Pressure-induced high-spin to low-spin transition in FeS evidenced by x-ray emission spectroscopy

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We report the observation of the pressure-induced high-spin to low-spin transition in FeS using new high-pressure synchrotron x-ray emission spectroscopy techniques. The transition is evidenced by the disappearance of the low-energy satellite in the Fe K\(_\beta\) emission spectrum of FeS. Moreover, the phase transition is reversible and closely related to the structural phase transition from a manganese phosphide-like phase to a monoclinic phase. The study opens new opportunities for investigating the electronic properties of materials under pressure.

The study of the electronic structure of highly correlated transition metal compounds has been an important subject in condensed-matter physics over the last several decades. The theoretical phase diagram proposed by Zaanen, Sawatzky, and Allen is one of the key steps leading to a better understanding of the materials. In addition to the on-site d-d Coulomb interaction (\(U\)) employed in the original Mott-Hubbard theory, the ligand-valence band width (\(W\)), the ligand-to-metal charge-transfer energy (\(\Delta\)), and the ligand-metal hybridization interaction (\(T\)) are explicitly included as parameters in the model Hamiltonian. This classification scheme has been very successful in describing the diverse properties and some seemingly contradicting behavior of a large number of these compounds. However, these high-energy-scale charge fluctuations are primarily characteristic of the elements involved, and thus cannot be freely adjusted for systematic study of their effects, although they can be varied somewhat by external temperature and magnetic field. On the other hand, pressure can introduce much larger perturbations of these parameters than can either temperature or magnetic field. Hence, it is of great interest to study the high-pressure behavior of these systems, and specifically, to correlate observed transformations with changes in electronic structure.

Unfortunately, high-pressure electronic structure studies have been severely handicapped because only a few standard spectroscopic techniques are compatible with high-pressure cells. Despite rapid developments in synchrotron-based x-ray spectroscopy, there have been limited investigations at high pressure beyond a few x-ray absorption studies that have focused mainly on local atomic coordination and structure. This limited study is due to the strong attenuation of x-ray photons below 10 keV through the pressure cell (e.g., diamond anvils), the energy range that covers all the 3d transition element K absorption edges, the 4f rare earth L absorption edges, and the 5f actinides M absorption edges, as well as their characteristic emission lines. This problem can be overcome by the use of beryllium as a gasket material in diamond anvil cells, and allowing both the incident and transmitted/scattered photons to pass through the low absorbing Be gasket instead of diamond. With this technique, the usable x-ray energy range can be extended to include the important spectral region from 3 to 10 keV, making possible a wide variety of x-ray spectroscopic studies of the electronic structure of materials under pressure.

Here we present a study of the high-spin to low-spin (HSLI) transition in FeS using new high-pressure, high-resolution x-ray emission spectroscopy (XES) techniques. Under ambient pressure, FeS is an anti-ferromagnetic insulator (\(T_N=598\text{K}\)) and has a NiAs-related (troilite) structure. More importantly, FeS falls at the boundary between charge-transfer and Mott-Hubbard insulators in the ZSA phase diagram (\(\Delta < U\) and \(U\) relatively small), so that its electronic structure is far more complicated, and has been very controversial. Pressure-induced structural phase transitions in FeS have been extensively studied, in part because the material is considered to be a major component of the cores of terrestrial planets. FeS undergoes two structural phase transitions at ambient temperature, from the NiAs-related to a MnP-related structure at 3.5 GPa, and then to a monoclinic phase at 6.5 GPa. The latter transition is further accompanied by an abrupt shortening of the \(c\) parameter from 5.70 Å to 5.54 Å. Conventional Mössbauer spectroscopy experiments have shown that the structural transition at 6.5 GPa is accompanied by the disappearance of the magnetic moment-induced hyperfine splitting. Resistivity measurements also hinted a possible insulator to semimetal transition at 3.5 GPa, and perhaps even a metallic phase above 7 GPa. We report the observation of a HS–LS transition in FeS under pressure. The spin state...
of the Fe in FeS is monitored by high-resolution measurement of the Fe Kβ emission line. The emission spectrum of HS Fe is characterized by a main peak with energy of 7058 eV, and a satellite peak located about 12 eV lower in energy. When the pressure exceeds 6.9 GPa, the satellite vanishes, indicating the transition to the low spin-state with the collapse of the Fe 3d magnetic moment.

