Understanding interlayer interactions in layered superconducting materials

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Background and motivations

The physics of layered functional materials is one of the most intriguing problems in solid state physics. Due to the low dimensionality, the presence of correlations and strong interplay between different degrees of freedom, this class of materials show many different functional properties from multiferroics to Mott insulators and intercalating materials for Li-ion batteries. Among these, high temperature superconductivity, discovered in 1986 by Bednorz and Müller\(^1\), is one of the most notable findings and it has been puzzling physicist for almost 30 years. However, unconventional superconductivity is not only present in copper-oxide based systems. The iron based superconductors (FBS), discovered in 2008 by Hosono and coworkers\(^2\) are layered multiband systems in which the active layer (responsible for superconductivity) is composed by iron atoms tetrahedrally coordinated with pnictogen (As) or chalcogen (Se,Te) anions. The active layers are arranged in a stacked fashion separated by alkali, rare-earth, oxifluoride or alkaline-earth layers. These “spacer layers” have fundamental importance even if they are not directly involved in superconductivity. Similarly, the newly discovered Bismuth-based superconducting family\(^14\) is composed by a stacking of BiS\(_2\) (or BiSe\(_2\)) active layers and rare earth oxide spacer layers. In all layered superconducting materials the parent compounds do not show superconductivity, they become superconducting after electron (or hole) doping via chemical substitution. In addition, some of the fundamental properties (Fermi surface topology, transport and magnetism, superconductivity) can be tuned by means of chemical substitution, mechanical pressure and/or chemical pressure exploiting the extreme susceptibility to the external conditions\(^3\).

It has been pointed out that, due to multiband nature of the Fermi surface and its tendency to instabilities, the local structure of the FeAs layers controls both the antiferromagnetic fluctuations and superconductivity\(^4\). In fact, structural quantities like bond angles (see Fig.2) and bond distances in the active layers show a clear correlation with T\(_c\). Chemical pressure via isovalent substitution, doping and external pressure can tune the basic properties via optimization of the local structure\(^4\).

The same holds for Bi-based superconductors as well, in which the Bi-S bond correlation and the local structure of the active layer is predicted to determine the electronic properties. It is well known also, that the unconventional superconductive properties depend on structural defects and on their arrangement, and knowing the average crystal structure is not sufficient. Therefore, an experimental technique which is sensitive to the local atomic arrangement in an element-selective way is strongly desired.

Even if the spacer layers are not directly involved in the superconducting mechanism, different features...
showed by compounds which share the same active layer underline the importance of the composition of spacer layers in tuning the basic properties. For this reason, understanding the interlayer coupling can provide a new control parameter to obtain desired properties. It is widely accepted that the local lattice structure in the active layers is related to superconductivity. However, the role played by spacer layers and interlayer interaction has not been investigated in depth.

My PhD project will be devoted to the study of local lattice distortions and disorder in the atomic structure of layered multiband superconductors. I will also provide indication about the role of interlayer interaction in controlling the above properties. The main experimental technique will be X-ray absorption spectroscopy (XAS) which is element-selective and provide local structural sensitivity. Space and angle resolved photoemission spectroscopy will be exploited to study possible inhomogeneous electronic states due to local disorder. The focus of my PhD project is on two representative systems: the skutterudite-type iron pnictides and the Bi-based superconductors.

