a) and 5(a), the thin-film spectra for MgO are clearly delivering excess intensity at high frequency, which provides the asymmetry. This compound is highly reflecting over a wide frequency range (Fig. 2a), which creates an artificially high apparent absorbance, in accord with equation (10). Using equation (10) requires reflectivity data, and it is desirable to obtain the intrinsic absorption independently. We devised the following procedure. For MgO, appearance of the overtone at 860 cm\textsuperscript{-1} indicates a film thickness near 1 \( \mu m \). The single-crystal absorption spectrum (Fig. 5a) was therefore scaled to \( t = 1 \mu m \). Although the absorbance values should have been adjusted for reflectance (equation 10), the scaling reduces the values to near zero, making the correction unimportant. The single-crystal spectrum is truncated at 745 cm\textsuperscript{-1}, because of the rapid rise in absorbance associated with the LO mode. The spectrum for the 6 \( \mu m \) thick film, scaled to \( t = 1 \mu m \), rapidly rises just below this frequency. This trend, extrapolated to meet the thin-film measurement, represents the closest approximation to the intrinsic absorption spectrum obtainable without reflectivity measurements. (A quantitative comparison will be made in Section 6.3.) A thicker film (~2 \( \mu m \)) is also shown. In this case, the rapid rise ends with a shoulder at the LA resonance (Fig. 7a). This data better constrains the join to the thinnest film.

Applying the same procedure to CaO indicates a rapid rise at 590 cm\textsuperscript{-1}, confirming the above assignment to the LO mode (Table 3). The thicker film of CaO appears to be 1.5 \( \mu m \), as this thickness provides the best joint between the thin-film data and the spectrum from \( t = 6 \mu m \). The rise to high \( v \) is scattering, and the intrinsic spectrum is approximated by a gradual decrease in absorbance above 750 cm\textsuperscript{-1}.

### 5.3.2 Sulphides

Far-IR absorption spectra of the cubic sulphides MgS and CaS also have one main peak, with some structure (Fig. 8). Mid-IR spectra revealed no additional features and are not shown. Their peak positions are very similar, but occur near 250 cm\textsuperscript{-1} rather than near 400 cm\textsuperscript{-1} for the oxides, consistent with the larger mass of the sulphur anion, and with the longer bond distances (Table 3). In addition, the peaks are much narrower than those of the oxides. Structure exists on the main band of MgS, which is attributed to a resonance with the acoustic modes. The positions of the shoulders are in reasonably good agreement with estimates of the acoustic frequencies (Table 3). The TO and LO positions are also compatible with frequencies observed for \( \alpha \)-ZnS and CdS using Raman spectroscopy (Arguello et al. 1969). The peak widths and the LO–TO splittings are smaller than those of the oxides and decrease as the reduced mass increases (Table 3). The narrower widths and low LO–TO splittings for MgS and CaS are consistent with the reflectivity being high over the narrow range where the sample mostly absorbs, and with the measured absorbance reasonably representing the intrinsic absorbance for the thin films.

FeS has an extremely weak IR spectrum, consisting of a few narrow, weak peaks superimposed on a scattering curve. The same type of baseline was seen for FeO, and it also has a weak peak compared with the other oxides, but for FeO a strong IR mode still exists, consistent with the wüsite structure being essentially that of rocksalt. FeS appears to lack a strong IR mode, which is attributed to

### Table 3. Thin-film absorption spectra parameters (in cm\textsuperscript{-1}) and related information. Width is twice the FWHM on the low-frequency side of the main peak. For comparison, acoustic frequencies, reduced atomic masses and bond lengths are included. Cation–anion distances and acoustic (Debye) frequencies are from compilations of structural (Wyckoff 1963; Gaines et al. 1997) and elastic data (e.g. Bass 1995; Knittle 1995). Acoustic frequencies of the sulphides were estimated (except for ZnS) because the shear moduli are not available. For MgS and CaS, resonances in the IR were used to estimate some acoustic frequencies.

<table>
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<tr>
<th></th>
<th>MgO</th>
<th>CaO</th>
<th>FeO</th>
<th>ZnO</th>
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</tbody>
</table>

*Present in thicker samples of MgS, whereas the main band at 255 cm\textsuperscript{-1} is no longer resolved. †Also seen by Jacobson & Nixon (1968) and Galtier et al. (1972). ‡The main peak in FeO shifts to 390 cm\textsuperscript{-1} for thicker samples. §Inferred from a resonance. \( ^\$ \)Troilite has several weak peaks, but no strong main peak. \( ^\| \)Troilite has six Fe–S distances at 2.359, 2.379, 2.416, 2.504, 2.565 and 2.721 Å (Evans 1970). The distances for the other hexagonal phases (ZnO and ZnS) are averages, with a spread in bond lengths of ~0.02 Å. #Raman data on ZnS (Arguello et al. 1970) are from averaging the polarizations of the hexagonal polymorph.
6 DISCUSSION

6.1 Useful relationships between spectral parameters and physical properties

For a simple harmonic oscillator

$$v = \sqrt{F/\mu}, \ F \propto X^{-3/2},$$

(12)

where $$\mu$$ is the reduced mass and $$F$$ is a force constant. The above power-law relationship of $$F$$ with bond distance ($$X$$) is phenomenological (Batsonov & Derbeneva 1969). In accordance with equation (11), the main peak position does not simply depend on atomic masses, but instead is determined by a combination of the mass and the bond distance. For example, the low frequency of CaO is related to its large bond length and intermediate reduced mass (Table 3, Fig. 7). Although equation (11) is not precisely adhered to, the trend for the oxides (Fig. 9) is consistent with the above phenomenological model, and suggests that the measured frequencies are reasonably correct.

The Lydanne–Sachs–Teller (LST) relationship relates the high- and low-frequency limits of the real part of the dielectric function to the IR frequencies:

$$\frac{\epsilon}{\epsilon_{\infty}} = \left(\frac{\nu_{\text{LO}}}{\nu_{\text{TO}}}\right)^2 = \prod_{i=1}^{m-1} \left(\frac{\nu_{\text{LO}}}{\nu_{\text{TO}}}\right)^2,$$

(13)

where the product pertains to multiple band substances. The LST relationship is derived by comparing the damped harmonic oscillator equations in the low- and high-frequency limits (Burns 1990). This relationship holds for each polarization separately. For the diatomics (except FeS), one band dominates, so the simpler formula is used and FeS is omitted from consideration. The TO positions were taken as 10 to 15 cm\(^{-1}\) (in round numbers) below the peak positions from the thin-film spectra, because this relationship was seen for MgO (cf. Tables 1 to 3). For non-opaque minerals, $$\epsilon_{\infty}$$ is very close to $$n^2$$ (equation 2). For the diatomic compounds examined here and previously (Table 4) for which data on all four parameters exist, good adherence to equation (12) exists, considering that $$\epsilon_0$$ is generally uncertain by 10 per cent.

