

X-Ray Absorption at High Pressure

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Initial measurements are reported on the extended x-ray-absorption fine structure (EXAFS) of the Fe *K* edge in FeS₂ to 64 kbar and FeF₂ to 21 kbar. With this new technique the Fe-Fe spacings are directly observed to vary in accordance with high-pressure x-ray diffraction measurements of the corresponding lattice parameters. In contrast, the Fe-S spacing in pyrite is found to be much less compressible. Pressure reduction of the mean-square deviations in the iron-ligand bond lengths are also given.

Pressure, as a fundamental thermodynamic variable, has long been of importance in studying phases of matter. Much of the current high-pressure research is particularly directed toward the production and study of new phases¹ (e.g., superconductors, superhard materials, lower mantle structures, and metallic hydrogen). Typical methods used in conjunction with high pressures have been electrical resistance, x-ray and neutron diffraction, as well as optical, Mössbauer, and magnetic resonance spectroscopy.

Here we report the first x-ray absorption spectroscopy at high pressures, and stress the utility of the extended x-ray-absorption fine structure (EXAFS) that characteristically appears within about 100 eV above an x-ray absorption edge.²⁻⁴ In this Letter we present high-pressure measurements on bond compressibilities and atomic spacings in FeS₂ and FeF₂. While these crystalline substances could also have been studied by single-crystal x-ray diffraction⁵ or neutron diffraction⁶ it is important to note that the present technique could be applied equally well to liquids, or to amorphous materials like glasses, polymers, etc., at high pressure. Thus we demonstrate a technique with wide applicability for study of the effect of pressure on the chemical bond.

In the present experiments high pressure was generated by the modified Bridgman-anvil method.⁷ The sample, a thin uniform film, approximately 0.3 mm × 0.7 mm, was mounted in a gasket of boron and lithium hydride. The sample area was thus parallel to the anvil axis but perpendicular to the collimated x-ray beam. Pressure calibration was based upon fixed-point electrical resistance discontinuities of bismuth samples in separate runs, but with identical geometry. The EXAFS experiments were all performed at room temperature at the Stanford synchrotron radiation laboratory (SSRL). Because of small sample size and relatively high attenuation of the x rays by the pressure-cell gasket (Fe *K* edge ≈ 7 keV),

we chose to use the high intensity of the new focused beam apparatus, available at SSRL for x-ray energies below 10 keV. It is estimated that our effective photon count was ~ 10⁸/sec with a bandwidth of ≈ 6 eV. Approximately 10 min were required for a single spectrum, several of which were obtained at each pressure.

X-ray absorption spectra of FeS₂ and FeF₂ at 21 kbar are shown in Fig. 1(a) and the background-corrected EXAFS, converted to wave number by the standard method,³ in Fig. 1(b). To a good approximation the EXAFS may be expressed as^{3,4}

$$\chi(k) = \sum_j (N_j / k R_j^2) |f_j(k)| \exp(-2\sigma_j^2 k^2) \times \sin[2kR_j + 2\delta_j(k)].$$

Here *k* is the photoelectron wave number, *R_j* is the distance from the absorbing atom to the *j*th shell of *N_j* neighboring atoms, $|f_j(k)|$ is an effective backscattering amplitude from shell *j*, and $\delta_j(k)$ is an associated phase shift. The factor $\exp(-2\sigma_j^2 k^2)$ contains the root-mean-square fluctuations, σ , in the distances *R_j*. By Fourier analyzing the EXAFS data one determines the radial distribution function⁴ as shown in Fig. 1(c). From this one is able to discern changes in the neighboring shell positions versus pressure [Fig. 2(a)]. It should be recognized that there are several alternative ways of arriving at the radial distributions in Fig. 1(c). This fact, coupled with uncertainties in obtaining atom positions from a given radial distribution, leads one to make a conservative estimate of the error bars in Fig. 2(a), which are equivalent to ~ ± 0.02 Å. (Under optimum circumstances the method is capable of at least an order of magnitude higher precision.)

In pyrite the Fe atoms form a face-centered cubic lattice while in FeF₂ they define a body-centered tetragonal lattice. In either case, the positions of ligand atoms, S or F, are defined

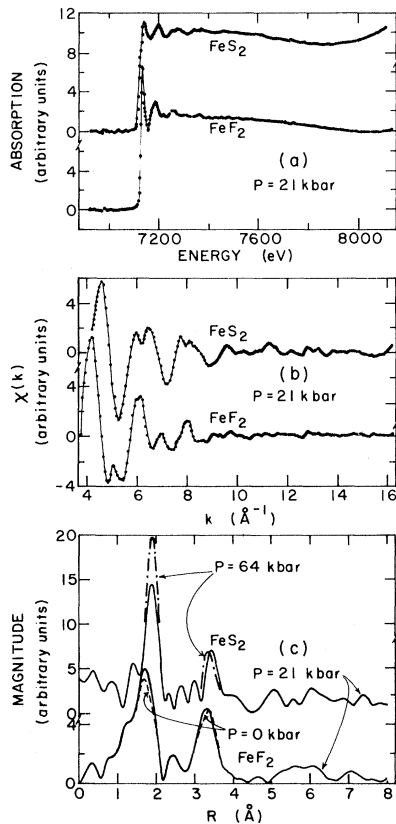


FIG. 1. (a) Fe K -edge x-ray absorption coefficient of FeS₂ and FeF₂ at 21 kbar. (b) The EXAFS from (a) plotted as a function of the photoelectron wave number. (c) Solid curve, magnitude of the Fourier transform of the 21-kbar data of (b). Broken curves, data at other pressures.