Iron pnictides with skutterudite spacer layers

Generally, in the FBS family the spacer layers are insulating and this is considered a kev feature for superconductivity. However, recent theoretical investigation have pointed out the promising potential of metallic intermediary layers as a novel route for superconductivity in iron pnictides. Discovery of superconductivity in layered \( \text{Ca}_{10}\text{Ir}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \) (so called 10-4-18 type, \( T_c \) of 40 K) and \( \text{Ca}_{10}\text{Pt}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \) (10-3-18 type, \( T_c \) 13K) compounds with complex spacer layers has further underlined importance of interlayer coupling as a key parameter for controlling physical properties of layered systems to find new superconductors with higher \( T_c \). Indeed, a new system \( \text{Ca}_{10}\text{Ir}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \) has been successfully synthesized with a \( T_c \) of 17K. Unlike other iron-based superconductors, the new families have very peculiar spacer layers with M (Ir or Pt) atoms in square planar geometry. The structure consists of alternating stacking of \( (\text{Fe}_2\text{As}_2)_5 \) and \( M_4\text{As}_8 \) (or \( M_3\text{As}_9 \)) layers with five Ca ions between them resulting in a relatively big unit cell (see Fig.1). Similar to other Fe-based superconductors, dominant contribution to the electronic DOS at the Fermi energy is driven from the iron 3d-electron orbitals. However, unlike most of the FBS having nonmetallic spacer layers, the new quaternary systems possess a fundamental difference of having metallic spacer layers with the non-negligible weight from M 5d states at the Fermi level suggesting larger interlayer coupling. The temperature dependence of the in-plane resistivity of Ir-based system, \( \text{Ca}_{10}\text{Ir}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \) shows a kink at 100K that has been assigned to some kind of structural phase transition (SPT) involving the Ir-As bond accompanied by an electronic orbital crossover transition. The \( T_c \) versus doping phase diagram clearly shows that SC takes place even without any doping due to interlayer carrier injection (the phase diagram is sketched in Fig.3). These very interesting properties come from the unusual interlayer interaction and one can expect to control it by means of certain tuning parameters such as pressure/doping. Generally speaking, low doping region of the phase diagram in Fe-based superconductors is characterized by the presence of a structural phase transition (SPT) from a high temperature phase to a low-\( T \) phase showing some kind of order (charge or magnetic). As doping level increase the SC appears with suppression of the low-\( T \) phase, e.g. the typical phase diagram in FBS family is presented in Fig.3 (left hand side). Interestingly, in \( \text{Ca}_{10}\text{Ir}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \) SC and SPT coexist and gets suppressed in the same manner as a function of electron doping (see sketch in Fig. 3) making it the only example of FBS in which superconductivity appears only in the low-\( T \) phase. Recently, Kitagawa et al found the same behavior of \( T_c \) and SPT as a function of external pressure. Nevertheless, no magnetic order has been found in the whole phase diagram making this system a suitable material to investigate the relationship between structure and SC in FBS disregarding magnetic effects.

PhD project: Early results on \( \text{Ca}_{10}\text{Ir}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \)

In the system \( \text{Ca}_{10}\text{Ir}_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \) with skutterudite intermediary layers strong interlayer interaction is expected. In particular i am interested in observe the local lattice distortions in the FeAs layers resulting from this interaction. In fact, this kind of local distortions are known to affect the electronic and superconducting properties. Moreover, from ARPES measurements high degree of disorder has been found with a so-called “glassy” non-dispersing electron band coming from Ir 5d orbitals. Electronic disorder may be linked to structural disorder,
the temperature evolution of Ir L$_2$ and Ir L$_3$ edge XAS spectra (see Fig. 4 a). By integrating the main peak (realted to 2p $\rightarrow$ 5d electronic transitions) and taking the ratio $R_{2,3} = I(L_3)/I(L_2)$ it is possible to estimate the spin orbit operator $\langle L \cdot S \rangle$. We found a rather low ratio of about 3 for every temperature investigated which point out the marginal role of spin orbit coupling in the electronic properties. In addition, we didn’t observe any anomaly or renormalization in the $(L \cdot S)$ operator so we concluded that the spin orbit interaction is not driving the SPT at 100 K.

This experiment has been published on Physical Review B$^{13}$.