The good agreement in Table 4 also allows estimation of $$\epsilon_0$$ if both the index of refraction and IR data exist. FeO has a high dielectric constant (Table 4), regardless of whether parameters from the thin-film measurements (Table 3) or classical dispersion analysis of reflectivity data (Table 5, discussed further below) are used. The value from Kramers–Kronig analysis [from Henning & Mutschke (1997), listed in Table 5] does not fit the LST relationship, indicating that $$R$$ is incorrect at either low or high frequency (see Section 6.2). Classical dispersion analysis of the thin-film data was also used to obtain $$\epsilon_0$$ (Table 2, see Section 6.6). The results are consistent with this mineral occupying a much different structure, related to that of NiAs. The correlation of peak positions with those of the diatomic sulphides listed in Table 3 is given for convenience. Our data differ somewhat from the optical functions derived from previous reflectivity measurements (Henning & Mutschke 1997) – see Section 6.4.

Figure 8. Thin-film IR spectra of diatomic sulphides. (a) Effect of thickness on MgS far-IR spectra. Thin, vertical lines connect features among the spectra. The main band in MgS is inferred to be a multiplet. Some of the differences are artificially enhanced by low instrumental throughput. (b) Effect of thickness on CaS far-IR spectra. These spectra mostly scale with data on commercial samples. Spectral artefacts near 385 and 440 cm\(^{-1}\) were removed. The absorbance of FeS is high because the films are relatively thick: otherwise the weak peaks could not be observed. The weak peaks below 180 cm\(^{-1}\) are artefacts of low throughput and small amounts of water vapour remaining in the instrument.

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the reflectivity measurements for CaO and MgO (Table 4), suggesting that the values for CaS and MgS obtained from fitting the thin-film data are reasonably accurate.

For FeS, data on the index of refraction are not available because this mineral is opaque in the visible. Two constraints exist. First, the low-frequency dielectric constant does not vary much among the sulphides (Table 4), suggesting that $\epsilon_0$ of FeS is 8.5 to 9. Comparison of the oxides with the sulphides with the same cation suggests that $\epsilon_\infty$ of FeS is roughly 6 to 7. Roughly, the index of refraction of FeS is about 2.6. Secondly, we use existing reflectivity values obtained by comparison with standards in a optical microscope. Such reflectivity values in the visible are available from the literature on ore minerals (mostly opaques, meaning that 30-µm thicknesses are impenetrable to visible light). For wavelengths near 590 nm, the compilation of Peckett (1992) provides $R = 18.4$ per cent for FeO, 11 per cent for $\alpha$-ZnO, 17 per cent for cubic ZnS, 22 per cent for MnS, 44 per cent for PbS, 50 per cent for FeS (troilite), 50 per cent for NiS and 40 per cent for FeS$_2$. The hexagonal minerals are birefringent and the values reported are the average. Some of these values can be checked against the index of refraction data ($\sqrt{\epsilon_\infty}$ in Table 4), which indicates that $R_{\text{vis}} = 15.8$ per cent for FeO, 11.4 per cent for ZnO and 16.5 per cent for ZnS. The match is excellent for ZnO and ZnS. The discrepancy for FeO is probably due to the variable structural chemistry of this mineral (Hazan & Jeanloz 1984), particularly the amount of magnetite exsolved in the wüstites specifically examined for these two different measurements. Because the same type of behaviour occurs for troilite, we infer that its high-frequency reflectivity should also be within a few per cent of the microscope determinations of 40 per cent. Because troilite is an opaque, $k$ is non-zero. For this case, equation (1) gives an upper limit of $n = 4.4$ for FeS in the visible (with $k = 0$). This value is significantly larger than that estimated from trends with chemistry and structure.

### Table 4. Dielectric constants and frequencies (in cm$^{-1}$). Values calculated from the LST relation are in parentheses and boldface. A value near unity in last column indicates adherence to the LST relation (equation 11). Dielectric data are from compilations (Arguello et al. 1969; Boswarva 1970; Cook & Jaffe 1979; Subramanian et al. 1989; Gaines et al. 1997). The $\epsilon_0$-values have uncertainties generally near ±10 per cent, whereas $n$ and $\epsilon_\infty$ are precise. For the other compounds, data are unavailable on $\epsilon_\infty$, but $\epsilon_\infty = 4.796$ for MnO, 5.617 for NiO and 6.200 for CdO, all of which crystallize in the rocksalt structure (Gaines et al. 1997). FeS is opaque, so data on $n$ are lacking.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\epsilon_0$</th>
<th>$\epsilon_\infty$</th>
<th>$\nu_{TO}$</th>
<th>$\nu_{LO}$</th>
<th>$\epsilon_0 / \epsilon_\infty$ ($\nu_{TO}$)</th>
<th>Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>BeO $\perp$</td>
<td>6.87</td>
<td>2.95</td>
<td>724*</td>
<td>1098*</td>
<td>1.013</td>
<td></td>
</tr>
<tr>
<td>BeO $\parallel$</td>
<td>7.66</td>
<td>3.00</td>
<td>680*</td>
<td>1083*</td>
<td>1.007</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>9.83</td>
<td>3.018</td>
<td>409</td>
<td>737</td>
<td>1.003</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>11.95</td>
<td>3.378</td>
<td>300 ± 5</td>
<td>3578 ± 2</td>
<td>0.953</td>
<td></td>
</tr>
<tr>
<td>FeO (14.4)</td>
<td>5.38</td>
<td>325#</td>
<td>534#</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoO</td>
<td>12.9</td>
<td>5.3</td>
<td>349$\parallel$</td>
<td>550$\parallel$</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>NiO</td>
<td>11.9</td>
<td>5.61</td>
<td>401$\parallel$</td>
<td>580$\parallel$</td>
<td>1.01</td>
<td></td>
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<tr>
<td>ZnO $\perp$</td>
<td>8.7</td>
<td>4.052</td>
<td>413$\parallel$</td>
<td>591$\parallel$</td>
<td>1.049</td>
<td></td>
</tr>
<tr>
<td>ZnO $\parallel$</td>
<td>11.3</td>
<td>4.117</td>
<td>380$\parallel$</td>
<td>579</td>
<td>1.182</td>
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<tr>
<td>SrO</td>
<td>13.1</td>
<td>3.28</td>
<td>233 ± 2</td>
<td>484 ± 4</td>
<td>0.93</td>
<td></td>
</tr>
<tr>
<td>BaO (37)</td>
<td>3.57</td>
<td>132$\parallel$</td>
<td>425$\parallel$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\beta$-ZnS</td>
<td>8.37</td>
<td>5.67</td>
<td>510$\parallel$</td>
<td>870$\parallel$</td>
<td>0.990</td>
<td></td>
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<tr>
<td>ZnS $\perp$</td>
<td>8.58</td>
<td>5.55</td>
<td>274$\parallel$</td>
<td>352$\parallel$</td>
<td>0.937</td>
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<tr>
<td>ZnS $\parallel$</td>
<td>8.00</td>
<td>5.65</td>
<td>274$\parallel$</td>
<td>352$\parallel$</td>
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<tr>
<td>CdS $\perp$</td>
<td>8.7</td>
<td>5.29</td>
<td>243$\parallel$</td>
<td>307</td>
<td>1.030</td>
<td></td>
</tr>
<tr>
<td>CdS $\parallel$</td>
<td>9</td>
<td>5.36</td>
<td>234$\parallel$</td>
<td>305</td>
<td>1.052</td>
<td></td>
</tr>
<tr>
<td>PbS (150)</td>
<td>16.8@</td>
<td>71@</td>
<td>212@</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Values by Henning & Mutschke (1997). †Raman data of Arguello et al. (1969). ‡Assumes that LO and TO values of the hexagonal polymorph are valid for the cubic phase. \#Classical dispersion analysis of Geick (1964).

