Magnetic and Structural Transition in Fe_3S at High Pressures

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Introduction

Fe_3S, containing 16.1 wt% sulfur, is the most iron rich compound in the Fe-FeS system. If sulfur is a dominant light element in an iron bearing planetary core, Fe_3S could be a major stable phase together with iron in a solid core. X-ray diffraction measurements indicate that Fe_3S is of tetrahedral structure and stable up to 43 GPa [1]. A recent synchrotron Mössbauer study shows a magnetic to non-magnetic transition at 21 GPa [2]. In this study, we have studied magnetic properties of Fe_3S at high pressures to 31 GPa in a diamond anvil cell, by measuring the pressure dependence of Fe K_β fluorescence line using x-ray emission spectroscopy. We have observed a magnetic transition in Fe_3S at pressures around 18-25 GPa and at room temperature. The relatively low transition pressure (18-25 GPa) suggests that the new high pressure phase of Fe_3S could be a stable phase at planetary (Martian or Earth's) core conditions. It is, thus, important to study the behavior of the new phase at high pressures and high temperatures.

Methods and Materials

K_β x-ray emission spectroscopy (XES) experiments on iron containing materials were performed at the station 16 IDD. In the XES, iron 1*s* electrons in the sample are excited by the incident monochromatic x-ray at 14.4 keV, leaving *K*-shell core-holes that immediately decay through radiative and nonradiative processes. One of those is K_β fluorescence, leaving 3*p* core-holes. Through exchange interaction, the 3*p* core holes interact strongly with the partially filled 3*d* shell, resulting in signatures in emission spectroscopy with a main peak and a satellite peak. The intensity of the satellite peak relates to the exchange interaction that mainly depends on spin states of 3*d* electrons. Therefore, x-ray emission spectroscopy provides information on the magnetic spin state of the 3*d* shell. This technique has been established by experimental studies on other transition metals and theoretical calculations [3]. With the development of the micro x-ray beam technique and x-ray window materials [4], XES has been successfully applied in high pressure studies with DAC [5].

Experiments on Fe_3S to 31 GPa were performed in a diamond anvil cell. The experimental setup is shown in Fig 1. The sample, analyzer and detector are located in a Rowland-circle (870 mm in diameter) with its plane vertical and perpendicular to the incident x-ray beam. The vertical configuration is chosen because it provides a reliable Bragg angle (or the energy). The Bragg angle is not dependent on sample position, but on the x-ray beam height that is usually well defined. The analyzer is Si(440) with 50 mm in diameter, which scans energies from 7020 to 7080 eV. The x-ray beam size is 43x65 μm^2 at FWHM. One XES spectrum takes about 6 hours.

The Fe_3S sample was synthesized in a large volume press [1] and loaded in a Be-gasket with a symmetrical DAC. The sample size was about 10 μm in thickness and 40 μm in diameter. The sample was excited by x-ray beam through diamond anvils. The emission signal was collected through the Be gasket.

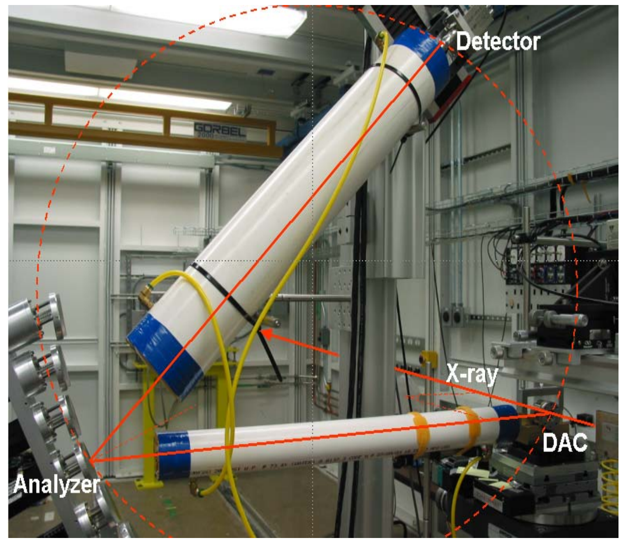

Fig. 1. High pressure x-ray emission spectroscopy setup at the 16ID-D station at the Advanced Photon Source. A Rowland circle is indicated with its plane perpendicular to the incident x-ray beam.