by a single coordinate, in addition to the lattice parameters. The results for the Fe-Fe bond distances in both materials compare well with those deduced from powder x-ray diffraction measurements of the corresponding lattice parameters.^{8,9}

Of more interest here, however, are the nearest-neighbor Fe-S and Fe-F distances, which as seen above are not required to scale with the unit cell, as are the Fe-Fe spacings. In Fig. 2(a) it is evident that the pyrite Fe-S bond is considerably less compressible than the unit-cell edge, reflecting strong covalent character. Conversely, in order to preserve the cubic symmetry, this behavior implies that the S-S molecular bond contracts at a rate which is roughly an order of magnitude greater than that of the unit-cell edge, approaching the high bond compressibility of pure sulfur itself. Thus, in our measurement described here, the determination of the Fe-Fe and Fe-S distances gives a complete description of

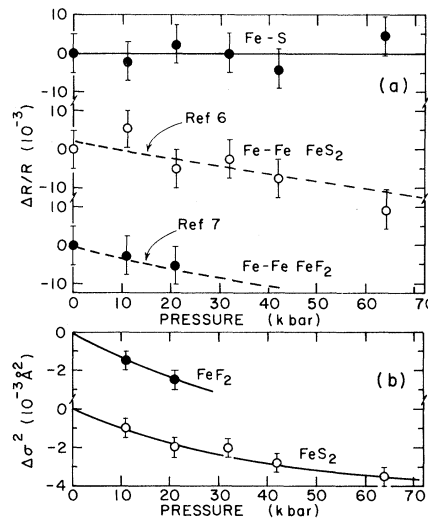


FIG. 2. (a) Fractional change in the atomic spacings as a function of pressure compared with x-ray diffraction results from the unit-cell dimensions from Refs. 6 and 7 (dashed lines). (b) Pressure-induced changes in the mean-square deviation of the nearest-neighbor bond lengths in FeF₂ and FeS₂. Solid lines indicate the trend of the data.

the pyrite structure's pressure dependence. Complete information of this type at high pressures can also be obtained from single-crystal x-ray diffraction⁵ or time-of-flight neutron diffraction⁶ studies. However, the EXAFS method can, in principle, be extended to the much higher pressure regions enjoyed by x-ray powder diffraction work (which generally only yields high-pressure lattice parameters), and is not limited to crystal-line substances.

In the case of FeF₂, there are two nearest-neighbor Fe-F distances. These differ by ~ 0.1 \AA and are presently unresolved in Fig. 1(c). (Experimental difficulties prevented us going to higher pressures.) However we note that this unresolved first-shell peak height increases with pressure while its width decreases. There exists a method⁴ for analyzing such changes in a peak in the radial distribution function by comparing samples under different conditions (e.g., temperature, pressure, crystal modification, etc.). That technique is to plot the logarithm of the ratio of the inverse Fourier transforms of the peak of interest under the various conditions. When plotted versus k^2 the slope gives the difference in the mean-square deviations $\Delta\sigma^2$ for the atom pair contributing to the peak.

The above procedure has been applied to the first-shell peaks for both compounds [Fig. 2(b)].

As in Fig. 2(a), the estimated errors are a result of uncertainties inherent in the transform procedure plus uncertainties in measuring the above slope. The decrease in σ^2 observed for FeF_2 is roughly twice that expected if the parameter u specifying the intracellular F position remains constant. Neutron diffraction results indicate such to be the case in the similar material NiF_2 .¹⁰ Thus although a decrease in the static disorder contributes partially to $\Delta\sigma^2$ in FeF_2 , thermal disorder undoubtedly contributes as well.¹¹ In the case of FeS_2 , the observed decrease in $\Delta\sigma^2$ must be entirely due to decreased thermal disorder since there is one near-neighbor bond length. In both cases the measurements are in reasonable agreement with crude estimates based upon the Debye-Grüneisen approximation.

In the above discussion we have focused on structural information from the EXAFS part of the x-ray absorption spectrum. The near-edge portion of the x-ray absorption spectrum (within 50 eV of the edge) contains information on the local *electronic* structure, namely the character of the lowest unoccupied single-particle and excitonic states. The pressure dependence of these near-edge regions will be reported elsewhere. Because of their nature, the interpretation is necessarily less straightforward than the EXAFS results presented above. Pressure-induced changes in the near-edge region are best observed with the finer resolution in the near-edge region are best observed with the finer resolution (≈ 1 eV) available with SSRL's other EXAFS beam lines.

In this preliminary x-ray absorption spectroscopy at high pressures we have found new information about materials even though they were already rather well characterized. Clearly similar experiments with liquids, amorphous or biological samples, and new high-pressure-induced phases, as well as with normal solids, will yield a wealth of new information. The technique is relatively simple and will undoubtedly see extensive use as more sources of continuous, intense x rays, such as synchrotron radiation facilities,

become available.

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¹Good reports on recent work are found in the following: *Proceedings of the Fourth International Conference on High Pressure, Kyoto, 1974*, edited by J. Osugi (The Physics-Chemical Soc. Japan, Kyoto 1975); *Proceedings of the Fifth International Conference on High Pressure Science and Technology, in High Temp.-High Press.* **7** 603 (1975); C. W. F. T. Pistorius, *Prog. Solid State Chem.* **11**, 1 (1976).

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