In Table 4, which suggests that either $k$ is significant (~2) or $\epsilon_0$ for troilite is greater than 9.

Reflectivity measurements on polycrystalline FeS (Henning & Mutschke 1997) give $R = 53.5$ per cent at 1000 cm$^{-1}$, which is inconsistent with microscope observations of $R = 40$ per cent in the visible. The excess is attributed to back reflections from the small crystals; see Section 6.4.

### 6.2 Re-analysis of FeO data

The wüstite sample from which IR reflectivity was obtained was synthesized by quenching (Henning & Mutschke 1997) and is polycrystalline (Mutschke, private communication). Grain sizes were not reported. At ambient conditions $R$ of FeO has a minimum near 125 cm$^{-1}$ and rises to lower frequencies (Fig. 10a). A reflectivity

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The rise in absorption coefficient at room temperature and derived functions. (a) Raw re-
Kronig analysis, line, left axis) from Henning & Mutschke (1997). For their Kramers–Kronig analysis, $R$ was assumed to be constant above the measurements. Reflectivity calculated from the classical dispersion fitting parameters in Table 5 is shown as open circles. $R$ calculated from a classical dispersion analysis using their Kramers–Kronig parameters is shown as a dot-dashed line. Classical dispersion analysis gives much lower $R$ at high $\nu$ in order to match $n$ in the visible. The raw data apparently have a secondary reflection. The rise in $R$ as $\nu$ approaches zero is probably also due to back reflections. Absorption coefficients (right $y$-axis) are determined from Kramers–Kronig of Henning & Mutschke (light solid line) and classical dispersion analysis spectrum of single-crystal Fe$_{0.95}$O obtained previously (Bowen, Adler & Auker 1975) resembles Fig. 10(a), but additional weak bands are seen at 300 and 569 cm$^{-1}$, the high-frequency side of the peaks is shifted to longer wavelength, the maximum peak reflectivity is about 10 per cent higher, and the minimum occurs at 270 cm$^{-1}$. Bowen et al. (1975) did not perform a quantitative analysis, so an in-depth comparison cannot be made. Kramers–Kronig analysis by Henning & Mutschke (1997) and previously (Henning et al. 1995), which assumes that $R = 1$ at $\nu = 0$ (Begemann et al. 1995) and that $R$ is constant at frequencies above the data, leads to a value of $n$ in the IR (Fig. 10b) that is larger than the $n = 2.32$ determined for the visible region from optical microscopy (Bowen & Schairer 1935). The high-frequency reflectivity is not correct because strong electronic transitions contribute negligibly to $k$ in the visible, as implied by equation (3) (also see Fig. 2). Only for opaque minerals such as FeS is $k$ affected. Thus $R$ of wüstite is determined by $n$ at high frequency through equation (1). The excess reflectivity at high frequency in the measurements is attributed to reflections from the back surface of the topmost layer of crystals in this polycrystalline sample as schematically shown in Fig. 1. As shown above for MgO, even thicknesses of 1 mm show back reflections in the mid-IR region. Sizes of this order are impossible to obtain through quenching, even thicknesses of 1 mm show back reflections are unavoidable in the polycrystalline samples studied by the Henning group. Consequently, the dielectric and optical functions obtained by Kramers–Kronig analysis (Henning et al. 1995; Henning & Mutschke 1997) err at high frequency.

The upturn in $R$ at frequencies below 125 cm$^{-1}$ is a spectral artefact for similar reasons, leading to $n$ and $k$ being suspect at all frequencies. Work in progress suggests that single crystals with compositions between MgO and Mg$_{0.41}$Fe$_{0.59}$O have constant reflectivity from 50 to 200 cm$^{-1}$. Henning and co-workers extrapolate their trend to $R = 1$ at $\nu = 0$ cm$^{-1}$, assuming that FeO is a free carrier. This assumption is contradicted by previous work. It is true that the electrical conductivity of single-crystal wüstite is high, 10 ohm$^{-1}$ cm$^{-1}$ at room temperature, but neither a Hall voltage nor intrinsic conduction has been observed (Bowen et al. 1975). FeO is thought to be a partially compensated semiconductor where the compensating defects are oxygen vacancies or trivalent impurities (Bowen et al. 1975). Thus the electronic properties depend on the non-stoichiometry of the particular sample. The wüstite prepared by Henning et al. (1995) has 10 per cent Fe$^{3+}$ from wet chemical analysis. The widths of the X-ray diffraction (XRD) peaks were sufficiently large that cell dimensions could not be accurately determined, suggesting a high degree of lattice disorder (Henning et al. 1995). In addition, in polycrystalline wüstites, Fe$_2$O$_3$ is commonly co-precipitated or exsolved (Hazen & Jeanloz 1984). Magnetite exsolution is expected for compositions similar to the sample examined by Henning & Mutschke (1997) (i.e. $x > 0.07$), and occurs rapidly and at scales too fine for detection by X-ray diffraction (Hazen & Jeanloz 1984). The variable structure and chemistry for individual samples and the differences in $R$ between the previous studies cast doubt on the rise in $R$ towards $\nu = 0$ being intrinsic behaviour, but

Figure 10. Re-analysis of FeO reflectivity data at quasi-normal incidence at room temperature and derived functions. (a) Raw reflectivity (thick solid line, left $y$-axis) from Henning & Mutschke (1997). For their Kramers–Kronig analysis, $R$ was assumed to be constant above the measurements. Reflectivity calculated from the classical dispersion fitting parameters in Table 5 is shown as open circles. $R$ calculated from a classical dispersion analysis using their Kramers–Kronig parameters is shown as a dot-dashed line. Classical dispersion analysis gives much lower $R$ at high $\nu$ in order to match $n$ in the visible. The raw data apparently have a secondary reflection. The rise in $R$ as $\nu$ approaches zero is probably also due to back reflections. Absorption coefficients (right $y$-axis) are determined from Kramers–Kronig of Henning & Mutschke (light solid line) and classical dispersion analysis (dotted line). (b) Dielectric functions determined from Kramers–Kronig (solid lines) and classical dispersion (broken lines). Heavier lines indicate $\epsilon_2$. One main peak is seen in $\epsilon_2$; no components are indicated, within the uncertainty of the data. (c) Optical functions determined from Kramers–Kronig (solid lines) and classical dispersion (broken lines). Heavier lines indicate $n$. The filled square is $n$ from optical microscopy. Problems in measured $R$ are apparent from comparing $n$ and $k$ from Kramers–Kronig and classical dispersion analysis at low and high frequency, as well as the value of $n$ in the visible (square).
rather suggest that the behaviour at low \( \nu \) could depend on the impurity content and on the presence of exsolved magnetite or iron metal (typically of \( 0.03 < x < 0.07 \)). More likely, the rise towards low frequency is an instrumental problem in that the pyroxene glass examined by Henning & Mutschke (1997) has a similar rise in \( R \) towards \( \nu = 0 \).

