High-pressure Raman spectroscopic studies of FeS$_2$ pyrite

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We report micro-Raman spectroscopic studies of FeS$_2$ pyrite in the diamond-anvil cell under hydrostatic and non-hydrostatic conditions to 55 GPa at room temperature. Four out of five Raman-active modes are resolved with helium as a pressure-transmitting medium to highest pressures. The fifth mode, $T_g(2)$ [377 cm$^{-1}$], is weak and unresolved lying ~2 cm$^{-1}$ from the intense $A_g$ mode [379 cm$^{-1}$] at 1 bar. We observe an increase in the separation of the $E_g$ [344 cm$^{-1}$] and $T_g(1)$ [350 cm$^{-1}$] modes under compression. All observed frequencies increase continuously with increasing pressure showing no evidence for a structural phase transition in accord with both X-ray diffraction and shock-wave studies. The $A_g$ and $T_g(1)$ modes gain significantly in intensity relative to the $E_g$ mode with increasing pressure probably resulting from Raman resonance effects. The $T_g(3)$ mode [430 cm$^{-1}$] broadens unusually compared to the other pyrite modes with pressure. The Raman data are consistent with a contraction of the S–S and Fe–S bonds under pressure. The main effect of non-hydrostatic conditions on the Raman modes is a strong pressure-induced broadening; the pressure-dependence of the frequencies and relative intensities are not affected within the error of the measurements.

KEYWORDS: FeS$_2$, pyrite, Raman spectroscopy, high pressure, diamond-anvil cell.

Introduction

The transition metal dichalcogenide FeS$_2$, pyrite, is the most abundant of the sulphide minerals and common in a variety of geological environments. Strong geophysical interest in its physical and chemical properties under high pressures and high temperatures has arisen in the context of the Fe-S system’s possible role in core formation, evolution and composition. It motivated studies of the equation of state (EOS) of pyrite, its structural stability, elasticity and shear strength (e.g. Merkel et al., 2002; Ahrens and Jeanloz, 1987; Jephcoat, 1985). Pyrite appears structurally stable to the highest pressures and temperatures: static compression experiments to 50 GPa and shock compression data to 320 GPa yielded no evidence for a structural phase transition in this mineral. Ahrens and Jeanloz (1987) suggested that the stability of FeS$_2$ pyrite might be due to the low-spin 3d-orbital configuration of Fe$^{2+}$. Diamond-anvil cell studies have shown that the EOS of pyrite depends strongly on the degree of non-hydrostatic stress in the sample (Merkel et al., 2002; Jephcoat, 1985). This study of pyrite is also motivated by interest in its electronic properties and the archetypal nature of dichalcogenides. FeS$_2$ pyrite is a semiconductor with an indirect band gap between occupied and unoccupied states of ~0.9 eV (e.g. Ferrer et al., 1990). Its electronic properties are strongly influenced by a complex interplay of largely covalent S–S bonds and mainly ionic Fe–S bonds (Cervantes et al., 2002). The possible use of pyrite as a solar cell and solid-state battery material has stimulated numerous theoretical and experimental studies of its electronic properties, in particular of its band gap (Cervantes et al., 2002; Ophahle et al., 1999; Eyert et al., 1998). In the most recent study, Cervantes et al. (2002) demonstrated with optical absorption spectroscopy that the indirect energy gap of pyrite decreases at a rate of 1.13(9) × 10$^{-2}$ eV/GPa with increasing pressure remaining.

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indirect to at least 28 GPa. Linear extrapolation of the decrease of the band gap to pressures above 28 GPa yielded a band gap closure and hence metallization pressure of 80(8) GPa.

