Fe-doping effects on magnetism in hole-type superconductors of \((\text{Bi,Pb})_2\text{Sr}_2\text{CuO}_6\)

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Abstract. We studied Fe-dopant effects on spin correlations in \(\text{Bi}_{1.75}\text{Pb}_{0.25}\text{Sr}_{1.90}\text{CuO}_{6+\delta'}\). Magnetic neutron elastic scattering, which is absent in a pristine sample, has been observed at incommensurate positions with an incommensurability of \(\delta \sim 0.2\). Surprisingly, this anomalously large \(\delta\) follows a linear relation \(\delta \sim p\) even in the overdoped region, unlike for \(\text{La}_{2-x}\text{Sr}_x\text{CuO}_4\). We discuss this specific feature observed in the overdoped phase from a dynamical stripe viewpoint.

1. Introduction

According to past neutron scattering studies, incommensurate spin correlations (ISC) are found to remain robustly even in the hole overdoped region and must be essential for driving high-\(T_c\) superconductivity in cuprates. One of the most striking feature of ISC in \(\text{La}_{2-x}\text{Sr}_x\text{CuO}_4\) (LSCO) and \(\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta'}\) (YBCO) should be a linearity between the incommensurability \(\delta\) and the hole-doping rate \(p\) in the underdoped region, and a saturated behavior of \(\delta\) in the overdoped region \([1, 2, 3, 4]\). Nonetheless, no magnetic neutron scattering has been reported yet for typical hole-type superconductors of \((\text{Bi,Pb})_2\text{Sr}_2\text{CuO}_{6+\delta}\), so-called \(\text{"(Bi,Pb)2201"}\).

In this paper, we study impurity-doped systems of \((\text{Bi,Pb})_2201\) to gain a clue of the “hidden” magnetic cross section. For Fe-dopant system, neutron diffuse scattering is discovered at incommensurate positions around \((\pi, \pi)\) and, unexpectedly, a large incommensurability of \(\delta \sim 0.2\) is found. We discuss a linear relation between the anomalous \(\delta\) and \(p\) in the overdoped phase in terms of dynamical stripe.

2. Sample characterization

Two series of single crystals were grown in air by the traveling-solvent floating-zone technique; \(\text{Bi}_{1.75}\text{Pb}_{0.25}\text{Sr}_{1.90}\text{Cu}_{0.97}\text{Tr}_{0.03}\text{O}_{6+\delta'}\) \((\text{Tr}=\text{Mn, Fe, Ni, Cu})\) and \(\text{Bi}_{1.75}\text{Pb}_{0.25}\text{Sr}_{1.90}\text{Cu}_{1-y}\text{Fe}_y\text{O}_{6+\delta'}\) \((y = 0.03, 0.06, 0.09,\) and \(0.15)\). The introduction of dopant was confirmed by X-ray-powder diffraction \([5]\) and ICP chemical analysis. The crystal structure analyzed at room temperature was consistent with the \(\text{Pnma}\) orthorhombic symmetry \([6]\). Only the 15%-Fe doped sample showed a deviation in the Cu concentration, due probably to excess CuO added during crystal growth.

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Unpolarized (polarized) neutron-scattering experiments were performed on triple-axis spectrometers TOPAN and AKANE (TAS-1) at the research reactor JRR-3 in the Japan Atomic Energy Agency, Japan. The incident neutron energy was set to 14.7 meV for TOPAN and TAS-1, and 19.4 meV for AKANE. The samples used for neutron scattering were approximately 30×5×2 mm³ in size, and 2θ < 0.5° for y ≤ 0.09 and ~1° for y = 0.15 in mosaicity. The scattering process in the CuO₂ plane was observed in the (h, k, 0) scattering plane by the triple-axis neutron spectroscopy, where a* ≈ 1.18 Å⁻¹ and b* ≈ 1.17 Å⁻¹.