One possibility is inaccuracies in ratioing the sample spectrum to the reference spectrum when the throughput is low. It is not trivial to obtain precise values of \( R \) below 100 cm\(^{-1}\). If a SiC globar was used as the source in this frequency region, its intensity is low. Mercury-arc lamps produce more light at low frequency, but their output is not completely stable, leading to baseline drift. The particular beamsplitter used also has an effect. The broad-range, coated mylar beamsplitters of various thicknesses requires merging multiple segments. In addition to these problems, the rise in \( R \) towards low frequency contains some contribution from back reflections from the small grains because the samples are partially transparent in this frequency region. Therefore at low frequency \( R \) should be flat-lying, as observed for MgO (Fig. 2) and Mg\(_{0.44}\)Fe\(_{0.56}\)O (Fig. 10a), to represent best the lattice dynamics of pure FeO.

To constrain \( n \) and \( k \) of FeO, a classical dispersion analysis was performed. The parameters obtained from the Kramers–Kronig analysis (Henning & Mutschke 1997) lead to a poor match to the reflectivity profile (Fig. 10a), and thus these values are inaccurate. The reflectivity above or below the peak cannot be used to determine the fitting parameters. As a first approximation, we assume that the shape of the strong main IR band represents the intrinsic behaviour of FeO (it is absorbing enough that back reflections are unlikely over the peak). The maximum reflectivity of 70 per cent is less than those of MgO with \( R = 92 \) per cent (Fig. 2a), Fe\(_{0.56}\)Mg\(_{0.44}\)O with \( R = 76 \) per cent (Fig. 10a), CoO with \( R = 80 \) per cent, and NiO with \( R = 90 \) per cent (Gielisse et al. 1965). The trends seem consistent, suggesting that the FeO values near the peak are reasonably correct. We altered the oscillator strength until a reasonable match across the main band was obtained (Fig. 10a). The final TO and LO parameters (Table 5) do not differ much from the Kramers–Kronig analysis of Henning & Mutschke (1997), but the dielectric and optical functions are affected to varying degrees (Figs 10b and c). The calculated \( R \) at \( \nu = 0 \) is 34 per cent, which is compatible with reflectivity data on Mg\(_{0.44}\)Fe\(_{0.56}\)O (Fig. 10a, details to be published elsewhere). The fit is also compatible with the LST relationship (Table 4), as is built into the damped harmonic oscillator model. The classical dispersion fit should therefore reasonably represent FeO, but may not be exact.

### 6.3 Comparison of measured and calculated absorption spectra

Qualitatively, the peak positions from thin films of the diatomic compounds are in generally good agreement with available reflectivity and Raman data (Tables 3 and 4). The small difference between the TO frequencies and the absorption positions (Fig. 9, Tables 3 and 4) suggests that this method documents the intrinsic behaviour (i.e. material properties) of these solids. The absorption peak lies closer to the TO position of ZnO with \( E \perp c \), as is expected because of the larger strength of the bands in this polarization because it is doubly degenerate, whereas bands in \( E \parallel c \) are singly degenerate. Note that the positions for FeO show the greatest disparity. This could be associated with the large amount of scattering or errors in the reflectivity from polycrystalline measurements.

![Ray paths (arrows) in a DAC. The trapezoids are the diamonds, the light grey represents an air gap, and the sample is the stippled grey area.](image)

- **(a)** Empty cell used as the reference. The reflections are caused by a small air gap. Using \( n = 2.387 \) for diamond, \( k = 0 \) in equation (1) gives 16.7 per cent as the ideal reflectance.
- **(b)** Ideal sample sandwiched between the diamonds.
- **(c)** More realistic lumpy surface with cracks, irregular thickness, and sections adhering to both diamonds.

Quantitative comparison of calculated and measured absorption spectra is made through equations (1) and (10). These equations presume that the light reflects upon entering and exiting the sample from a medium (Fig. 1). The situation in the DAC is slightly different (Fig. 11). The empty cell, serving as the reference, has two air–diamond reflections, whereas the loaded cell could have two sample–diamond reflections. However, the thin film is not bonded to the diamond, and an air gap could exist between at least one of the diamonds and the film. The diamond faces are very smooth, whereas the films contain grain boundaries. One approximation would be that the air–diamond reflections are eliminated when the raw data are ratioed to the reference spectrum, leaving air–sample reflections that need to be accounted for. Another approximation would be that the air–diamond and sample–diamond reflections are roughly equal, and thus this effect need not be necessarily be accounted for. However, because the reflectivity for MgO is high and variable (~100 per cent between 400 and 600 cm\(^{-1}\), ~80 per cent between 600 and 740 cm\(^{-1}\), and drops rapidly to either side) which contrasts strongly with the constant reflectivity of air–diamond as 17 per cent, reflections at the sample surface could affect the absorption experiment. We therefore calculated spectra allowing for extra reflections, both sample–diamond and sample–air, for comparison both with the calculated absorbivity and with the thin-film measurements. The results show that the peak position of the film is very close to that of the intrinsic absorption spectra (Fig. 12a) but is altered if reflections are accounted for (Fig. 12b). Reflections both broaden and shift the peak, and in particular increase the effective peak height. Calculated values for the thinner films are most affected by the additional reflections (Fig. 13). Such behaviour is not observed: instead, intensities tend to scale upon thinning (Figs 7 and 8), suggesting that these are essentially absorption spectra.

The lack of a match suggests that equation (10) does not adequately describe the situation. It appears that the intrinsic spectrum (Figs 12 and 13) dominates, but a mismatch exists. The imperfect correspondence (Fig. 12) is attributed to the departure from ideal behaviour in the cell.

(i) The coverage of the diamond tip is not perfect, and the slight amount of light leakage will ‘round’ the top of the peak and decrease the overall absorbance (as shown in Fig. 6). The intensity of the shoulders and weaker peaks will be exaggerated compared with the main peak (Hofmeister et al. 2000), and the profile will be flattened and have lower absorbance than an ideal film (Fig. 6).
(ii) The incident angle is high inside the diamond, owing both to the use of converging light and to the fact that diamond has a high index of refraction. Whilst \( n = 1 \) for air or vacuum, the dielectric constant \( \epsilon_0 \) is 5.7 and \( n = 2.4099 \) at 15 237 cm\(^{-1}\) for diamond (Fontanella et al. 1977), implying that \( n \) is close to 2.387 across the far-IR. Effectively, the diamonds act like lenses, making the relevance of Fig. 1 questionable. The sample, being thin, is also analogous to a coating, which is used in the optical industry to prevent surface reflections.

