High-pressure X-ray Emission Spectroscopy at Sector 13

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Introduction

The Kβ x-ray emission has been used for several decades at ambient conditions to study the spin state and valence state of transition metal ions. Recently we applied this technique to compressed materials. The pressure-induced high-spin to low-spin transition was observed in FeS [1]. A similar study on FeO [2] provided a probe of the spin state of Fe^{2+} to 140 GPa (close to pressure conditions at the Earth's core-mantle boundary). In this report, we present an outline of the setup used in these studies and briefly describe recent results.

Methods and Materials

Below is a short list of the components for the x-ray emission spectroscopy (XES) experiment at high pressure:

- Upstream collimating and focusing optics. At Sector 13 we used focusing Kirkpatrick-Baez (K-B) mirrors that provided an x-ray spot that was less than 10 μm in diameter.
- Rowland-circle spectrometer, including the Si or Ge crystal analyzer and the detector. The x-ray beam path should be filled with He gas or placed in vacuum to minimize signal losses and background radiation due to the x-ray scattering in air.
- High-pressure cell with a beryllium gasket to allow measurements of the x-ray emission at low energy.

The third-generation synchrotron source provides an intense x-ray beam; however, the x-ray emission may be completely absorbed by traditional stainless steel gaskets and severely attenuated in diamond in the range of the Kβ emission in 3-D elements. Fig. 1 shows the attenuation of the x-ray radiation in the Be gasket and in the diamond anvils.

The process of the Kβ emission is illustrated in Fig. 2. The emission results from the $3p \rightarrow 1s$ decay. The Kβ line shape can be described, in a good approximation, by using a two-step model (absorption followed by emission). In the final state, the 3*p* core hole strongly interacts with the incomplete 3*d* shell. The consequence is the splitting of the Kβ spectrum into two peaks; the separation is controlled by the configuration interaction in the final state. The splitting usually exceeds the 3*p*-3*d* simple exchange interaction *J*. Furthermore, calculations

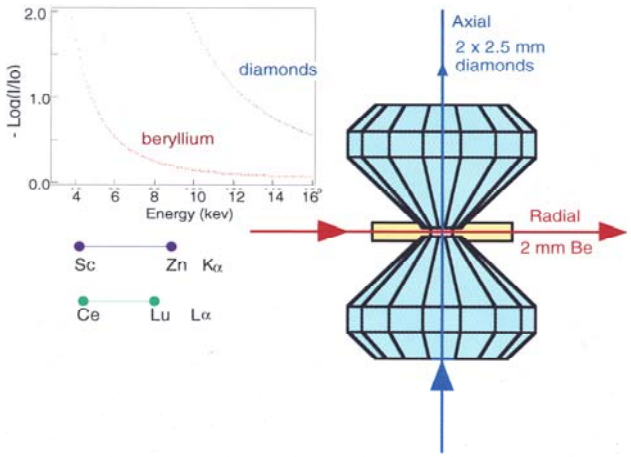

FIG. 1. Absorption of the x-ray radiation by 2 × 2.5-mm diamonds and by 2-mm Be gasket.

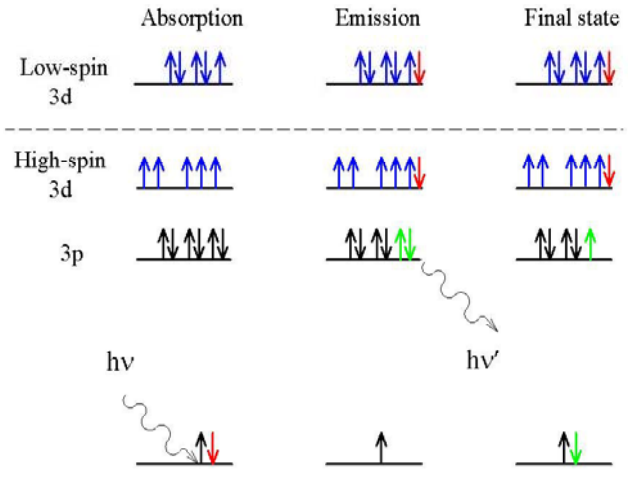

FIG. 2. Schematic diagram of the Kβ emission process.

show that the Kβ′ satellite at lower energy results predominantly from the 3p↑3d↑ final state, whereas the $K\beta^{1,3}$ line comes mainly from the 3p↑3d↓ final state, with a small contribution from 3p↑3d↑, which appears in the spectrum as a low energy shoulder in the main peak. We

illustrate the change in the Kβ emission line shape between high- and low-spin states in Fig. 3 [1].

Results

Previous high-pressure experiments on the Kβ emission have not addressed the pressure-induced shift of the Kβ line because of the strict requirements for the reproducibility in the sample position [1-3]. Recently, we designed high-pressure experiments that take advantage of the tight x-ray focus (better than 10 μm) after the K-B mirrors. Reproducible sample positioning and the small sample size (20-30 μm) allowed the Kβ line position in iron to be measured with an accuracy of 0.15 eV (0.002%). The line shift was about 1 eV/100 GPa (Fig. 4).