The experiments were carried out at the X25 hybrid wiggler beamline at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The beamline consists of a Pt-coated double-focusing mirror located upstream of a two-crystal monochromator. Collimated by 150 µm from the detector produced an energy resolution of about 1.2 eV at 7 keV. Two-dimensional scans were carried out to ensure accurately measured lineshapes [7]. The emission spectrum was then reconstructed by extracting the maximum of intensity in the detector scan at each Bragg angle. Typical collection times were about 90 minutes per spectrum.

High-purity FeS was loaded into a diamond cell together with 4:1 mixture of methanol-ethanol as pressure medium [17]. The diamond-cell gasket was initially a 5 mm diameter by 1 mm thick Be foil. The pressure was measured by the ruby fluorescence technique. In order to reduce background signal, the incident white beam was collimated by 150-50 µm water-cooled 1 mm thick Ta slits. The slit assembly was in turn mounted on a water-cooled copper block located in front of the cell, which was oriented vertically so that both the incident and collected x-rays passed through the Be gasket. The emitted x-rays were detected at a 90° scattering angle to further reduce background signal. To evaluate the signal from the Be gasket (known to contain small amount of Fe impurities), a spectrum measured 150 µm from the sample was subtracted from that measured at the sample position.

Figure 1 shows the Fe Kβ XES of FeS between ambient pressure and 11.5 GPa. All spectra show a main peak located at 7058 eV, usually referred to as the Kβ1,3 line. More importantly, a well-defined satellite located at 7045.5 eV, denoted Kβ′ in the following, appears only in spectra measured for pressures below 6.3 GPa. The satellite intensity disappears in spectra for pressures ranging between 6.3 and 11.5 GPa. The width of the main line also shows significant narrowing in this pressure range. The spectrum taken at 6.1 GPa shows intermediate behavior between these two groups of spectra. It is probably due to the pressure gradient in the sample, which is estimated to be less than 0.5 GPa. Moreover, the observed changes are reversible as the pressure reduced back to ambient.

To illustrate the pressure-induced effects more clearly, the intensity of the satellite as a function of the applied pressure is shown in Fig. 2. The intensity of the 7045.5 eV satellite of each spectrum was determined by subtracting the spectrum at 11.5 GPa (with no satellite) and fitting the resulting profile with two Voigt functions (at 7045.5 and 7056 eV). The difference spectra are shown in the inset of Fig. 2. In addition to the satellite peak in the difference spectra, a peak around 7056 eV is observed, which is also a signature of the HS state (as discussed below). Although the position and intensity of this peak are subject to some uncertainty due to the subtraction procedure, the peak disappears around 7 GPa (like the 7045.5 eV satellite). From Fig. 2, a reversible transition occurs between 6.0 GPa and 7.0 GPa. Since the uncertainty in pressure due to the relaxation processes and the pressure gradient in the cell is about 0.5 GPa, the observed change thus coincides with the pressure of 6.5 GPa at which the magnetic splitting disappeared in the Mössbauer measurement. Notably, there is no appreciable change in the satellite intensity at 3.5 GPa, the pressure corresponding to the NiAs- to MnP- related structural phase transition.

To interpret the observed spectral changes, a brief review of the theory of Kβ x-ray emission spectra is given. The Kβ emission lines are characteristic x-ray lines originating from the 3p→1s decay. For a large number of transition metal compounds, the Kβ spectra has been interpreted using atomic multiplet calculations and configuration interaction. It is now widely accepted that the spectral shape of Kβ emission line for these compounds is dominated by final state interaction between the 3p core hole and the electrons of the partially filled 3d shell. Qualitatively, the main effect is due to the exchange interaction between the core hole and the local moment, which results in splitting of the Kβ spectrum into HS and LS final states. This simple picture also predicts that the energy separation between the two peaks is given by the product of the exchange integral J and (2S+1), where S is the total spin of the 3d shell; and that the intensity ratio between the two is given by S/(S+1) [18]. Both the energy splitting and intensity ratio are modified when configuration interaction is taken into account [19]. These calculations show that the 3p3d final state is characterized by a single peak that constitutes most of the intensity of the main emission line. On the other hand, the 3p3d final state is further split into two components, one at significantly lower energy than predicted by simple theory and one at slightly lower energy than the main emission line (3p3d) which appears as a shoulder. However, the simplified picture does point out the qualitative changes expected for the 3d electrons going from HS to LS states, namely smaller energy splitting between the main peak and the satellite as well as a reduction in the satellite to main peak intensity ratio.
The above theoretical approach has been successfully applied to the interpretation of the Kβ emission spectra of a number of Mn [20, 22], and Fe [23, 24] compounds recently. The sensitivity of the Kβ₁,3 emission lineshape to the spin state of the system is demonstrated Fig. 3, where the Fe Kβ₁,3 line from FeO and FeS₂ are shown. These spectra were recorded at ambient pressure, and the nominal oxidation state is +2 for Fe in all three compounds; however, Fe is in the HS state in FeO and in the LS state in FeS₂. Note the pronounced satellite structure in the Kβ spectrum of FeO, and the lack of a satellite feature for FeS₂. Detailed inspection shows that there is a small shoulder on the low energy side of the main peak for FeO, indicating the presence of the small HS component discussed above. On the other hand, the main peak for FeS₂ is narrower and more symmetric, suggesting that in addition to the disappearance of the low energy satellite, the higher energy HS component is absent as well. These two examples clearly show that the spectral shape of the Kβ emission line can be used to characterize the spin state of the transition-metal ions in these systems.