(iii) The film is not perfectly smooth, so the loss of light may involve scattering rather than the specular reflection effect assumed in deriving Fig. 12.

(iv) The film does not have a uniform thickness, which enhances the shoulder.

(v) Non-normal incidence exaggerates the LO mode (Berreman 1963).

Discerning the microscopic behaviour is difficult because some of these effects compete: for example, light leakage lowers the absorbance from intrinsic values whereas a reflection raises it, and excitation of the LO mode raises \( a \) for the high-frequency side of the peak. However, the imperfect correspondence of Fig. 12 is most likely connected with light leakage (compare Figs 6b and 12b) and also with the surface roughness of the sample (which reduces the reflectance) compared with the smoothness of the diamond and the focusing effect. Fig. 11(c) probably best describes the sample, which touches both diamonds, with some air gaps and some light leakage. Thus, equation (10) provides excessive reflection. A smaller amount than the ideal, roughly 10 per cent, and a mixture of sample–air and sample–diamond reflections would provide a better match. The spectrum is also affected by the light leakage depicted in Fig. 7. The excess intensity on the high-frequency side is ascribed to the non-normal incidence. MgO, with its broad peak and strong LO mode,
is a worst test case (Fig. 12) with its extreme changes in $R$ across the peak (Fig. 2) and with the reflectivity being high near the LO mode, but the absorbance being moderate, rather than strong. It is also the hardest of the materials studied, which makes it difficult to obtain an even film without cracks. The comparison for FeO (Fig. 13) with lower $R$ and less contrast (Fig. 10), and a little softer, is better, but the reflectivity data are uncertain. Much better agreement is seen for CaO which has a narrower peak, and is soft: see below. Excellent agreement was seen for garnets (Hofmeister 1995). These complex silicates have 13 bands with widths about 1/10th those of the oxides, and thus the reflectivity is only high where the sample absorbs strongly.

The thicknesses created by compression are tenths of a µm to 1 µm, as ascertained by transmission electron microscopy measurements of garnet samples (Hofmeister 1995). The films are too thin to be removed without damage, and so thicknesses cannot be reliably determined from comparison with a microscope reticle. From relief observed visually in a binocular microscope, all films prepared in this study have thicknesses below 1 µm. The lack of precise correspondence of calculated and measured spectra does not allow film thickness to be ascertained exactly from comparison. However, the above discussion suggests that the rough comparisons in Figs 12 and 13 are valid. The thicknesses of the MgO films are estimated to be 0.5 µm, consistent with visual observations, and a small amount of reflection.

Similar relationships exist between the absorption data on FeO and the classical dispersion calculation (Fig. 13). Specifically, the profiles from a calculation that assumes no exit reflection best match the data, and film thicknesses of about 0.15 and 0.4 µm are suggested for the two films. However, the peak maximum of the film occurs at a higher frequency than the calculation, which did not occur for MgO. Perhaps the difference in peak positions represents a larger amount of reflection for FeO. For FeO, a strong peak is seen above the LO position. Assuming that the peak at 564 cm$^{-1}$ is the LO mode and that the TO mode occurs at 15 cm$^{-1}$ below the thin-film peak gives a reasonable value for $\epsilon_0$ from the LST relation (Table 4). These values may be just as valid as the classical dispersion analysis, given the obvious problems with the reflectivity data obtained from polycrystalline material. Providing exact values for the peak parameters and for the optical functions of FeO will require single-crystal reflectivity measurements.

6.4 Assessment of FeS reflectivity data

The thin-film measurements show that the peaks of FeS are weak. It is difficult to resolve the features in the thin samples, whereas increasing the thickness mainly increases the baseline (owing to high overall reflectivity) without enhancing the peaks (Fig. 8). Our data are consistent with the essentially featureless spectrum obtained from a dispersion (Nuth et al. 1985), because in a dispersion, light leakage can overwhelm such small absorption features. Reflectivity measurements in the visible provide $R = 40$ per cent (Peckett 1992), which is much lower than $R > 53$ per cent at 1000 cm$^{-1}$ determined by Henning & Mutschke (1997). This discrepancy at high $v$ is clearly due to back reflections, which exist in the transparent spectral regions of our reflectivity measurements of thick (1 mm) MgO crystals. Henning & Mutschke (1997) did not report the grain sizes of their FeS sample, but such a synthesis by quenching would provide grain sizes closer to µm than to mm. It is clear that the high-frequency region of FeS has enhanced reflectivity because of secondary reflections (Fig. 1).

![Figure 14. Comparison of measured absorbance of FeS (solid black lines) with that calculated for a thickness of 0.5 µm using Kramers–Kronig analysis (heavy black line) of reflectivity data (grey line, right y-axis, Henning & Mutschke 1997). The thin films are less than 1 µm thick, from relief. The positions of the absorption features agree well, but the calculations overestimate the strengths by about four-fold.](image)

Our absorption data imply that problems exist in the previous reflectivity data at low frequency as well. Comparing FeO and FeS absorption spectra in the far-IR (Figs 7 and 8) suggests that the reflectivity of these samples should behave the same at low frequency. Free-carrier absorption is unlikely to be the cause of the rise in $R$ towards low frequency.

Although the maximum value of $R$ obtained for the main IR peak of FeO appears to be correct (cf. Figs 10 and 13), the same behaviour is not necessarily true for FeS. For FeO, $R$ ranges from about 5 to 70 per cent, whereas $R$ of FeS ranges from about 40 to 60 per cent. The smaller range in $R$ is consistent with the peaks being weak, and further suggests that the reflectivity across the entire spectrum could be artificially enhanced by back reflections. Such problems were seen by Long et al. (1993), who compared optical functions obtained from reflectivity of single crystals and pressed powders of calcium carbonate and calcium sulphate. This inference is confirmed by comparing the data sets (Fig. 14). Peaks in $R$ occurring at 230, 255 and 295 cm$^{-1}$ for FeS at room temperature (Henning & Mutschke 1997) correspond well with the peaks from the thin-film measurements (Table 3). The shoulder in $R$ at 200 cm$^{-1}$ is not resolved in the thin-film measurements at room temperature. This feature is close to the level of noise in the reflectivity data, and may not be real. This correspondence of reflectivity and absorbance suggests that the reflectivity spectrum of FeS (Fig. 14) is a mixture of absorption and reflection, as occurred for the weak overtone-combination bands at high frequency of MgO (Fig. 4). Fig. 1 shows the process schematically. This superposition enhances the features in the reflectivity, giving overly large intensities in the absorption spectrum calculated from Kramers–Kronig analysis. Fig. 14 shows the absorbance calculated for $t = 0.5$ µm, compared with the measurements on two different films with thicknesses of 1–2 µm. Even if the films are as thin as 0.2 µm, the previous calculations still provide excessively large absorbance. The positions are in good agreement for the three well-resolved bands below 300 cm$^{-1}$ (>33 µm). In contrast, the broad peak extending from 370 to almost 600 cm$^{-1}$ obtained from Kramers–Kronig (Henning & Mutschke 1997) is not present in any
of the six absorbance measurements on two different samples of troilite. In fact, a depression is seen over this frequency range in some of our spectra (Fig. 8c). This band is not evident in the raw reflectivity data, and we conclude that this feature between 17 and 30 µm is a spectral artefact, probably induced by back reflections and the use of constant R as an extrapolation of the data to high frequency.

