Symphonic use of quantum beams for materials science -now and future-

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Abstract.

Symphonic use of multiple probes for materials science is discussed through two recent studies on high-$T_c$ superconductors, and a future prospect of the symphonic use is given. For a hydrogen-doped iron-based superconductor, which shows a double-peaked superconducting dome as a function of hydrogen concentration, symphonic use of neutron, muon and synchrotron x-ray probes discovered a second antiferromagnetic (AF) phase and its contrasting feature compared to the first AF phase. A drastic change of the AF order by Ni impurities in slightly hole-doped La$_2$CuO$_4$, a Mott insulator, has been studied by using neutron and synchrotron x-ray probes. The symphonic use of these probes clarified the microscopic dual electronic states for both Cu and Ni in this system.

1. Introduction

Recent research in materials science has widely utilized quantum beams such as synchrotron x-ray, neutron and other beams to understand the origin of novel properties. In particular, many researches on novel materials such as multiferroic materials and high-$T_c$ superconductors require “symphonic use” of quantum beam probes or multi-probe use (MPU). There are two main reasons for such MPU. One is the recent development of quantum beam techniques. For example, an energy tunable x-ray beam with high brilliance and intensity is produced in advanced synchrotron facilities. Also, intense pulsed neutron beams are produced in spallation neutron facilities. Then these quantum beams can provide detailed information on crystal, magnetic and electronic structures of a wide variety of materials. The other reason is complicate coexistence of hierarchical structures with different length, energy and temporal scales in novel materials. Such coexistence is possibly related with inter-coupled electronic, vibrational and magnetic properties in novel materials. Therefore, only single probe use is not enough to obtain invaluable information on these multi-scale materials. In general, use of different types of beam is done one by one. On the other hand, future MPU of different types of probe or symphonic use will be done simultaneously and the information by each probe can be exchanged and can affect running experiments. MPU then enhances the effectiveness of each experiment, helps to understand unknown phenomenon, and is suitable for heterogeneous multi-scale systems. In the following session, we present several examples of MPU.
2. Examples of symphonic use for superconducting materials

2.1 Discovery of the second magnetic phase of an iron-based superconductor

Role of magnetism is one of the most important and longstanding issues for the novel superconductors. In these systems, the superconductivity appears by destroying a magnetic phase in a parent compound by carrier doping or band filling control. In that sense, a magnetic phase transforms to a superconducting phase. A recent study reported an advanced doping method using a hydrogen anion instead of fluorine in the La1111 type iron-based superconductor that has surpassed the doping-limit of fluorine, and uncovered the concealed second superconducting dome (SC2), in addition to the first superconducting dome (SC1) [1]. If the origin of two superconducting domes is different or two distinct superconducting phases exist, the existence of a second magnetic phase is highly suggested. Then to search for a hidden magnetic phase started beyond the SC2 doping region, MPU has been performed using neutron, muon, and x-ray beams.

Shortly after the start of the MPU project, a second anti-ferromagnetic phase (AF2) was discovered and the overall phase diagram of AF2 and the detailed properties were determined (Figure 1). In the project, muon spins injected in the hydrogen-doped sample first detected a local magnetic field developing at low temperature, which strongly suggests the existence of magnetic order for $x > 0.4$ in Figure 1. Then neutron scattering confirmed a long range magnetic order and determined the spin...
structure as well as the size of the ordered moment, both of them were found to be different between AF1 and AF2 as shown in Figure. 1. Just above the magnetic phase transition in AF2 synchrotron x-ray diffraction observed a structural phase transition and determined the anomalously large atomic shifts at the transition.

Furthermore, the muon experiment strongly suggests a heterogeneous feature near the boundary of SC2 and AF2 due to the imperfect antiferromagnetic volume fraction at the base temperature (Figure. 2 (b)). On the other hand, the peak-width of the magnetic Bragg reflection by neutron diffraction experiment is instrumental resolution-limited (Figure. 2(a)) at $x = 0.51$, which means the length scale of the magnetically ordered region is larger than 10~100 nm. A neutron diffraction experiment at $x \sim 0.4$ will clarify if the coexistence between magnetic and superconducting phases near the boundary is microscopic or mesoscopic in nature.