The structure of FeS$_2$ pyrite is cubic, space group Pa3 with four formula units per unit cell (e.g. Stevens et al., 1980). The Fe atoms occupy the sites of a face-centered cubic sublattice and the S atoms are arranged in dumb-bell pairs along <111> directions located at the mid-points of the cube’s edges and body centre. Each Fe atom is coordinated by six nearest-neighbour S atoms in a distorted octahedron and each S atom is bonded to three Fe and one other sulphur atom forming a distorted tetrahedron. The FeS$_6$ octahedra are linked by corner sharing. The pyrite structure is fully characterized by the lattice constant $a = 5.4160(2)$ Å and the Wyckoff parameter $x = 0.385$ Å. The number and symmetries of the Raman and infrared-active modes of pyrite have been predicted using group theoretical methods (Lutz and Willich, 1974). The irreducible representation of the vibrations of FeS$_2$ pyrite is $\Gamma = A_g + E_g + 3T_g + 2A_u + 2E_u + 6T_u$. The gerade vibrations ($A_g + E_g + 3T_g$) are all active in the first-order Raman spectrum; the ungerade modes $5T_u$ are infrared active whereas the $(2A_u + 2E_u)$ modes and the rigid lattice translations ($T_u$) are optically inactive. The Raman active modes comprise one totally symmetric mode ($A_g$), one doubly degenerate mode ($E_g$), and three triply degenerate modes ($T_g$). The $A_g$ and $T_g(2)$ mode correspond to in-phase and out-of-phase stretching vibrations of the S$_2$ dumb-bells, respectively (Fig. 1). In the $E_g$ librational mode the S atoms are displaced perpendicular to the S–S bond axis. $T_g(2)$ and $T_g(3)$ correspond to various librational and stretching motions or their combinations (Sourisseau et al., 1991). The Raman-active modes involve only movements of the S atoms, and therefore the phonon frequencies give information on the forces determining the stretching and librational motions of the S$_2$ units.

Ambient Raman and IR spectra of FeS$_2$ pyrite have been published (e.g. Mernagh and Trudu, 1993; Anastassakis and Perry, 1976; Ushioda, 1972). Vogt et al. (1983) were the first to report a complete, ambient Raman spectrum of FeS$_2$ from polarized Raman measurements with four different scattering configurations. Light-scattering studies of opaque minerals at high-pressure are rare. Takahashi et al. (1985) reported a positive pressure dependence of the $A_g$ and $E_g$ Raman mode of FeS$_2$ to 4.8 GPa and no Raman spectroscopic characterization of pyrite has been performed at pressures >5 GPa. We have recently shown that Raman scattering can be applied to high-pressure metallic phases in the 100 GPa range using the diamond-anvil cell (DAC) (Olijnyk and Jephcoat, 1999). Here we investigate the vibrational properties of natural iron pyrite with micro-Raman spectroscopy in the

**FIG. 1.** Displacement vectors for the five Raman-active modes of FeS$_2$ pyrite (after Sourisseau et al., 1991). Small, filled circles represent Fe atoms and the larger, hollow circles, the S atoms.
DAC to 55 GPa, comparing measurements made under hydrostatic conditions with helium as a pressure-transmitting medium and non-hydrostatic conditions (no pressure-transmitting medium) in order to determine any possible influence of the applied stress state on the vibrational properties of FeS$_2$. We also report the use of Zn as an internal pressure gauge in optical experiments.