The n- and k-values extracted by Kramers–Kronig analysis by Henning & Mutschke (1997) clearly err. This inference is corroborated by the large values of about 6 so obtained for n, whereas equation (1) sets an upper limit of n = 4.4 in the visible (for k = 0) from independent observations of R. Lower values of about 2.5 for n are seen for the compounds FeO, ZnS and CdS, but these compounds are more transparent. If the lower n holds also for FeS, then k is substantial in the visible, not near 0 as derived by Henning & Mutschke (1997).

Given the uncertainty in the thickness of the thin film of FeS, and the likelihood of back reflections pervasively altering the reflectance data, we cannot extract the optical functions using either Kramers–Kronig or classical dispersion analyses. Reflectivity data on larger crystals are needed.

6.5 Comparison with previous absorption spectra of iron sulphides and oxides

Keller et al. (2002) provide mid-IR absorption spectra of the diatomics examined here, pyrrhotite (Fe1−xS) and magnetite (Fe3O4). Their data are at odds with the thin-film far-IR spectra, and give overly large absorption strengths compared with those extracted from reflectance data (Henning & Mutschke 1997). This difference in absorption strengths can be attributed to Keller et al. (2002) not applying the correction of Shankland et al. (1979). This correction (equation 10) is particularly important for FeS, as R is large. However, omitting the correction is unlikely to create the pronounced peaks reported for FeS and pyrrhotite, although it could create a weak peak. Moreover, absorption strengths obtained from the reflectance data were shown above to be too large, and thus additional problems exist in the FeS and FeO absorption spectra reported by Keller et al. (2002). To probe the source of the discrepancies, we collected mid-IR data from the above minerals as well as from pyrite (FeS2).

The pyrrhotite spectra (Fig. 15), like that of troilite, show no evidence of an extremely broad band from about 400 to 600 cm−1. Pyrite has a fairly narrow bands at 600 and 1644 cm−1 and overlapping peaks at 1000 and 1200 cm−1. The pyrite structure contains S2 dimers which should be active in the mid-IR, and probably produce the higher frequency modes. Pyrite peak widths are similar to those of the iron oxides. Our thin-film data on sulphides do not provide evidence of extraordinarily broad bands for these phases in the mid-IR (Fig. 15) or in the far-IR (Fig. 8c).

Our wüstite (FeO) spectrum has a shoulder at 560 cm−1 on the main band at 363 cm−1 (Figs 7c and 13), whereas the FeO spectrum of Keller et al. (2002) consists of a single peak at ~550 cm−1 on a flat lying baseline. Our spectra were collected from a thickness of about 0.2 µm. Keller et al. (2002) do not provide thickness or absorbance values, but state that the sulphides have τ < 0.2 µm. The spectra of FeO should thus be equivalent, and we conclude that their main, far-IR peak of FeO was removed during baseline subtraction by Keller et al. (2002).

For magnetite, four IR bands are observed in the far-IR (Fig. 7c), as expected from symmetry analysis (Chopelas & Hofmeister 1991; Hofmeister & Mao 2001). The pattern of two strong and two weak bands is typical for the IR spectra of minerals with the spinel structure. The highest frequency band occurs at 570 cm−1, and is similar in position and width to the LO mode of FeO (Fig. 7c). (Probably the similar peak positions in FeO and Fe3O4 reflect similar atomic motions and bonding.) This band and the other moderately strong band in magnetite at 353 cm−1 are seen in the spectra of Keller et al. (2002), although the 353 cm−1 band is lower in intensity. It is likely that their spectral profile of the 353 cm−1 band was altered because it occurs at the limit of detection. The two weak bands at 421 and 479 cm−1 were not detected by Keller et al. (2002). This comparison corroborates the assumption that problems exist below 500 cm−1 in the absorption spectra of Keller et al. (2002). Because differences exist between all four minerals in the same frequency range, the mismatch with our sulphide spectra is not due to slightly different samples being examined (e.g. from differences in Fe3+ content, vacancies, disorder or polytypism), but is related to experimental technique.

We ascribe the extraordinarily broad features reported in FeS and pyrrhotite to spectral artefacts. Baseline subtraction is probably the major cause. Another contributing factor may be use of carbon films to support their samples. Carbon is both highly reflective and absorbent, like FeS. The surface reflections (equations 1 and 10) would thus depend on frequency and may contribute to spectral artefacts. A third consideration is that KBr beamsplitters have low throughput below 500 cm−1, which can create problems near the end of the spectral range. Fourthly, it is highly likely that the detector was saturated and responding in a non-linear fashion to intensity input. Although a small aperture of 32 × 32 µm2 was used by Keller et al. (2002), the synchrotron beam is intense. Mid-IR detectors are prone to saturation, which can occur even if only a small spot on the detector element is flooded with light. A low overall throughput does not guarantee that detector response is linear over the whole frequency range. Saturation was avoided in the present study by use of wire mesh screens to reduce throughput or by restricting

![Figure 15](image-url)
the aperture near the source. The phase correction spectra were examined in all cases to ensure that saturation had indeed been avoided. Because the throughput of our relatively dim globar was too much, even when a DAC was used which reduces throughput by a factor of 1000, one might reasonably conclude that a bright synchrotron source requires special measures to avoid saturation.

Because no peak exists for iron sulphides in the vicinity of 25 \( \mu \)m, identification of this material in protoplanetary discs is predicated on a match with the weak features of troilite near 250 cm\(^{-1}\) (Figs 8c and 14). Of the objects examined by Keller et al. (2002), only M2-43 has features in this region, but these are at or barely above the noise level. The spectral match is unconvincing.

6.6 Estimated optical constants for CaO, CaS and MgS

In principle, absorption data from a known thickness, corrected for reflections (equation 10), can be fitted using a classical dispersion analysis (equations 4 and 5). The other input is the index of refraction in the visible (\( n_{\text{vis}}^2 = \epsilon_{\infty} \)). An additional constraint could be provided by values of \( \epsilon_0 \), but such data seem unavailable for MgS or CaS. Data for \( \epsilon_0 \) of CaO are available (Table 4), along with reflectivity measurements (Jacobson & Nixon 1968; Galtier, Montaner & Vidal 1972). Because we found these sources after classical dispersion analysis had been carried out, and because the oscillator strengths were not reported, we fit the thin-film data and compare the resulting parameters with the previous reports.

For CaO, the film thickness was ascertained by comparison with thick-film data (Fig. 7b). For CaS and MgS, thicknesses are estimated as about 1 and 0.75 \( \mu \)m, respectively, by comparison with results for the oxides (Figs 7, 12 and 13). These are rough numbers. The fit is made by scaling the spectrum to correspond to \( t = 1 \mu m \) and to provide the true absorbance. This allows direct comparison with the calculated absorption coefficient.