As shown in this topic, MPU made it possible to discover a new magnetic phase (AF2) and to extract the contrasting feature compared to AF1. Scientifically, the discovery of AF2 reconfirmed the appearance of magnetic and superconducting phases in pairs. Also, the contrasting feature between AF1 and AF2 strongly suggests contrasting superconducting property and origin between SC1 and SC2.

In general, each probe in a MPU study not only contributes to solve a target issue but also sometimes provides supplemental information by applying the unique feature of each probe. For this example, high sensitivity to hydrogen atoms of neutron beam discovered a tunneling motion of the doped hydrogen atoms in the iron-based superconductor. Interestingly, the tunneling motion was found to be drastically affected by the opening of superconducting gap. Therefore, the detail analysis of the tunneling motion can provide valuable information on the superconducting gap [2].

2.2 Ni impurity effect in a doped cuprate superconductor

MPU plays important roles to understand unusual phenomena. It has been well known that a tiny amount (~1%) of hole-carrier doped into La$_2$CuO$_4$, an antiferromagnetic Mott insulator, drastically destroys the antiferromagnetic order. Such effect has been believed to occur by forming a so-called

![Figure 3](image1.png)

**Figure 3.** Schematics of the Ni-doped CuO$_2$ plane in the (a) Ni-rich and (b) hole-rich groups (reprinted with permission from [5], copyright 2009, the American Physical Society). The red (blue) clouds around Ni (Cu) represent spatially trapped (mobile) holes. Spin direction of Ni$^{2+}$ ($S = 1$) in (a) is not confirmed experimentally. With increasing the number of Ni$^{2+}$, the spin direction should rotate 90 degrees and form a spin structure of La$_2$NiO$_4$.

![Figure 4](image2.png)

**Figure 4.** Magnetic phase-diagram of La$_{2.13}$Ni$_{0.5}$O$_4$ determined by neutron scattering (reprinted with permission from [4], copyright 2005, the Physical Society of Japan). The data point at $y = 0$ (closed circle) was taken from a magnetization measurement. The curved broken line presents results from susceptibility measurements [3] and the thick broken line represents $T_N$ for La$_{2.13}$Ni$_{0.5}$O$_4$. 
Zhang-Rice (ZR) singlet state which rapidly moving on the antiferromagnetic ordered CuO$_2$ plane (Figure 3(b)). However, a fascinating phenomenon was discovered when a tiny amount of Ni-impurity is compensated for the doped hole in the magnetically diminished samples. In contrast to common sense Ni-impurities recover the magnetic order! This recovery only occurs in hole-doped samples. Ni-impurities in non-doped La$_2$CuO$_4$ weakly affect the magnetic order due to the dilution effect of magnetic moment (as shown by a broken line in Figure 4). The first observation of this effect was made by a magnetization measurement [3]. But there was no interpretation for the reason. Then a neutron diffraction measurement has been performed using single crystals of La$_{1.99}$Sr$_{0.01}$Cu$_{1-y}$Ni$_y$O$_4$ [4]. The neutron scattering not only reconfirmed the recovery of magnetic order by Ni but also discovered the change in the magnetic structure with increasing Ni concentration. A switch of spin structure from the La$_2$CuO$_4$ type to the La$_2$NiO$_4$ type occurs by a spin rotation in CuO$_2$ planes by 90 degrees. This effect strongly suggests that for $y > 0.05$ the Ni spin direction should be equal to that of La$_2$NiO$_4$ and each Ni spin has $S = 1$ (Ni$^{2+}$). Then the question is the Ni spin state for the dilute region $y < 0.03$ where the magnetic order recovers with Ni impurity. A hypothesis to explain the effect is the “blotting paper effect”, when the substituted Ni absorbs or traps a hole, the effective Ni spin state changes to $S_{\text{eff}} = 1/2$ (Ni$^{2+}$, more exactly Ni$^{2+}L$, where $L$ represents a ligand hole bound on oxygen atoms around Ni), the same as Cu$^{2+}$. The local spin direction at the Ni-site is also expected to be identical to that of Cu. Thereby, the hole-trapped Ni decreases the number of ZR singlets and recovers the magnetic order (Figure 3). In order to experimentally confirm this hypothesis local information on the electronic state of Ni is indispensable. Then x-ray-absorption fine structure (XAFS) experiment to study the element-selective electronic as well as crystal structure around a Ni dopant has been performed using single crystals over a wide hole-doping range. Then the near-edge structure is found to be consistent with that of Ni$^{2+}$ for the Ni rich and Ni$^{2+}L$ for hole-rich samples. Furthermore, as shown in Figure 5, the two types of extended XAFS (EXAFS) pattern were obtained only for the x-ray polarization parallel to CuO$_2$ plane. The two types of EXAFS pattern correspond to two types of in-plane Ni-O bond length as shown in Figure 6 (a).