We also used a setup similar to the one shown in Fig. 5, but with the Rowland circle plane perpendicular to the incoming x-ray beam. In this configuration, the detector is mounted above the sample, and the Be gasket is perpendicular to the x-ray beam. The tight x-ray focus provides a much better local probe of the sample than that accomplished by the setup shown in Fig. 5. The sample position is actually defined by the x-ray beam focus, which is extremely stable and well-defined. In this arrangement, the incoming x-ray beam is directed through the diamonds, and the intensity on the sample is attenuated by the absorption of one of the diamond anvils. The attenuation of the x-ray intensity at 12 keV is about a factor of 2 for the diamond height of 1.3 mm, and it increases rapidly for larger diamonds. With this setup, we recently measured the Kβ emission and x-ray diffraction of FeO and $Mg_{0.5}Fe_{0.5}O$ in the 100-GPa pressure range with and without pressure media, by using laser heating to relieve the stresses in the compressed samples. We

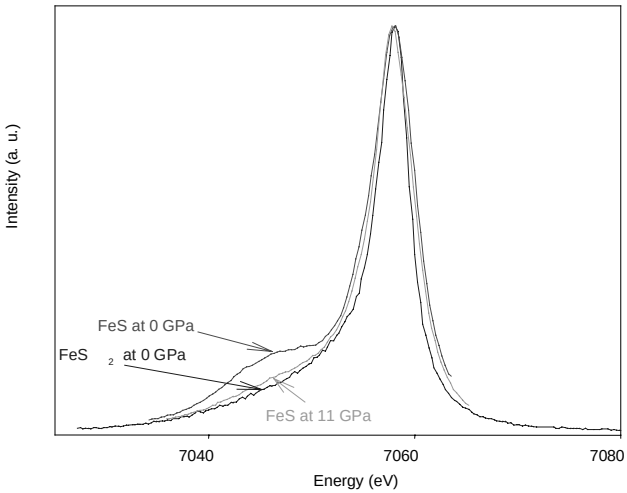

FIG. 3. Kβ emission spectra of FeS at 11.5 GPa (low spin) and ambient (high spin) [1]. The FeS_2 (low-spin configuration) emission is shown for comparison.

observed the pressure-induced shift of the main Kβ emission peak, which was similar to the pure Fe. The observed changes in the Kβ emission line shape correlate with the structural changes in the material and suggest the low-spin or metallic state is at about 100 GPa [4]. Further studies of electrical and optical properties are underway to resolve the stability field of the low-spin and metallic states in FeO at high-pressure conditions.

Discussion

Unambiguous identification of the high-spin to low-spin transition in insulating materials similar to FeS

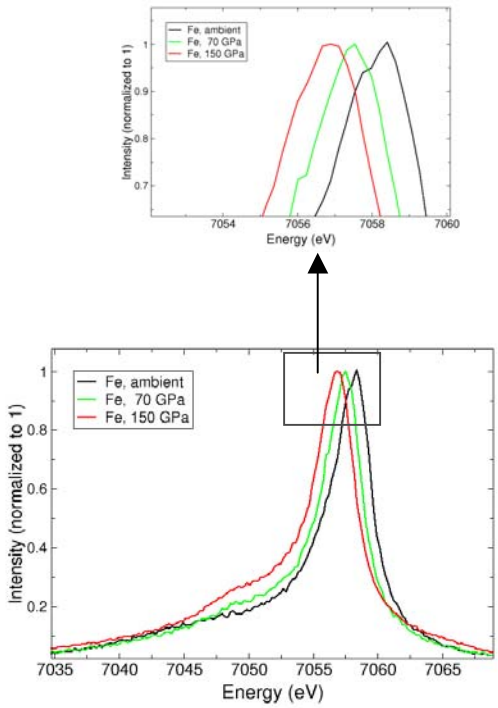

FIG. 4. Kβ emission spectra of pure Fe to 150 GPa.

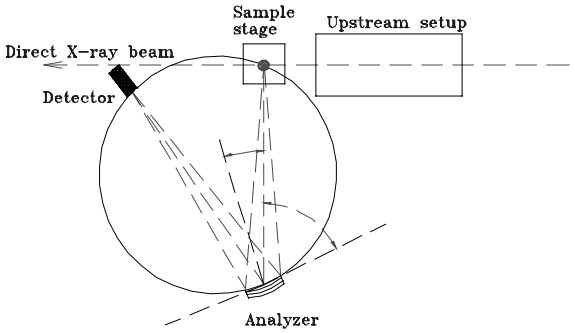

FIG. 5. Experimental setup for the high-resolution XES. We have used Ge and Si analyzers [1, 2].

(Fig. 3) is not easily possible in metals. For example, the high-spin satellite feature is much lower in pure iron (Fig. 4) than in FeS, FeO, or Fe_2O_3 [2-3]. Despite these difficulties, the transition to the low-spin state in pure Fe was observed to be between 13 and 20 GPa [3] from the precise measurements of the Kβ emission. However, additional complications are involved when an insulator-metal transition accompanies the changes in the Kβ emission line shape. Our experimental data [4] suggest that the metallic state is stabilized in FeO above 100 GPa. The identification of the low-spin state of Fe^{2+} ion at these conditions requires better theoretical understanding of the Kβ emission process in the metallic state.

At low pressures, iron-oxygen alloys form immiscible melts consisting of iron-rich metallic and iron oxide nonmetallic components. Thus, for oxygen to be an important alloying constituent of iron in the core, it must become miscible with liquid iron at high pressure. According to current understanding, the more compact low-spin Fe^{2+} ion already favors metallic bonding in FeO at moderate temperatures above 140 GPa. The identification of the metallic low-spin state of iron in iron oxide may provide an explanation of the FeO miscibility with liquid Fe in the Earth's outer core.

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