Good fits were obtained for all substances (Fig. 16). The results are consistent, in that fitting the peak resulted in structure near the inferred position for the LO component. Relevant parameters (given in Table 2) must be considered as estimates for MgS and CaS. However, the results for CaO should be fairly accurate because thickness could be constrained through comparison with spectra obtained from a \( t = 6 \mu m \) film. The parameters are not affected by changing the thickness by 20 per cent, which is roughly the uncertainty in \( t \). The resulting frequencies for CaO (Table 2) are within a few cm\(^{-1}\) of those obtained from reflectivity of single crystals (Table 4). The uncertainty given in Table 4 is derived from the range of reported frequencies (Jacobson & Nixon 1968; Galtier et al. 1972): our results for the LO mode are slightly high, and as a result \( \epsilon_0 \) is high, cf. Tables 2–4. If we had altered the damped harmonic oscillator parameters to fit the low-frequency dielectric measurements of Jacobson & Nixon (1968), better agreement would have been obtained for the LO mode. As is, our results are within 1.2 per cent.

Results for MgS and CaS are less accurate, as thickness is uncertain and because the spectrum consists of two overlapping bands. The spectrum for MgS appears to have a baseline problem at the high frequency, probably due to high reflectance. Even with these problems, for frequencies above about 1200 cm\(^{-1}\), the results for \( n \) and \( k \) (Fig. 17) are independent of the peak parameters, but instead are determined by \( n_{\text{vis}} \). The results suggest that if the thin-film thickness for MgS could be determined from interference fringes or if the reflectance at high frequency could be minimized by collecting data from a thicker film, then fitting the absorption spectra would set a limit on \( n \) in the visible, and better constrain \( k \).

The peaks of CaO, CaS and MgS are narrower than those of MgO and FeO, resulting in a better match of ideal absorption coefficients with the measurements. The better match is largely due to the reflectivity and absorptivity being high over the same frequency interval. An additional factor is that the CaO and the sulphides are soft, which is conducive to preparing thin, even films. The existence of multiple, overlapping peaks contributes some uncertainty to the fits, but is of less importance. We conclude that materials such as silicates with relatively narrow peaks, and which are frequently softer than MgO, would provide absorption spectra closer to intrinsic values.
6.7 Effect of temperature

MgO reflectivity has been obtained from 8 to 1950 K (Jasperse et al. 1964) and analysed using the classical dispersion model (Kachare et al. 1972). However, the data at room temperature vary slightly from the present results (Fig. 2), which is probably due to alignment or resolution problems with the dispersive technology used at that time. The main IR band was assumed to consist of one strong peak and one shoulder, whereas our analysis indicates that four poorly resolved peaks are present (Tables 1 and 2). Neither were the previous data adequately fitted by two oscillators. An additional problem is that high resolution is needed to measure the steep pro-
ductions may cause these inconsistencies. Undersampling rounds the peaks. Therefore the temperature response of MgO deduced by Kachare et al. (1972) has some degree of associated uncertainty. The measurements show that, for both peaks, the frequencies decrease as temperature increases (dv/dT = −0.0186 cm⁻¹ K⁻¹), whereas the damping coefficients and oscillator strengths increase. All parameters depend linearly on T. The product of $\Gamma$ and $f$ causes the peaks in $k$ (and also the absorption peaks) to become less intense as temperature increases. This deduction is consistent with the trend in reflectivity wherein the main peak becomes shorter and broader as T increases. Such behaviour is expected. As T increases, more states are populated and the number of phonon–phonon scattering events increases, leading to larger widths. The number of Mg–O dipoles producing the main IR band should be unaffected as it is the ground state, and thus the area under the peak should remain the same. The broader peaks must therefore be shorter. If the population of the main band does increase, as is possible at very low temperatures, then the band area and height could increase as temperature increases.

The reflectivity data of FeO and FeS with temperature (Henning & Mutschke 1997) may be problematic as these involve measurements of polycrystals. Specifically, the raw data indicate that the maximum R of FeO decreases as T increases, consistent with the behaviour of MgO, but the FeO peaks become narrower, and the TO position is constant (in both raw R data and derived functions). Frequency being independent of T is consistent with finite thermal expansivity, particularly in that the IR band of diatomic solids involves stretching and compression of the cation–anion bond. Moreover, wüstite and MgO have nearly identical values of the thermal expansivity (e.g. Fei 1995) and thus their frequencies should shift at about the same rate. Errors in the absolute value of R due to secondary reflections may cause these inconsistencies. Undersampling due to low resolution is a contributing factor, and this effect probably explains the small degree of change in R for the pyroxene sample and the glasses examined in the same study (Henning & Mutschke 1997). It is particularly revealing that the main band decreases in both intensity and breadth as T increases. Although the intensity decrease is compatible with the behaviour of MgO (Jasperse et al. 1964), the width decrease is not. Moreover, simultaneous decreases in intensity and width require that the vibrational energy states become decreasingly populated at T increases, which is incompatible with statistical thermodynamics. We did not try to use classical dispersion to obtain optical functions from the reflectivity measurements at low temperature because data on n in the visible at cryogenic temperatures may be needed to constrain the results. Single-crystal reflectivity data on FeO and FeS at temperature, and probably measurements of $n(T)$ or of $R(T)$ in the visible, are needed for accurate determination of the optical functions at temperature of these materials.

![Figure 18. Emissivity of MgO at room temperature for various grain sizes. Black lines = calculations based on classical dispersion analysis (light solid line = thickness of 0.1 μm; light dots = t of 0.2 μm; light dashes = 0.5 μm; heavy solid = 1 μm; heavy dots = 2 μm; heavy dashes = 5 μm; long dashes = 10 μm). Grey lines = calculations from measured absorbance of a 100-μm crystal (dashes = t of 100 μm; dots = 50 μm). For grain sizes above about 20 μm, the overtone bands contribute to the emissivity. For grain sizes of about 2 to 10 μm, the emissivity is roughly unity over the peak and minimal elsewhere. For grain sizes 1 μm or below, the emission peak strongly resembles the absorption profiles.](https://example.com/fig18)

6.8 Calculation of emissivity and emissions

Equation (7) provides emissivity. From Fig. 2, ideal absorptions for MgO obtained from Kramers–Kronig and classical dispersion analyses are nearly identical. Because back reflections may be present near 1000 cm⁻¹, the synthetic spectra are used to compute ε. The emissivity mimics absorption spectra at low grain sizes (Fig. 18). For larger grains, emissivity is pinned at unity for the absorbing region, and extends into the overtone combination region for the largest grains (submillimetre sizes). Higher temperatures would cause additional broadening, whereas cryogenic features would be narrower than those presented here. The peak shifts expected are relatively small.

Emission spectra are a convolution of the emissivity and Planck’s blackbody curve. If the grains are only MgO, then the emission spectra for temperatures above 200 K are quite similar to the emissivity with the intensity being highly temperature-dependent (Fig. 19). Below 200 K, the higher frequency side of the emissions is truncated by the decrease in blackbody radiation: only the TO mode is manifest. The peaks shown in Fig. 19 are broader than expected at cryogenic temperatures, because room-temperature spectra were used in the calculation. However, a distribution of temperatures among the dust grains would also cause peak broadening, and thus the results of Figs 18 and 19 should be relevant.

