

11 Element Strategy Initiative to Form Core Research Center for Electron Materials

– Multi-probe study using X-rays, muons and neutrons –

*Youichi Murakami, Hiroshi Kumigashira,
Kenji Kojima, Jun-ichi Yamaura*

11-1 Introduction

The national project “Elements strategy initiative to form core research center for electron materials” was started in 2012. We are aiming to develop entirely new materials that use ubiquitous elements. We are developing materials based on successful experience far away from development policy, and are pioneering electronic materials to create new guidelines for material design using harmless elements to open up new fields of material science. We are researching the crystal, local, electronic, and magnetic structures of new functional materials using synchrotron radiation, and muon and neutron sources.

11-2 Observation of electrider bands in Y_2C by means of ARPES

“Electrider” is a fascinating material in which “free electrons” are confined in the cage or void space in ionic crystals. Recently, Y_2C , formerly predicted to be a two-dimensional (2D) electrider by *ab initio* calculations, has been synthesized successfully. Y_2C ($[Y_2C]^{2+} \cdot 2e^-$) has a unique layered structure with anionic electrons within the interlayer space as illustrated in Fig. 1(a).

Ab initio calculations revealed that Y_2C is a semimetal: an almost fully occupied hole-like electrider band and a slightly occupied electron-like electrider band overlap each other near E_F as shown in Fig. 1(b). The sizes of the circles indicate the calculated interlayer eigenstates, i.e., the electron is found inside the sphere of radius 1.7 Å at the interstitial site between Y_2C layers. Note the strong interlayer (electrider) character of the two semimetallic bands near E_F .

We have measured the energy-band disper-

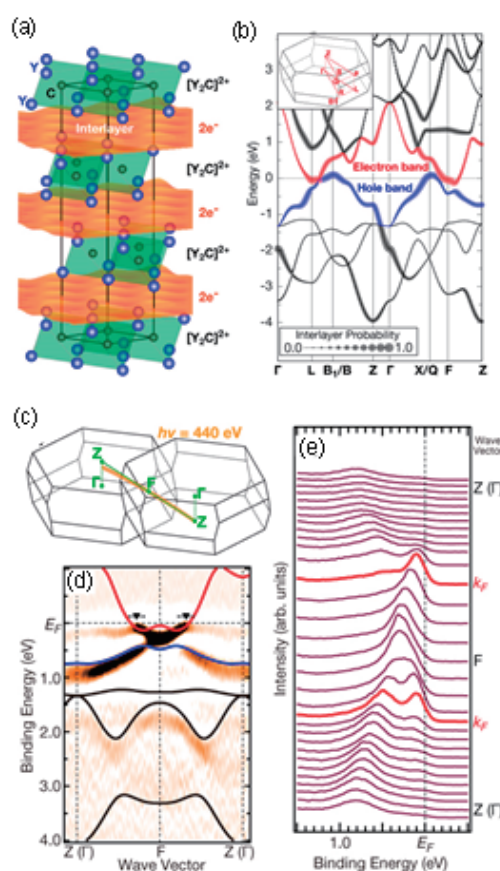


Fig. 1: (a) Crystal structure of Y_2C with a schematic illustration of the anionic electron layer. (b) Theoretical band structure of Y_2C . (c) Measured k -path going through the F point in the rhombohedral BZ by ARPES with $h\nu = 440$ eV. (d) Experimental band structure obtained by plotting the second derivative of ARPES spectra. The energy bands along the Z-F-Z direction calculated by the FLAPW method are superimposed by solid lines. (e) ARPES spectra near E_F and around the F point.

sion along the representative high-symmetry lines at the beamline BL-2A MUSASHI of PF. Figure 1(d) shows the band dispersion determined by ARPES along the Z-F-Z direction with an orange line in the BZ [see Fig. 1(c)]. It is clear that the

electron bands exist near E_F and make small electron-pockets around the F point, which is more clearly seen in the ARPES spectra as shown in Fig. 1(e). The overall band structures observed by ARPES are in good agreement with theoretical band structures. We present convincing evidence from ARPES and band structure calculations that there are “void electrons” with quasi-2D semimetallic “electride” bands in Y_2C .

11-3 Pressure effects in iron oxypnictide superconductor $LaFeAsO_{1-x}H_x$

$LaFeAsO_{1-x}H_x$ is the hydrogen anion substituted version of the pioneering iron oxypnictide superconductor $LaFeAsO_{1-x}F_x$, which shows a unique phase diagram of two superconducting (SC) domes and two magnetic/structural ordered parent phases. A systematic study of the crystal structure for $LaFeAsO_{1-x}H_x$ ($0 < x < 0.51$) was performed using synchrotron X-ray diffraction up to ~ 8 GPa at the beamline NE1A of PF-AR and BL-8B of PF.

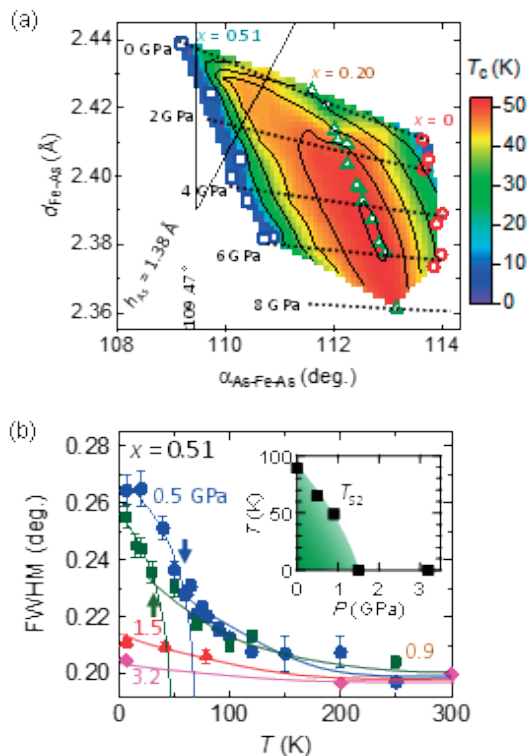


Fig. 2: (a) Contour plots of T_c for $LaFeAsO_{1-x}H_x$ as a function of $\alpha_{As-Fe-As}$ and d_{Fe-As} . Broken lines represent the regular tetrahedron of $FeAs_4$ and the $h_{As} = 1.38$ Å as empirically believed structural parameters of the highest- T_c . (b) Temperature dependence of FWHM of 220 reflections at several pressures for $LaFeAsO_{0.49}H_{0.51}$. The arrows indicate the T-O structural transitions of T_{S2} . Inset shows the phase diagram of T_{S2} under pressure.

From the structure analyses of powder samples, we established that the $As-Fe-As$ angle of the $FeAs_4$ tetrahedron widens on application of pressure due to the interspace between the layers being nearly infilled by the large La and As atoms. This rarely observed behavior in iron pnictides implies that the $FeAs_4$ coordination deviates from the regular tetrahedron in our systems, breaking a widely accepted structural guideline regardless of the increase of the superconducting transition temperature (T_c) from 18 K at ambient pressure to 52 K at 6 GPa for $x = 0.2$ as shown in Fig. 2(a). In the phase diagram, the second parent phase at $x \sim 0.5$ is suppressed by low pressure at ~ 1.5 GPa in contrast to the first parent phase at $x \sim 0$, which remains robust to pressure [see Fig. 2(b)]. We suggest that the spin/orbital fluctuation from the second parent phase gives rise to the high- T_c under pressure. The pressure responses of the $FeAs_4$ modification, the parent phases, and their correlation are previously unexplained peculiarities in 1111-type iron pnictides.

References

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