We can now describe more precisely the pressure induced electronic transition in FeS. Under ambient condition, Fe in FeS is considered to be divalent with a HS electron configuration \((t_{2g}^3e_g^2t_{2g}^1)\). This result is now well established through both Mössbauer spectroscopy and magnetic susceptibility measurements [10]. The Mössbauer spectra clearly indicate divalent Fe. The isomer shift of +0.76 mm/s found in FeS is consistent with Fe²⁺ in the HS configuration, which is further confirmed by the large effective moment (estimated to be 5.5 \(\mu_B\) by magnetic susceptibility measurements [10]). In the LS state \((t_{2g}^3e_g^2t_{2g}^1)\), the two final states of the Kβ emission line, \(3p^3↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑↑∪
For the relatively low Bragg angles used in these measurements, the accurate tracking of analyzer and detector was crucial because misalignment between the two can cause an apparent reduction in intensity, thereby modifying the measured emission lineshape. For each Bragg angle, the detector was scanned over a range of 600 µm.

Pure polycrystalline FeS was synthesized from high-purity Fe metal and sulfur (both 99.999+%) in evacuated silica tubes. It was annealed at 675 K for several days until all of the sulfur reacted with the iron. The tubes were then transferred to 1275 K and annealed for one week before quenching rapidly in an ice-water bath. The homogeneity and purity of the sample was confirmed by electron microprobe analysis. A slight excess of iron was included to remain in the troilite side of the phase diagram and to insure that the material is stoichiometric.

Although possible metallization was suggested in Ref. 14, only a slight increase in resistivity with increasing temperature was measured.

FIG. 1. Fe XES in FeS as function of pressure. The spectra were normalized with the intensity of the main peak set to unity, and aligned so that the (pressure independent) energy of the main peak is set to 7058 eV. At low pressure, the satellite at 7045.5 eV is characteristic of the high-spin state (solid line) whereas the absence of satellite at high pressure denotes the transition to the low-spin state (dotted lines). The dashed line shows an intermediate spectrum obtained on decompression at 6.1 GPa. The sequence of pressures was 1.25, 2.0, 2.7, 3.5, 6.3, 7.5, 10.0, 11.5, 8.2, 6.9, 6.1, 5.2, 1.4, and 0.2 GPa.

FIG. 2. Integrated intensity of the structure in the satellite region of the spectra shown in Fig. 1 obtained from a Voigt profile fitted to the difference spectrum upon compression (circles) and decompression (squares). The intensity was calculated from the difference spectra obtained by subtracting the 11.5 GPa spectrum from each scan (inset). The pressure in the inset follows from top to bottom the loop as indicated in the caption to Fig. 1 and given on the left-hand side of the inset. The second peak in 7056 eV region is distorted by the subtraction procedure; consequently its intensity is not shown. Spurious peaks in the K\textsubscript{\beta} shoulder at 7058 to 7062 eV arise from uncertainties associated with the subtraction procedure. The solid line is a guide to the eye; the dashed line shows zero intensity level.

FIG. 3. XES spectra of FeS in the high-spin (room pressure) and low-spin (11.5 GPa) states, along with room pressure reference spectra of two iron compounds with +2 oxidation states for iron, namely FeO (HS) and FeS\textsubscript{2} (LS). The difference between the low-spin spectra of FeS and FeS\textsubscript{2} is within the measured error.