Polarized XAFS experiments were performed on the beamline BL14B1 at SPring-8, Japan. An energy resolution of approximately ~1 eV was achieved by using a Si(111) double-crystal monochromator. Fe K-edge XAFS spectra were measured using a y = 0.15 single crystal and a Fe₂O₃ powder sample at room temperature. In case of y = 0.15, two types of absorption Iₓab and Iₓ were measured, in which an electric field of X-ray directs in the CuO₂ plane and along the c-axis, respectively.

3. Results and Analyses

3.1. Sample characterization

First, we surveyed which dopant can induce magnetic correlations effectively. Figure 1(a) shows a 3%-Tr dependence on the in-plane magnetic susceptibility χₓab, in which a magnetic field (H) of 1 T was applied in a direction parallel to the CuO₂ plane. Interestingly, there is little change in the Ni-doped sample. It strongly suggests a non-magnetic feature of Ni dopant, as proved in La₂₋ₓSrₓCuO₄ [7]. On the other hand, because of a substantial increase for Fe dopant, we below focus on Fe-doped compounds.

Figure 1(b) shows χₓab(T) of the series of Fe-doped samples. The Curie-Weiss law for high-temperature susceptibility was used to calculate the Curie constant C and the Weiss temperature (1/θ) ∼ 10 K. As can be seen in the inset of Fig. 1(b), C linearly increases up to y = 0.09. The effective number of Bohr magnetons ρₑff was found to be 4.4 using the equation C = (Nµ²∥HB/3kB)ρₑff, by assuming that only the Fe spins contribute to C. The deviation of the C-y relation from linearity for y = 0.15 suggests that the effect of the additional magnetic interactions was pronounced in this case. The peak width in the Q-scan was actually narrower for y = 0.15 than for y = 0.09 [see Fig. 2(a)]. Therefore, crystals with y = 0.09 were used for measurements with a priority to estimate the inherent Cu-spin correlations in (Bi,Pb)₂201.

In order to evaluate ρₑ, Tₑonset is determined from magnetic shielding effect. Tₑonset is ~6 K and 23 K for the as-grown and Ar-annealed (600 °C×5 days) pristine samples, respectively. Hence,

![Figure 1](image-url)

**Figure 1.** (a) Dopant-element and (b) Fe-doping dependence on χₓab. The inset in (b) shows the Curie constant of Fe-doped samples as a function of y. (c) ρₓab from as-grown samples with y = 0.09 and y = 0, together with that from the Ar-annealed pristine sample. (d) Fe K-edge XAFS spectra of as-grown single crystal with y = 0.15. The polarization dependence is weight-averaged to compare the edge energy with that of (Fe³⁺)₂O₃ powder sample.
the pristine as-grown sample is expected to be overdoped. The in-plane resistivity $\rho_{ab}$ of the as-grown pristine sample actually shows a normal metallic transport above $T^\ast_{\text{inset}}$ [Fig. 1(c)]. Using a dome-shaped superconducting phase diagram [9], the effective hole number of the pristine as-grown sample is evaluated to be $p \sim 0.25$, being consistent with a value (0.27) in Ref. [8]. Indeed, from recent ARPES measurements on as-grown crystals, $p$ is found to be 0.28(2) and 0.23(2) for the pristine and the 9% Fe-doped samples, respectively [10]. Such the reduction in $p$ caused by Fe doping indicates a formation of Fe$^{3+}$ charge states. This conjecture is supported by a comparable edge energy of Fe $K$-absorption of $y = 0.15$ with that of a Fe$^{3+}$ standard sample of Fe$_2$O$_3$, as shown in Fig. 1(d). Fe doping of 9% is sufficient for destroying the superconductivity in the heavily overdoped phase, and it causes an increase in the residual resistivity and carrier localization at low temperatures, as is evident from the upturn in $\rho_{ab}$ [Fig. 1(c)].

