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Pressure induced high spin-low spin transition in FeSe superconductor studied by x-ray emission spectroscopy and ab initio calculations

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FeSe is a simple binary system in the iron based superconducting family and exhibits a significant pressure induced increase in the superconducting transition temperature (T_c). In addition to pressure effect, spin fluctuations, magnetic ordering, and crystal structure all play vital roles in altering T_c. Even though various experiments and theoretical simulations explain the connection among them and superconductivity, the interplay between these important parameters is still not clearly understood. Here, we report the pressure effect on the spin state of Fe in FeSe superconductor studied using synchrotron x-ray emission spectroscopy at ambient and low temperatures down to 8 K near T_c. Pressure induced high spin to low spin transition was observed at both ambient and low temperatures with continuous suppression of Fe magnetic moments under increasing pressure. The spin transition is closely related to the pressure induced tetragonal to orthorhombic structural transition. © *2011 American Institute of Physics*. [doi:10.1063/1.3621859]

Recent discovery of superconductivity in the iron based compounds has sparked tremendous interest as these systems are very similar to the high T_c layered superconductors and have possible connection between magnetic ordering and superconductivity which can be tuned by chemical substitution or application of physical pressures. Among the iron based superconductors the simple FeSe binary system with anti-PbO type tetragonal structure shows a transition temperature of 8 K.[1] The FeSe system has several common features to other FeAs iron pnictides. It has layered structure with planar sublattice and displays spin density wave (SDW) and magnetic instability. Furthermore, similar to iron pnictides the superconductivity in this system is also sensitive to external pressure. The rise in the transition temperature (T_c) to 37 K around 4-6 GPa demonstrates a strong correlation between superconductivity and crystal structure.[2] Application of high pressure at room temperature transforms the tetragonal phase to an orthorhombic/hexagonal phase around 7 GPa.[3–5] Upon cooling, FeSe undergoes a structural transformation from tetragonal to an orthorhombic phase (*Cmmm*) below 90 K.[6] A pressure induced transition to *Pbnm* above 1.2 GPa at 8 K is reported[7] and the *Pbnm* phase is stable above 12 GPa (Refs. 7 and 8). Structural inhomogenities are further observed near transition temperature in the extended x-ray absorption fine structure measurements at low temperatures.[9] Besides crystal structure, spin and magnetic orderings are also crucial to understand the superconducting mechanism. Phonon density of states measured around 8 K at high pressures shows an increase in the optical and acoustic phonon modes[7,10] which implies an increase in the density of states under pressure. Recent high pressure nuclear magnetic resonance (NMR) studies show a close correlation between the spin-lattice parameter and T_c (Ref. 11) and strong spin fluctuations near the superconducting (SC) state.

As the Fermi surface of FeSe is dominated by Fe 3*d* electrons and that have a strong hybridization with interacting Se orbitals, it is important to understand the Fe spin state. X-ray emission spectroscopy with synchrotron radiation and diamond anvil cell is an excellent technique to study the spin state of elements under high pressure conditions. Here we report the Fe spin change as a function of pressure both at room temperature (RT) and low temperatures (LT) up to 16 GPa. In addition we have performed the DFT and spin moment calculations. Our results show suppression of Fe spin under pressure near T_c.

Polycrystalline FeSe samples were synthesised by conventional solid state reaction technique by mixing and reacting appropriate weight ratio of high purity starting materials in an evacuated quartz tube described elsewhere.[7] The samples exhibited a T_c of 7.5 K, and the Se concentration was found to be close to 0.9 from energy dispersive x-ray analysis and Rietveld refinement of the ambient x-ray diffraction pattern.[7] The sample was loaded into a 150 μm hole of a high purity Be gasket of a membrane driven symmetric type diamond anvil high pressure cell with helium pressure medium and ruby pressure marker. The x-ray emission experiments were carried out at the IDD station of Sector16 of HPCAT, Advanced Photon Source at Argonne National Laboratory. X-ray emission spectrometer in the Rowland geometry and a spherically bent Si (440) single crystal analyzer at a Bragg angle corresponding to 7058 eV of the Fe K-β emission line were used for data collection. The pressure inside the cell was measured offline at ambient temperature. For low temperature experiments, the symmetric cell was mounted into a continuous helium flow type cryostat, and the pressure was measured *in situ* using ruby fluorescence technique with thermal correction. Spin-polarized total energy calculations and structure relaxations were