**Experiment**

Two high-pressure micro-Raman spectroscopic experiments were performed on natural FeS$_2$ pyrite. In the ‘hydrostatic’ run an ~12 µm thick chip of a single-crystal of FeS$_2$, ~20 × 30 µm in size, was mounted in a diamond-anvil cell together with a 10 µm diameter ruby sphere for pressure calibration (Mao et al., 1978). Culets of 400 µm diameter compressed a fully hardened T301 stainless steel gasket preindentated to 40 µm with a 110 µm drilled hole. Fluid helium was loaded at 0.2 GPa (Jephcoat et al., 1987) as a pressure-transmitting medium to ensure the best possible hydrostatic conditions. In a second, non-hydrostatic run a fine-grained powder sample was prepared by grinding pyrite crystals under ethanol. Culets of 300 µm in diameter and a stainless steel gasket preindentated to 35 µm with a 100 µm hole formed the sample chamber. Compacted pyrite powder was loaded without a pressure-transmitting medium in order to maximize the stress gradient across the sample. In this non-hydrostatic run we placed a 2.5 µm thick and 20–25 µm wide Zn-foil strip on top of the pyrite powder across the centre of the hole (Fig. 2) to utilize the Raman-active $E_{2g}$ mode of Zn as a pressure sensor (see below). Unpolarized Raman spectra to 51 GPa (hydrostatic run) and 55.2 GPa (non-hydrostatic run) were measured in 135º scattering geometry with a SPEX Triplemate equipped with a back-illuminated liquid-N$_2$-cooled CCD detector. Data were recorded for both increasing and decreasing pressure, and in the non-hydrostatic run at the centre and the edge of the sample chamber. The spectra were excited by the 514.5 nm line of an argon-ion laser focused to a 5 µm spot on the sample (with powers low enough to avoid heating the sample) and collected through a spatially-filtering (confocal) aperture giving high spatial resolution at the sample. The intrinsic resolution of the spectrometer is 1.5 cm$^{-1}$ and calibrations are accurate to ±1 cm$^{-1}$.

**Zinc as an optical pressure sensor**

Olijnyk et al. (2000) reported the pressure dependence of the Raman-active doubly degenerate $E_{2g}$ phonon mode of Zn to 58 GPa at 300 K using a diamond-anvil cell and the ruby fluorescence method as pressure scale. The $E_{2g}$ mode of Zn is a single, sharp and intense line at 71.1 cm$^{-1}$ at ambient conditions. With increasing pressure this mode shifts to higher wavenumbers without significant intensity loss. No phase transition is known or expected to occur in the 100 GPa range. The measured frequency-pressure data of the $E_{2g}$ mode can be expressed as

$$P = \frac{\delta_0}{\delta_0} \left( 1 - \left( \frac{\nu(P)}{\nu_0} \right)^{-\delta_0/\delta_0} \right)$$

where $\nu_0 = 71.1$ cm$^{-1}$, $\delta_0 = (\partial \ln \nu / \partial P)_{\nu_0} = 0.05315$ GPa$^{-1}$, and $\delta_0 = -0.00728$ GPa$^{-2}$ (Olijnyk et al., 2000) and provides a useful alternative to the ruby pressure scale for optical studies. The measured $E_{2g}$ frequencies are determined within ±0.2 cm$^{-1}$, corresponding to ±0.05 GPa at 1 GPa and ±0.2 GPa at 55 GPa. The properties of the $E_{2g}$ mode of Zn make the metal an ideal secondary pressure sensor with

![Fig. 2. View into the DAC through the cylinder diamond onto the non-hydrostatic pyrite powder sample with a Zn foil strip as pressure marker at 55.2 GPa in the centre of the sample chamber. The colourful pattern of birefringence develops when the diamond-anvils are stressed under pressure in polarized light.](image-url)
distinct optical advantages especially in non-hydrostatic experiments. The metal does not contribute any broad-band emission to the Raman measurement and is optically clean. Furthermore, the frequency shift of the Zn phonon mode is insensitive to non-hydrostatic conditions and its half width remained <12 cm\(^{-1}\) at pressures up to 55 GPa in the non-hydrostatic pyrite run. The \(E_{2g}\) mode of Zn was separated by >250 cm\(^{-1}\) from the modes of the FeS\(_2\) sample and did not interfere to the highest pressures. At various points across the sample, the Zn and FeS\(_2\) modes were recorded together in one spectrum giving a precise local pressure (Fig. 3).