Combined with previous results on hole-localization effects (“blotting paper effect”) of Ni, two types of charge states are strongly indicated for Ni. This duality disqualifies a magnetic-impurity picture for Ni dopant in the superconducting phase of cuprates. In order to understand the microscopic reason why the “blotting paper effect” occurs by Ni in hole-doped La$_2$CuO$_4$ it is important to distinguish the four types local charge state, Cu$^{2+}$, ZR-singlet, Ni$^{2+}$ and Ni$^{2+}L$. One of the best probes is a resonant inelastic x-ray scattering (RIXS). In fact, a preliminary RIXS experiment has been performed for both Ni-substituted La$_2$CuO$_4$ and Cu-substituted La$_2$NiO$_4$ [6]. The capability of RIXS to investigate the local excitations around the substituted

**Figure 5.** Raw data of polarized XAFS at Ni K-edge of La$_{2-2x}$Sr$_x$Cu$_{1-y}$Ni$_y$O$_4$ for polarization of x-ray beam parallel (a) and perpendicular (b) to CuO$_2$ plane (reprinted with permission from [5], copyright 2009, the American Physical Society). The Ni$^{2+}$ standard sample of (5–100) is included (closed symbol). Here, the hole and Ni concentrations are expressed as (100x -100y).
element was demonstrated; that is, electronic excitations in La$_2$Cu$_{0.95}$Ni$_{0.05}$O$_4$ and La$_2$Cu$_{0.05}$Ni$_{0.95}$O$_4$ were successfully observed at the K-edge of the substituted element. When the incident photon energy is tuned to the well-screened core hole state, charge transfer excitations from O 2$p$ to substituted Cu or Ni 3$d$ states appear in the spectra. The edge position of the charge transfer excitations is found to be different between the bulk state and the substitute state even if the same element is targeted by RIXS. These observations strongly suggest that RIXS on the substituted atoms can be useful for exploring their electronic states affected by their surroundings.

3. Future of symphonic use of quantum beams

In the near future, thanks to further development of quantum beam probes, symphonic use of multi-probe will open a new paradigm for materials science. In one way, such development will expand the accessible region in a length-frequency ($Q$, $\omega$) space of each probe. For example, both x-ray and neutron inelastic scattering will observe the same elementary excitations in materials such as phonons and magnons with the same instrumental resolution. Then one can discuss an “inner structure” of elementary excitations. For example, since neutrons are sensitive to nuclei while x-rays are sensitive to the surrounding electrons, phonons by neutron dominantly reflect the motions of nuclei, while those by x-ray reflect the motion of surrounding electrons. Therefore, by combining information from each probe one can extract the inner structure of phonons or, in other words, valuable information on electron-phonon interaction in materials. In the other direction, symphonic use will be carried out to elucidate a phenomenon from multi-direction in ($R$, t)$\times$($Q$, $\omega$) space, for example, elucidation of phonons in heterogeneous multi-scale system requires both information on atomic motion in the local($R$)-real time (t) space and wave-like nature in length-frequency ($Q$, $\omega$) space.

The ultimate symphonic use of multiple probes does not simply mean a combination of various probes but means a new type of research complex where inter-correlated and inter-affected experiments (or sometimes including theories) are performed using different types of probes.

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