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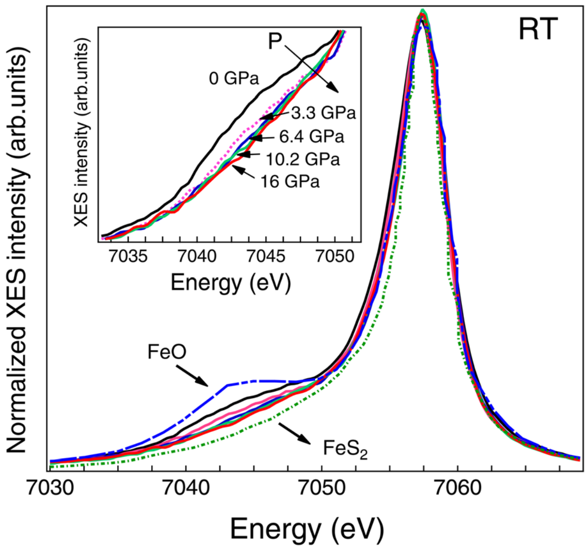

FIG. 1. (Color online) X-ray emission spectra collected for FeSe at RT at various pressures up to 16 GPa. The normalized XES intensity is plotted as a function of pressure. The inset shows expanded view of the satellite peak.

performed up to 16 GPa to support and understand the experimental results.

The Fe *K*-β emission spectra obtained as a function of pressure up to 16 GPa at ambient temperature is shown in Fig. 1. We have observed a main peak ($K\beta_{1,3}$) at 7058 eV and a satellite peak ($K\beta'$) around 7045 eV due to the *3p* and *3d* shell interaction. The $K\beta$ emission spectra, corresponding to FeO, in which Fe is in the high spin state, and FeS_2, in which Fe is in the low spin state, are shown for comparison. Under ambient conditions, Fe is reported to be in a high spin divalent configuration with varying degree of co-valency in FeSe as established by previous Mossbauer experiments.[12,13] The satellite peak in the emission spectrum obtained for FeSe at ambient conditions lies just below the FeO spectrum, indicating a nearly high spin configuration for the Fe 2+ state. As seen in Fig. 1 the intensity of the satellite peak is noticed to decrease upon increasing pressure. An appreciable change in the satellite peak intensity is observed near the structural transition pressure (∼6–7 GPa). A similar high spin-low spin transition accompanying a structural transition is also reported for FeS (Ref. 14). Around 16 GPa, the satellite peak intensity is considerably reduced, and the emission spectrum tends to become a single peak structure which closely resembles the XES spectrum of low spin Fe in FeS_2.

In Fig. 2 we show the XES spectra obtained at 8 K at various pressures up to 8 GPa. The satellite peak intensity as a function of pressure is shown in the inset. We have also plotted the integrated intensity of the satellite peak as a function of pressure at RT and at 8 K as shown in Fig. 3 for comparison. It is noted that the suppression of XES intensity at low temperature and high pressure is gradual and sluggish compared to that at RT. As reported earlier, FeSe undergoes a structural phase transition from the *Cmma* phase to *Pbnm* at very low pressures around 1.2 GPa, and the two phases co-exist up to 8 GPa. The spin transition at this region is hence found to be gradual. The spin-lattice relaxation measurements in the NMR experiments indicate enhanced spin fluctuations with pressure and show competing antiferromagnetic spin fluctuations with superconductivity at low pressures.[11] This result is consistent with the observed spin transition, and such spin fluctuations are mainly caused by the Fe d-electrons in the conduction band since the *s*-electron density is reported to be less sensitive to applied pressure.[10]