Bismuth based superconductors

Very recently a new class of SCs with a layered structure has been discovered$^{14}$. The active layer is composed by Bi atoms coordinated with S (or Se) atoms to form a square lattice while the spacer layer is composed by rare earth (RE) oxide (the structure is sketched in Fig.1). In REOBi$_2$ superconductivity takes place upon substitution of oxygen with optimal amount of fluorene. Despite a rather low Tc (maximum at about 10.6 K) these systems are considered valid candidates as a new family of non-conventional superconductors. In fact, evidence of multiband character$^{16,21}$ and indication of Fermi surface nesting$^{16,21}$ in a quasi 2D layered structure are reminiscent of Fe-based superconductors. Several studies indicate usual BCS-like superconductivity coming from electron-phonon coupling. Strong electron-phonon coupling has been predicted$^{16}$ and found experimentally$^{17,18}$ along with the finding of low electron-electron correlations$^{22,28}$. On the other hand, no anomaly in the phonon spectrum has been observed across Tc from neutron scattering$^{29}$ and an anomalous value of 2D/Tc = 16.8 has been observed from STS$^{30}$ indicating a pairing mechanism which is beyond the usual BCS-like. In addition, from specific heat measurement$^{31}$ indication of a quantum critical point has been found. As a result, debate between a BCS and non-conventional superconducting scenario in bismuth based materials is still far to be settled. As in the Fe-based family, superconducting dome can be reached by electron doping $(O_{1-x}F_x)$ in the spacer layers. One of the most notable experimental results is the large enhancement of Tc (from 3K to 11K) by applying external pressure$^{18,19}$ and by high pressure annealing techniques in sample preparation$^{20}$. Along with external pressure effects, chemical pressure can directly affect the superconducting properties$^{22}$. The above peculiar features are shared with Fe-based superconductors and underline the interplay between local structure and the electronic and superconducting properties.
FIG. 5: In panel a) the Ce L$_3$-edge XAS spectrum of CeO$_{1-x}$F$_x$BiS$_2$ at different F-doping level is presented, the inset shows the background subtracted XAS. The peaks labeled $4f^1$ and $4f^0$ are related, respectively to Ce $3^+$ and $4^+$ components. Panel b) shows the behavior of the relative weight of $4f^0$ peak as a function of doping level ($x$). The side panel show the crossover between coupling and decoupling between the active and spacer layers above and below the critical F-concentration of $x_c = 0.4$.

**PhD project: Early results on REO$_{1-x}$F$_x$BiCh$_2$**

Among different Bi-based superconductors, the CeO$_{1-x}$F$_x$BiS$_2$ system shows very peculiar properties as a function of F-doping. In fact, for $x < 0.4$ it is non-magnetic and non-superconducting while for $x > 0.4$ it show coexistence of superconductivity and ferromagnetism. We have exploited XAS spectroscopy in order to answer the following questions: (i) What is the origin of the coexistence of FM and SC? (ii) How is it related to the valence of Ce atoms? (iii) What is the role played by the local structure?

From Ce L$_3$-edge XAS we studied the evolution of electronic structure and valence fluctuation upon F-substitution and we provided understanding of the coexistence of ferromagnetism and superconductivity. We found that the Ce $4^+$ component disappears at $x > 0.4$ where the system start to show the coexistence of superconductivity and ferromagnetism (see Fig.5) and the effect of F-doping is to break the Ce-S-Bi interlayer coupling channel. This system is known to be susceptible to external pressure, namely Tc increases from 2 to 10 K under high pressure or with high pressure synthesis (HP) in sample preparation. From combined Ce L$_3$ and Bi L$_3$-edge EXAFS spectroscopy we observed the evolution of disorder and local lattice distortions in CeO$_{1-x}$F$_x$BiS$_2$ upon F-doping for both ambient and HP prepared samples. Local structure of both active and spacer layers showed clear doping evolution (e.g. local bond distances are presented in Fig.6a), the effect of HP annealing is prominent in the BiS$_2$ layer which shows structural disorder. The local buckling of the BiS$_2$ layer decreases with increasing F-content confirming the scenario of structural instability. In terms of electronic structure there is disagreement between different ARPES studies due to microscale phase separation and band reconstruction at the surface. To address these issues we decided to investigate the electronic structure of LaO$_{1-x}$F$_x$BiSe$_2$ using space resolved ARPES with sub-micrometer spatial resolution. Our measurement revealed microscale inhomogeneity allowing us to measure the actual bulk electronic structure avoiding inhomogeneity effects. Our findings are in good agreement with band structure calculations suggesting that electron/polaron correlations are irrelevant. Moreover, we found rather broad features indicating disorder in the BiSe$_2$ plane. The results on REO$_{1-x}$F$_x$BiCh$_2$ has been reported in three publications.