Grain sizes larger than 1 μm would provide broader emission spectra at 298 K and above, whereas below 200 K the blackbody function would dominate as shown in Fig. 19. Smaller grain sizes would provide emission spectra that more closely resemble absorption spectra from samples of the same grain size. Another complicating factor is the possibility of temperature gradients within the
could be identified in the TO positions, whereas for large grains the data and thus the amount of reflection is lower, consistent with the non-normal incidence and some surface roughness of the films. However, this effect is most pronounced in the transparent regions and near the LO mode, where the sample reflects, and it is weakly absorbent. The mismatch of ideal and measured absorption worsens as the LO–TO splitting increases, as the frequency interval of high reflectivity with low absorbance increases concomitantly. As the LO–TO splitting depends on the band strength, the Si–O stretching band at 10 μm and the bending mode near 20–25 μm could be affected by these problems, but the low-frequency, weak modes of silicates should not. Spectra collected from dispersions have similar problems to the thin-film data. This method is useful as the conditions in space involve distributions of particles. However, laboratory spectra and astronomical data differ in several important ways. Foremost, the processing differs. In laboratory experiments light is forced through some sort of aperture, and the raw data are ratioed to a baseline involving this aperture, whereas astronomical data are processed by subtraction of a baseline. Thus the artefacts induced by light leakage shown in Fig. 6 (which is equivalent to mismatching the apertures, or ratioing to an inappropriate baseline) will not as strongly affect observational data, but will affect laboratory measurements from dispersions more than measurements from thin films. For well-dispersed dust in space with various grain sizes, the largest, opaque particles will simply reduce the overall throughput in the observational data, and the signal received is either that which misses the grains or light that is partially absorbed by the smaller grains. The features will essentially scale, although rounding of the strongest peaks will be seen because each dust particle provides a range of thickness. Because large grains (≥ 1 μm) in dispersions can induce artefacts, comparisons with astronomical data should be made using dispersions with fine grain sizes. The lack of parallel surfaces in space also means that secondary reflections are weaker than that predicted by the equations here. Therefore the thin-film data with minimal reflections are appropriate. This can be met by merging spectra from films of varying thicknesses (i.e. obtaining data in the transparent regions from thicker films). Dust peaks in observational data will occur at the same positions as the ideal absorption spectra, and the higher frequency side of the peaks will be stronger than the ideal. The angle of incidence is essentially normal, so the LO modes should not be as prominent as in the thin film. The peak absorbance should roughly indicate the optical depth of the dust.

Dense dust clouds with large particles can have the same spectral artefacts as seen for the thicker films, and as schematically indicated in Fig. 6. Interpretation of the features based on comparison is less robust in the optically thick regime. For the oxides, with one strong peak, special conditions of fairly uniform and fine grain sizes are needed for a definitive identification. The spectral signatures of MgS and CaS, with their relatively narrow peaks, should be easier to recognize in astronomical data.

Emission peaks should not be as prey to artefacts, and the calculations based on ideal absorption coefficients should provide the appropriate comparison. As discussed above, the temperature of the object determines which vibrations are excited, and affects the width and intensity of the peaks.

7 SUMMARY AND CONCLUSIONS

Interpretation of observed astronomical spectra is made through comparison with laboratory data. The correctness of an interpretation is predicated on the observational and laboratory data being

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**Figure 19.** Emission spectra of MgO. Dots = temperatures of 298 K; dashes = 200 K; light solid line = 100 K, but intensity is scaled by x10; Heavy solid line = 50 K, scaled by x10^5. The second peak at 50 K is due to the finite reflectivity at low frequency, coupled with the steep climb for Planck’s blackbody function. The calculation presumes that the emissions are solely due to MgO grains.
collected under similar conditions. We cannot control the conditions in space (temperature, dust density, grain size, phase and chemistry), and thus it is imperative that we understand the effect such variables have on laboratory measurements in order to gauge the relevance of the laboratory spectra to the astronomical environment. This paper not only presents new optical data on oxides and sulphides, but also provides methods to ascertain the accuracy of such measurements. Analysing IR spectra in detail reveals the limitations inherent in laboratory data. In particular, the absolute values of $n$ and $k$ and the positions of absorption features can be compromised by sampling techniques. Understanding these issues allows astronomers to be able to judge whether imperfectly fitted observed spectra are due to variance of the conditions in the laboratory from those remotely probed, or to the presence of different phases.

Specifically, new reflectivity data on MgO at room temperature are cross-checked against existing independent dielectric measurements at low frequency and measurements of the index of refraction in the visible. Secondary reflections were found to exist even for very large thickness (~1 mm) over frequency regions where the sample essentially transmits, and for the ideal conditions of a nearly perfect polish on only one side. The Kramers–Kronig analysis of the raw data was therefore used as the starting point for fitting the spectrum to a series of damped harmonic oscillators. Such a classical dispersion analysis provides the optical functions, dielectric functions, absorption coefficients and emissivity from the far-IR to the visible. Above about 25 000 cm$^{-1}$, the tail of strong, metal–oxygen charge transfer bands affects the values of $k$, and the classical dispersion results are no longer valid. The same approach was applied to previous reflectivity data on FeO (Henning & Mutschke 1997). Because of the small grain size, spurious reflections affect the results at low as well as high frequencies. We presume that the region of strong absorbance is not affected, but single-crystal measurements are needed to confirm this. For FeS, with its weaker peaks, $R$ from polycrystals appears to be corrupted at all frequencies, so that the functions extracted from the available measurements have substantial errors, particularly in $n$ and $k$ at high frequency, and in overly large absorption band strengths. Inference of FeS in protoplanetary objects based on these $R$-values and problematic absorption data (Keller et al. 2002) is not well founded.

The diatomic solids studied here, with their one strong IR band, represent an extreme of behaviour because the high reflectivity near the absorption peak contrasts strongly with the low baseline reflectivity at high and low frequency. Reasonable agreement was obtained between the thin-film measurements and calculated spectra for MgO and FeO which have broad bands, and good fits could be obtained to the absorption data of the compounds with narrower peaks (CaO, CaS and MgS), suggesting that ideal spectra will represent dust features of polyatomic compounds in astronomical environments, e.g. complex oxides and silicates. Only the strongest peaks (such as the Si–O stretching bands near 10 μm) may be altered from the ideal by light leakage and surface reflections. None the less, under certain conditions, even the broad bands of simple oxides and sulphides can be distinguished. Fine grain sizes, well dispersed in an optically thin cloud, should provide spectra closely resembling the intrinsic absorption or emissions of the phase.

ACKNOWLEDGMENTS

This work is supported by NSF–AST–9805924. We thank N. Johnson (Washington University) for providing synthetic powders of MgO and FeS, and for dehydrating the samples. We thank T. C. Hoering, I. Kushiro and B. Mysen (Geophysical Laboratory) for synthesiz-

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