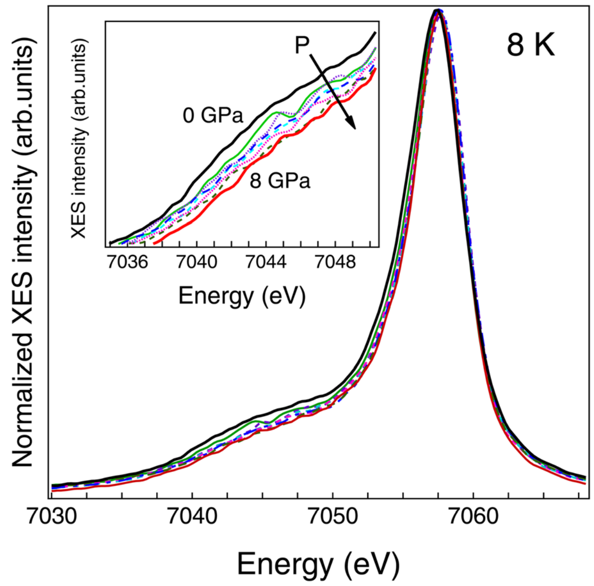

FIG. 2. (Color online) Low temperature XES spectra at selected pressures up to 8 GPa collected at 8 K. The inset shows XES spectra zoomed between 7038 and 7050 eV.

In order to correlate the current experimental results with theory, first-principles calculations were performed using the generalized gradient (GGA) approximation and local density approximation (LDA) as implemented in the VASP package.[15] The projector augmented wave (PAW) pseudo-potential method is used with a plane wave basis set limited by the cutoff energy of 500 eV (Ref. 16). The spin magnetic moments and strip-like anti-ferromagnetic (AFM) ordering in FeSe with a larger $\sqrt{2} \times \sqrt{2}$ supercell [see Fig. 4(b)] and a $9 \times 9 \times 9$ Monkhorst-Pack k-point grid. Fe atoms were initialized in high spin and low spin states, as well as in AFM ordering. After relaxation, we obtain an orthorhombic *Cmma* structure with the lattice vectors a and b differing slightly. Our results are consistent with the tetragonal-

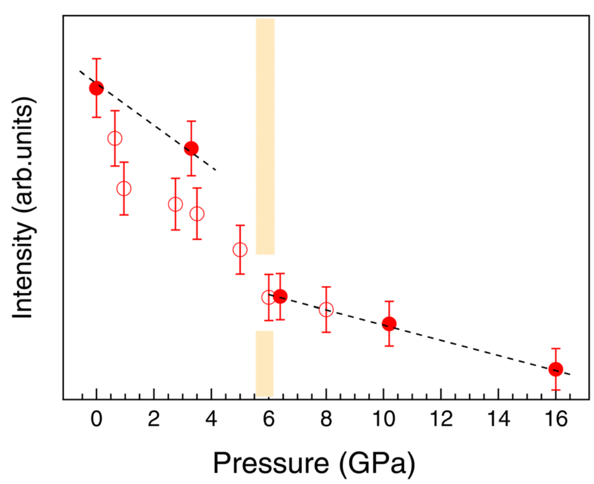

FIG. 3. (Color online) Integrated XES intensity plotted as a function of pressure at RT (solid symbols) and LT (open symbols) at 8 K.