Results

By measuring the pressure dependence of Fe K_β fluorescence line, a magnetic transition in Fe_3S was observed at pressures around 18-25 GPa and at room temperature (Fig. 2). The relative intensities of the satellite peak indicate the collapse of the 3*d* electron magnetic moment at the transition (Fig. 3). This magnetic transition is found to be reversible with pressure. The pressure range of this magnetic transition is consistent with a recent syncrotron Mössbauer study [2]. The relatively low transition pressure (18-25 GPa) indicates that the new high pressure phase of Fe_3S could be a major stable phase in planetary (e.g. Martian) cores.

The magnetic tranistion is found to be associated with a structural transition as evidenced by x-ray diffraction measurements at GSECARS sector. However, the structure of the new phase remains to be solved. We have recently performed more diffraction experiments on Fe_3S at GSECARS and confirmed the structural change. These diffraction data are still in process.

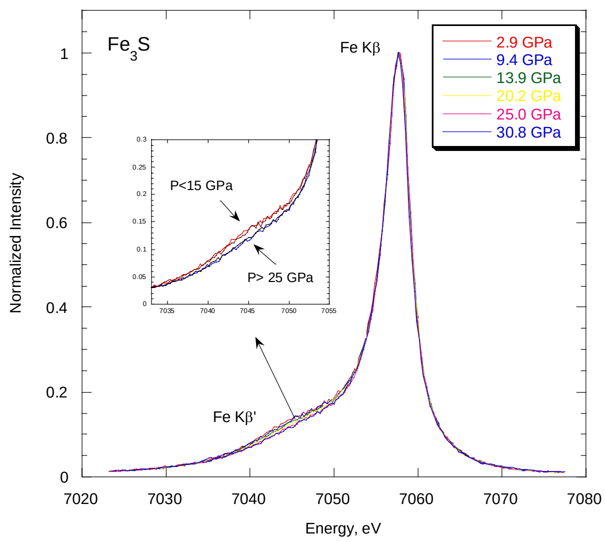

Fig. 2. K_β emission spectra of Fe_3S at high pressures. The intensity change of the satellite peak reflects a magnetic transition in Fe_3S (see the insert). The main peak position is aligned to 7058 eV.

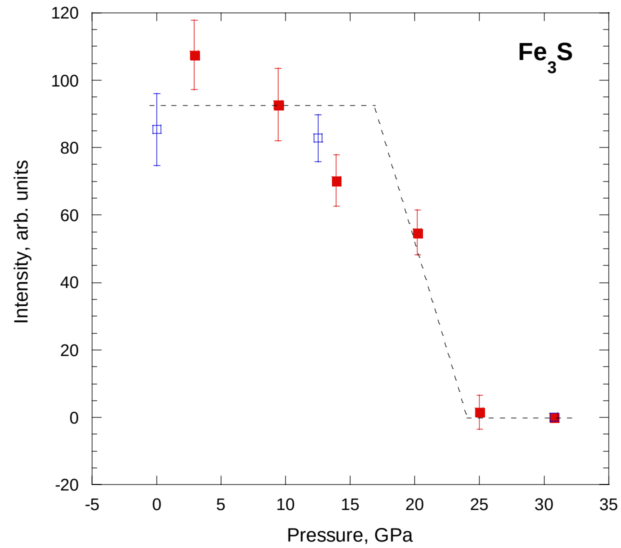

Fig. 3. Integrated intensity of the satellite peak shown in Fig. 2. The intensity was calculated from the difference between the normalized spectra and the one at 30.8 GPa in the energy range of 7030 – 7055 eV. Solid symbols are those on compression; while open symbols denote those on decompression. The dashed line is a guide to eyes.

Acknowledgments

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