**Results**

**Hydrostatic run**

The ambient Raman spectrum of FeS\(_2\) pyrite agrees well with previously published data (Table 1) (Mernagh and Trudu, 1993; Vogt et al., 1983). Four modes are observed. The \(A_g\) and \(T_g(2)\) mode occur \(\leq 2\) cm\(^{-1}\) apart (Vogt et al., 1983) and cannot be resolved in the present

![Raman spectrum showing the modes of the Zn pressure marker and the pyrite sample under non-hydrostatic compression at 22.5 GPa.](image)

**Fig. 3.** Raman spectrum showing the modes of the Zn pressure marker and the pyrite sample under non-hydrostatic compression at 22.5 GPa.

**TABLE 1.** Ambient Raman frequencies of the FeS\(_2\) and their full width at half maximum (FWHM) under hydrostatic and non-hydrostatic compression. A comparison with literature data including mode assignment is given.

<table>
<thead>
<tr>
<th>(v_i) (cm(^{-1}))</th>
<th>Hydrostatic FWHM (cm(^{-1}) at 51 GPa)</th>
<th>Non-hydrostatic FWHM (cm(^{-1}) at 55.2 GPa)</th>
<th>Symmetries and assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Present study</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>344</td>
<td>3.2</td>
<td>9.2</td>
<td>(E_g), S(_2) libration</td>
</tr>
<tr>
<td>350</td>
<td>2.7</td>
<td>9.2</td>
<td>(T_g(1)), coupled libration and stretch</td>
</tr>
<tr>
<td>379</td>
<td>4.5</td>
<td>10</td>
<td>(T_g(2)), S–S out-of-phase stretching</td>
</tr>
<tr>
<td>430</td>
<td>4.8</td>
<td>57*</td>
<td>(A_g), S–S in phase stretching</td>
</tr>
<tr>
<td>Vogt et al. (1983)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>343</td>
<td>30</td>
<td></td>
<td>(T_g(1)), coupled libration and stretch</td>
</tr>
<tr>
<td>350</td>
<td>377</td>
<td></td>
<td>(T_g(2)), S–S out-of-phase stretching</td>
</tr>
<tr>
<td>379</td>
<td>379</td>
<td></td>
<td>(E_g), S(_2) libration</td>
</tr>
<tr>
<td>430</td>
<td>430</td>
<td></td>
<td>(T_g(3)), coupled libration and stretch</td>
</tr>
</tbody>
</table>

* at 39.6 GPa; at higher pressures the mode was a flat feature not easily fitted with a single peak (Fig. 4)
unpolarized, high-pressure Raman study. We observe a variation in the relative intensities of the Raman modes with changing orientation of the crystal relative to the incident laser beam, but this does not reveal the Tg(2) mode. The spectra show only one peak at 379 cm\(^{-1}\) agreeing with the reported frequency of the A\(_g\) mode. The underlying Tg(2) mode does not influence the fitted A\(_g\) peak position because its intensity is weak compared to the intensity of the A\(_g\) mode that dominates the spectrum. Under compression to 51 GPa, all modes shift continuously to higher frequencies (Figs 4, 5). Above 10 GPa, some spectra (e.g. at 14.9, 20.1 and 30.8 GPa) do show a weak and broad shoulder on the high-frequency side of the A\(_g\) mode. This shoulder seems to shift faster to higher frequencies than the A\(_g\) mode itself, but no pressure dependence can be established as it is not uniformly observed. The pressure dependence of the Tg(1) mode is larger than that of the E\(_g\) mode (2.91 cm\(^{-1}/\text{GPa}\) compared to 2.80 cm\(^{-1}/\text{GPa}\)) leading to an increasing separation between them with pressure. The intensity of the E\(_g\) mode decreases relative to the intensity of the A\(_g\) and Tg modes with increasing pressure (using 514.5 nm laser excitation and fixed sample-to-laser beam orientation) particularly above 30 GPa. The full width at half maximum (FWHM) of the FeS\(_2\) modes increases from 3--5 cm\(^{-1}\) to ~10 cm\(^{-1}\) at 51 GPa (Fig. 6, Table 1). The Tg(3) mode broadened more strongly and became a flat feature not easily fitted with a single peak at pressures above 40 GPa. We cannot exclude a splitting of the

Fig. 4. Selected Raman spectra of FeS\(_2\) pyrite with solid helium as the pressure-medium as a function of increasing pressure at 300 K. The ambient Raman spectrum was collected outside the DAC. Data are unsmoothed and no background was subtracted; rising background at higher wavenumbers is caused by the fluorescence of the diamond anvils and the internal scatter from the ruby.

