Pressure Dependence of Electronic Structure and Spin State in $Fe_{1.01}Se$ Superconductors

High-temperature superconductivity has been discovered in Fe-based quaternary oxypnictides. This is the first system in which Fe is crucial for superconductivity. This is quite interesting since, usually, Fe has magnetic moments and tends to form ordered magnetic states which is apt to destroy superconductivity. The binary superconductor FeSe is another emerging Fe-based superconductor. It has the simple tetragonal structure which is isostructural with the FeAs layer in quaternary iron arsenide, suggesting it may provide valuable information to the superconductivity in Fe-based compounds. We have proposed that superconductivity in this material is the result of the interplay among structural, magnetic and electronic properties. Comprehensive studies of the evolution of magnetic spin states and the hybridization of the Fe 3d and Se orbitals with pressure are presented to elucidate the superconducting properties.

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The discovery of unconventional high-T_c superconductors in iron-based oxypnictide compounds $LaFeAsO_{1-x}F_x$ with T_c ~26 K has sparked interest in layered FeAs systems. A new superconductor in an arsenic-free PbO-type β-$FeSe_x$ compound with T_c ~8 K was reported. A large enhancement of T_c was observed in a tetragonal $Fe_{1.01}Se$ superconductor under pressure. T_c of $Fe_{1.01}Se$ increased to as much as 27 K on applying pressure up to 1.5 GPa and then increased up to 34-37 K with pressure from 8.9 to 22 GPa.

The electronic states near the Fermi level in FeSe chalcogenide and FeAs pnictide are given by the Fe 3*d* orbitals and Se/As 4*p* orbitals. The interaction of Fe 3*d* orbitals with the neighbouring Se/As orbitals in the Fe-based superconductors affects their fundamental transport properties and physical nature. As interlayer Se-Se interactions of $Fe_{1.01}Se$ are weak, the application of external pressure has a profound influence on the local distortion around the Fe atoms and the hybridization between Fe 3*d* and interacting Se orbitals. Authors proposed that superconductivity in $Fe_{1.01}Se$ is likely the result of an intricate interplay between their structural, magnetic and electronic properties. A comprehensive understanding of the evolution of magnetic spin states and the hybridization of the Fe 3*d* and the neighboring Se orbitals in $Fe_{1.01}Se$ with pressure is thus of key importance for the elucidation of superconducting properties of Fe-based materials. However, detailed information about the pressure dependence of electronic structures and spin states of $Fe_{1.01}Se$ is sparse.

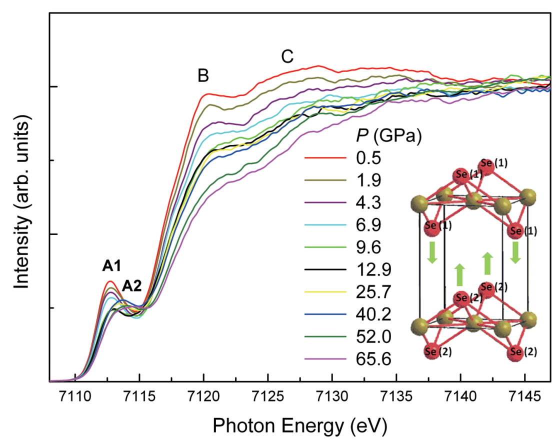

Fig. 1: Fe *K*-edge X-ray absorption spectra, recorded with partial fluorescence yield, of polycrystalline $Fe_{1.01}Se$ for pressure varied in the range 0.5 – 65.6 GPa. The inset displays the crystal structure of $Fe_{1.01}Se$.

Figure 1 shows Fe *K*-edge X-ray absorption spectra of polycrystalline $Fe_{1.01}Se$ recorded at pressure varied in the range 0.5 – 65.6 GPa. The spectra were obtained in partial fluorescence yield, with the spectrometer energy fixed at the maximum of the Fe $K\beta_{13}$ emission line (~7058 eV). At ambient pressure, the Fe *K*-edge XAS spectrum of tetragonal $Fe_{1.01}Se$ consists of a pre-edge peak A1 and two pronounced broad lines B and C on the side of greater photon energy. Because the Fe atom in $Fe_{1.01}Se$ is in a tetrahedral site without center of symmetry, the Fe 3*d* orbital is hybridized with Fe 4*p* orbitals. As the quadrupole transition Fe 1s→3*d* is very weak, the observed pronounced pre-edge peak A1 in Fe *K*-edge X-ray absorption spectra of $Fe_{1.01}Se$ in Fig. 1 predominantly originates from the dipole transition of a Fe 1*s* electron to unoccupied Fe 3*d*-Se 4*p* hybrid bands. The high-energy features B and C are dominated by dipole transitions from the Fe 1*s* core electron to Fe 4*p* unoccupied states. Feature B at ~7120 eV is ascribed to unoccupied Fe 4*p*-Se 4*d* hybrid bands. Feature D at greater energy is due mainly to the photoelectron multiple scattering of Fe atoms with their nearest neighbours.