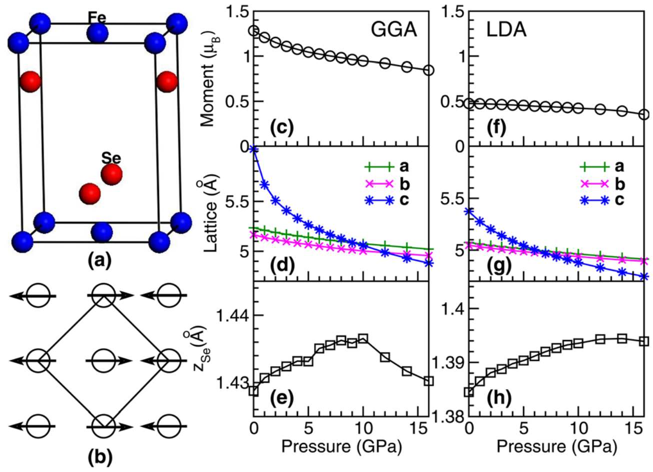

FIG. 4. (Color online) (a) Unit cell of tetragonal FeSe. (b) Top view of AFM phase in cmma FeSe. The black square represents one unit cell. (c)–(e) and (f)–(h) The calculated spin moment per Fe, lattice parameters, and Se anion height with respect to Fe layer by GGA and LDA.

orthorhombic phase transition at low temperatures.[8] The AFM phase stability is then investigated under pressure. The total energy of AFM phase is 14.3 meV (GGA) or 1.93 meV (LDA) lower than that of non-magnetic (NM) phase at ambient pressure. The AFM phase stability is then investigated under different pressures. The total energy difference of E_{NM}-E_{AFM} decreases monotonically with pressure in LDA calculations. In GGA calculations, the E_{NM}-E_{AFM} first decreases to 9.0 meV at 10 GPa and then increases to 10.3 meV at 16 GPa. The magnetic moments of Fe ion were calculated within the Wigner Seitz radii defined in the VASP pseudopotentials. Their absolute value as a function of pressure are presented in Fig. 4 for the unit cell shown in Fig. 4 for GGA and LDA, respectively.

In Fig. 4, the spin moment decreases continuously with pressure increase, and no drastic spin collapse is observed. This result agrees well with the smooth HS-LS transition in the present experiment. From the GGA calculation, we obtain a moment of 1.283 μ_B at ambient and 0.846 μ_B at 16 GPa; LDA moments are much smaller but in good agreement with previous work.[17] This spin moment change can be attributed to pressure-induced electron delocalization or the spin crossover of Fe atomic spin S from high spin $S = 2$ [Fe^{2+}(3d):$4t_{2g}\uparrow 2e_g\uparrow$] to low spin $S = 0$ [Fe^{2+}(3d):$6t_{2g}\uparrow 0e_g\uparrow$] state. This result agrees well with the smooth HS-LS transition in the present experiment. The lattice parameters as a function of pressure are shown in Fig. 4 for GGA and LDA, respectively. The volume collapse under pressure comes mainly from the reduced interlayer distance along the c axis, which increases the crystal-field energy Δ_{cf} and suppressed HS states. LS state is thus favored by the lower spin-pairing energy.

The inter-layer distance change also causes the change of Se anion height z_{Se}. As has been suggested previously,[18] the anion height is important to the stability of the magnetic phase as well as the superconductivity. In GGA calculations [see Fig. 4(e)], the z_{Se} reaches its maximum of 1.436 Å at 9 GPa, then it decreases to 1.430 Å at 16 GPa. This behavior can be correlated with the weakest AFM stability at 10 GPa in our GGA calculations. The z_{Se} calculated by LDA is presented in Fig. 4(h). In this case the z_{Se} increases with pressure and saturates at 1.430 Å near 16 GPa. It corresponds to the decreasing AFM stability from LDA calculations.

In summary we have investigated the high pressure effect on Fe spin in the FeSe superconducting compound at ambient and low temperatures (8 K) up to 16 GPa. We identify a pressure induced high spin – low spin transition under pressure. Our results indicate that Fe local spin changes may play a vital role in altering the superconducting properties in addition to structural and electronic properties in the FeSe compounds.

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