Fig. 5. Pressure dependence of the Raman modes of pyrite with helium as the pressure-transmitting medium. Errors in both frequency and pressure are within the size of the symbol. All modes were fitted with a weak quadratic term for the whole pressure range. For the Tg(3) mode, only data up to 40 GPa are given because its weakness and large half width (>50 cm\(^{-1}\)) at higher pressures do not allow us to determine its frequency reliably.
triply degenerate $T_g(3)$ mode due to the possible presence of small, non-hydrostatic stresses in the solid helium at pressures $>12$ GPa. Table 2 gives the pressure derivatives and mode Grüneisen parameters. The mode Grüneisen parameters $\gamma_{iT} = \frac{\partial \ln v_i}{\partial \ln V}$ were obtained from fitting the $\ln v_i(P)$ vs. $\ln V(P)$ values linearly. The $V(P)$ values were taken from Jephcoat (1985) using a Birch-Murnaghan equation of state with bulk modulus $K_T = 133.5$ GPa and its pressure derivative $K'_T = 5.73$.

Non-hydrostatic run

The most obvious effect of non-hydrostaticity on the Raman spectrum of pyrite is the strong pressure-induced broadening of all modes (Fig. 7, Table 1). This substantial broadening of the modes leads to peak overlap and therefore lower resolution than in the hydrostatic run. The $E_g$ and $T_g(1)$ modes are unresolvable at all pressures. We observe only one symmetric peak at a frequency that corresponds to the frequency of the more intense $E_g$ mode in the hydrostatic run. With increasing pressure, the $A_g$ and $T_g(3)$ mode gain in intensity relative to the $E_g$ mode as is observed with helium as the pressure medium. Frequency-pressure data were collected from two different spots of the pyrite sample, close to the centre of the sample chamber and close to the edge of the gasket hole, in order to check for possible effects of different, local stress conditions on the FeS$_2$ modes and their pressure dependence. No detectable difference between the data collected at the centre and the edge of the gasket hole, either in the pressure dependence of the frequencies (Fig. 8) nor in the half widths of the modes was observed. Furthermore, the pressure dependence of the mode frequencies under non-hydrostatic and hydrostatic conditions agrees remarkably well within the errors of both measurements (Fig. 8, Table 2). The frequencies and half widths of the FeS$_2$ modes exhibit no hysteresis on pressure release and the ambient Raman spectra before and after the pressure application are identical.

**Table 2.** Pressure dependence and mode Grüneisen parameters of FeS$_2$ pyrite under hydrostatic and non-hydrostatic compression.

<table>
<thead>
<tr>
<th>$v_i$ (cm$^{-1}$)</th>
<th>Hydrostatic run to 51 GPa</th>
<th>Non-hydrostatic run to 55 GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\left(\frac{\partial v_i}{\partial P}\right)_{T}$ (cm$^{-1}$/GPa)</td>
<td>$\gamma_{i0}$</td>
</tr>
<tr>
<td>344</td>
<td>2.80p–1.21 × 10$^{-2}$p$^2$</td>
<td>1.36</td>
</tr>
<tr>
<td>350</td>
<td>2.91p–1.20 × 10$^{-2}$p$^2$</td>
<td>1.39</td>
</tr>
<tr>
<td>379</td>
<td>3.10p–1.20 × 10$^{-2}$p$^2$</td>
<td>1.40</td>
</tr>
<tr>
<td>430</td>
<td>3.43p–8.36 × 10$^{-3}$p$^2$*</td>
<td>1.42</td>
</tr>
</tbody>
</table>