As noted, the intensity of the pre-edge line A1 at ~7112.7 eV decreases progressively with pressure up to ~10 GPa, indicating a varying local distortion around Fe atoms and a suppression of the Fe 3*d*-Se 4*p* hybridization. A new pre-peak A2 at energy ~7113.7 eV develops for pressure above 13 GPa and attains its maximum intensity at P = ~40 GPa, indicating formation of a new phase. After $P > 40$ GPa, the intensity of pre-edge peak A2 decreases slightly. Upon increasing pressure, a substantial decrease of absorption features B and C, particularly feature B, was observed along with an energy shift. This upward shift of energy for absorption features B and C is due to the fact that the bond lengths of both Fe-Fe and Fe-Se in $Fe_{1.01}Se$ decrease upon applying pressure. The rising absorption edge of Fe *K*-edge spectra of $Fe_{1.01}Se$ gradually shifts towards greater energy with increasing applied pressure, probably associated with the charge transfer between Fe and Se due to the shrinking of the bond lengths of Fe-Se upon pressurization.

Figure 2 shows Fe $K\beta$ emission spectra of $Fe_{1.01}Se$ with pressures 0.5, 40.2 and 65.6 GPa with reference emission spectra of two iron-containing compounds with iron in +2 oxidation state, FeS (high spin) and FeS_2 (low spin) at ambient pressure. The Fe $K\beta$ X-ray emission spectrum is divided into a main line $K\beta_{1,3}$ (~7058 eV) and a satellite line $K\beta'$ (~7045 eV) due to the exchange interaction between the 3*p* core hole and the unfilled 3*d* shell in the final state of the emission. The intensity of the satellite line $K\beta'$ is proportional to the net spin of the 3*d* shell and thus is indicative of the spin magnetic moment.

The position of the $K\beta_{1,3}$ line is shifted toward lower energy by about 0.6 eV with pressure increased to ~52 GPa. Above 52 GPa, the main line $K\beta_{1,3}$ for $Fe_{1.01}Se$ is narrower and more symmetric, accompanied with the intensity of the $K\beta'$ line and the position of the $K\beta_{1,3}$ line remaining nearly unchanged. As noted, the $K\beta'$ intensity of $Fe_{1.01}Se$ is notably less than that of FeS with the high-spin Fe^{2+} state. $Fe_{1.01}Se$ hence shows a small net magnetic moment of Fe^{2+} at ambient pressure, consistent with other measurements from neutron scattering and Mössbauer spectra for Fe-based superconductors. The profile of the $K\beta'$ line for $Fe_{1.01}Se$ at P = 65.6 GPa is almost coincident with that of FeS_2 with the low-spin Fe^{2+} state. This indicates that $Fe_{1.01}Se$ shows the low-spin state of Fe^{2+} ions upon applying pressure up to ~66 GPa.[1]

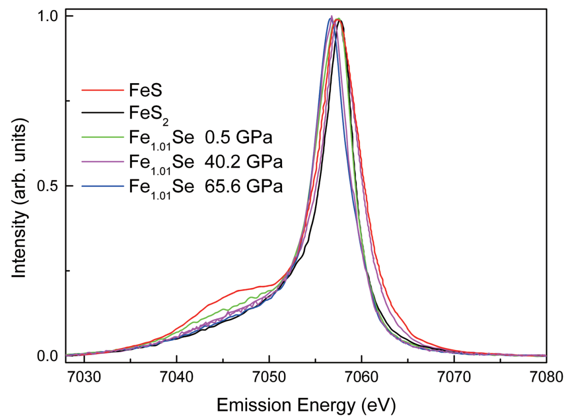

Fig. 2: Fe $K\beta$ emission spectra of $Fe_{1.01}Se$ for P = 0.5, 40.2 and 65.6 GPa with reference emission spectra of FeS (high spin) and FeS_2 (low spin).

Based on spin-lattice relaxation in ^{77}Se NMR spectra for $Fe_{1.01}Se$, the Fe spins are collinearly antiferromagnetically ordered. For tetragonal β-FeSe, the Fe-Fe exchange coupling between nearest-neighbor (NN) spins is ferromagnetic, and that between next-nearest-neighbor (NNN) spins is antiferromagnetic, because Fe-Se-Fe angles relevant to their superexchange interactions are nearer 90° for the former and 180° for the latter. Based on first-principles electronic structure calculations for β-FeSe, the NN FM superexchange interactions (J1) and NNN AFM superexchange interactions (J2) are J1 = 71 meV/Fe and J2 = 48 meV/Fe at ambient pressure. The increased $FeSe_4$ tetrahedral distortion away from regular tetrahedra shape in $Fe_{1.01}Se$ upon pressurisation reduces the Fe 3*d*-Se 4*p* hybridization, as evident in Fig. 1, and is expected to suppress the NN FM superexchange interactions mediated by Se 4*p*-orbitals. The competition between the NN FM and the NNN AFM superexchange interactions in $Fe_{1.01}Se$ upon pressurisation accordingly enhances spin fluctuations. A subtle balance of the competition between the NN FM and NNN AFM superexchange interactions produces collinear antiferromagnetic spin arrangement in $Fe_{1.01}Se$. The Fe-Fe spin fluctuations in $Fe_{1.01}Se$ thus decrease strongly the net magnetic moments of Fe ions, generating small net magnetic moments of Fe^{2+} at ambient pressure.

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Reference

1. J. M. Chen, S. C. Haw, J. M. Lee, T. L. Chou, S. A. Chen, K. T. Lu, Y. C. Liang, Y. C. Lee, N. Hiraoka, H. Ishii, K. D. Tsuei, E. Huang, and T. J. Yang, Phys. Rev. B **84** , 125117 (2011).

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