**PhD project: Summary and perspectives**

It is well known in the field of layered superconductors that the superconducting properties depend on defects and on their arrangement and knowing the average or ideal structure is not enough. In addition, in the iron based family local distortions in the active layers strongly affects Fermi surface shape and hence superconductivity. In this context, the knowledge of interaction between different layers and its effects on the electronic transport mechanism is crucial. The goal of this research field is to shed light on basic physical mechanisms for SC and also provide indication for fabrication of new SC materials with desired properties. The focus of my PhD project is on two representative and recently discovered systems, in particular:

Disorder and local lattice distortions in the iron
pnictide \( \text{Ca}_{10}M_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \) will be studied as a function of control parameters like temperature and pressure. By changing stoichiometry, going from \( M = \text{Ir} \) to \( M = \text{Pt} \), the system \( \text{Ca}_{10}M_4\text{As}_8(\text{Fe}_2\text{As}_2)_5 \) show different properties due to effect of 5d-metal vacancies in the spacer layer.

In \( \text{REO}_{1-x}\text{F}_x\text{BiCh}_2 \), disorder and local lattice distortions as a function of control parameters like temperature, pressure and chemical pressure in the spacer (\( \text{RE} = \text{La}, \text{Ce}, \text{Nd}, \text{Sm} \)) and in the active (\( \text{Ch} = \text{S}, \text{Se} \)) layers will be investigated.

A natural question which arise is What is the effect of the local structure in the electronic properties? From X-ray absorption spectroscopy we can extract information on the unoccupied electronic states. In fact, XANES spectroscopy is capable to probe both atomic and electronic structure, being sensitive to both. In order to disentangle the structural and electronic contribution to the XANES features I will exploit the comparison with theoretical calculations using multiple scattering approach. In order to obtain a complete view I will study the effects of nanoscale distortions in the functional properties. In this class of materials the nanoscale distortions can be polarized in space giving rise to non-homogeneous distributions and intrinsic phase separation even in the electronic structure. These effects will be observed by means of \( \mu \)-ARPES which is a space resolved photoemission probe, capable to give a microscopic view in the electronic structure.

Experiments and collaborations

This work will be mainly done using the local and element sensitivity of EXAFS spectroscopy to unveil the local lattice distortions. XANES spectroscopy will be performed and compared to multiple scattering calculations, in order to observe the local unoccupied electronic states and band filling as well as the local atomic arrangement. The extreme susceptibility of this class of materials from external conditions allows tuning of some of the fundamental properties by applying pressure, chemical or mechanical. Along with chemical pressure (obtained by element substitution), hydrostatic pressure effects will be investigated by means of diamond anvil cells (DAC). In order to look for non-homogeneities and intrinsic phase separation in the structural and electronic features we will use space resolved probes like micro-XAS and micro-ARPES. Our results will be integrated with other techniques like synchrotron X-ray diffraction and Raman spectroscopy. The hard X-ray absorption measurements require high intensity and energy-tunable sources, for this reason this kind of measurements will be carried out in international synchrotron facilities like ESRF in Grenoble (France) and ELETTRA in Trieste (Italy). In our laboratory i will do preliminary studies for morphological and photoemission characterization of the samples.

To carry out the proposed work a long standing collaboration with the following groups will be exploited:

**Space resolved ARPES** (Prof. Takashi Mizukawa’s group from the University of Tokyo)

**Raman and high pressure measurements** (Profs. Paolo Dore and Paolo Postorino from the HPS group @ La Sapienza)

**X-ray diffraction** (Dr. Boby Joseph from ELETTRA synchrotron)

**Sample preparation of 10-4-18 family** (Prof. Minoru Nohara’s group from Okayama University)

**Sample preparation of Bi-based family** (Profs. Yoshihiko Takano from NIMS institute and Yoshikazu Mizuguchi from Tokyo Metropolitan University)

**Sample preparation of Fe-based family** (Prof. Marina Putti’s group from Genova University).

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