* to 39.6 GPa
Discussion and summary

The present study shows a continuous increase of all observed Raman frequencies of pyrite to the highest pressure of 55 GPa. There is no indication of a structural phase transition in FeS$_2$ in accord with high-pressure X-ray diffraction and shock-wave data (Merkel et al., 2002; Ahrens and Jeanloz, 1987; Jephcoat, 1985). The mode Grüneisen parameters are very similar for all observed modes with the average mode Grüneisen parameter $\gamma_i = 1.39$ being close to the value of the thermal Grüneisen parameter of 1.59 (Ahrens and Jeanloz, 1987). The effect of pressure on the bond lengths in pyrite, S–S, Fe–S and Fe–Fe, is of fundamental interest regarding the properties of the band gap of FeS$_2$. Eyert et al. (1998) showed, based on first-principles calculations that small changes in the S–S bond length strongly influence position and width of the optical band gap. The observed positive pressure dependence of the stretching and librational mode frequencies of pyrite suggests a pressure-induced contraction of the S–S and Fe–S bonds, respectively. The frequency increase of the in-phase S–S stretching frequency ($A_g$) under compression is in accord with a shortening of the S–S bond length, because this stretching vibration is mainly determined by the S–S force constant (Lutz and Zwinscher, 1996). As the librational mode ($E_g$), and the coupled librational and stretching modes ($T_g(1,3)$), are largely governed by the Fe–S force constant (Lutz and Zwinscher, 1996; Sourisseau et al., 1991), a pressure-induced increase in their mode frequencies agrees with a shortening of the Fe–S bond under compression. The effect of pressure on the S–S and Fe–S bond lengths in pyrite has been investigated previously with direct structural and theoretical methods: Fujii et al. (1986) reported single-crystal XRD data of FeS$_2$ to 4.2 GPa, and Sithole et al. (2003, 1999) calculated pressure-dependent bond lengths in pyrite. Both studies yielded a decrease in the S–S and Fe–S bond length under compression. On the other hand Will et al. (1984) reported a lengthening of the S–S bond from an energy-dispersive powder XRD experiment up to 40 GPa. The present, positive pressure dependence of the Raman modes of pyrite is compatible with a contraction of the S–S and Fe–S bond under compression. Non-hydrostatic conditions do not influence the pressure-induced frequency shifts of the Raman modes of iron pyrite within the experimental errors.

The striking gain in intensity of the $A_g$ and $T_g(1)$ modes relative to the intensity of the $E_g$ mode with increasing pressure is probably caused by inter-band resonance effects. Above band-gap (>0.9 eV) resonance Raman scattering from FeS$_2$ pyrite was first reported by Macfarlane et al. (1974). The authors observed a near order of magnitude increase in the intensity of the $A_g$ mode on tuning the incident Ar$^+$ laser energies from 2.41 eV (514.5 nm) to 2.73 eV (454.6 nm). By coincidence, we also observe a near order of magnitude increase in the intensity ratios $I(A_g/E_g)$ and also $I(T_g(1)/E_g)$ by compressing FeS$_2$ to 51 GPa and probing with 514.5 nm excitation. Hence, to first order, pressure moves the resonance to lower energies, from ~2.73 eV at 1 bar to ~2.41 eV at 51 GPa. Macfarlane et al.
suggested that the resonance Raman scattering in FeS$_2$ is mainly caused by two direct inter-band electronic transitions occurring at 2.47 and 2.85 eV. Assuming that these inter-band transitions underlay the pressure-induced enhancement of the $A_g$ and $T_g(1)$ intensity too, then the energy separation of the inter-bands involved in the resonance effect decreases with pressure, shifting the resonance towards lower excitation energies. Investigations of resonant Raman scattering of FeS$_2$ pyrite under pressure are underway and further study into the 100 GPa range, where metallization is expected, would also be worthwhile.

Acknowledgements

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