3.2. Elastic neutron scattering
Spin correlations distinctly induced by Fe doping were first studied by unpolarized neutron scattering experiments. As shown in Fig. 2(a), incommensurate elastic scattering, which is absent in pristine sample, occurs at low temperatures at around $(1, 0, 0)$ and the peak intensity grows with Fe doping. The elastic diffuse peaks, which start appearing below $T^\ast \sim 40$ K for $y = 0.09$ [Fig. 2(b)], correspond to antiferromagnetic short-range modulations propagating along the Cu-O-Cu bond axes. The direction of spin modulation is found to be identical to that observed for the superconducting LSCO and YBCO systems. Further, results of the polarized-neutron analysis performed in a spin-flip channel confirm that the diffuse incommensurate peaks appearing below $T^\ast$ are of magnetic origin, as shown in Fig. 2(c). We fitted the magnetic cross sections of the difference plot [Fig. 2(a)] to a pair of Lorentzian peaks at $Q_\pm = (1 \pm \delta, \pm \delta, 0)$.

Figure 2. (a) Difference plots with a relative scale using offset. The curved lines show fits by a pair of Lorentzians and a constant. Dependence of the $q$-integrated intensity on Fe doping quantity is shown in the inset. (b) The thermal evolution of the incommensurate peak at $Q_- = (0.8, -0.2, 0)$. The solid line is drawn as a guide. (c) Temperature variation of $Q$ spectra observed using polarized neutrons in the spin-flip channel with a horizontal field of $\sim$20 Oe applied in a direction parallel to that of the scattering vector. (d) Comparison of $\delta$ between Fe-doped (Bi,Pb)2201, pristine LSCO [1, 2, 3], and YBCO samples [4]. Dynamical data are plotted for LSCO ($\omega = 3 - 6$ meV at $T \sim T_c$) and YBCO ($\omega \ll$ (resonance energy) at $T < T_c$). The $p$ range of the superconducting phase is indicated by a thick bar at the base line. The solid line is drawn as a guide for LSCO and YBCO data.
with HWHM $\kappa$. As a result, $\delta = 0.21(1)$ and $\kappa = 0.086(17)$ Å$^{-1}$ were extracted for $y = 0.09$, for example. $\delta$ changes little upon Fe doping within the concentration range, but the peak width at $y = 0.15$ becomes smaller than that at $y = 0.09$. The normalized $q$-integrated intensity presented in the inset of Fig. 2(a) shows a linear increase up to $y = 0.09$ but a slight increase at $y = 0.15$, thereby indicating the non-linear dependence of $y$ on $C$.

4. Discussions
Since the average Fe-Fe separation $R_{\text{Fe-Fe}} (= a_{\text{tet}}/\sqrt{3})$ nearly corresponds to $\xi$ when $y = 0.09$, small clusters with diameter $\xi$ must be formed around Fe. The linear dependences of $C$ and the neutron scattering intensity on $y$ below $y = 0.09$ and the nondependence of $\delta$ on $y$ suggest that the noninteracting clusters are induced. However, Fe doping beyond $y \sim 0.1$ may introduce additional effects of Fe-Fe and/or inter cluster interactions, which cause the upper deviations in $C$ and the scattering intensity.

Although the local charge state of Fe is likely Fe$^{3+}$, the obtained $p_{\text{eff}}$ is much smaller than that expected for $S = 5/2$ ($p_{\text{eff}} = 5.9$). To explain the decreasing $p_{\text{eff}}$, we speculate that the Fe spin strongly couples with neighbor Cu spins and/or ligand hole spins in the anti-parallel way, thus resulting in a reduction in $p_{\text{eff}}$. Note that a similar reduction in the effective spin value is observable in Ni-doped LSCO [7].

The most distinct feature in current ISC should be the anomalously large $\delta$. Interestingly, $\delta$ for $y = 0.09$ of (Bi,Pb)2201 obeys the linear relation $\delta = p$ even if $p$ exceeds 0.2, whereas $\delta$ for LSCO [1, 2, 3] and YBCO [4] shows a saturation in the overdoped region. A possible scenario is that even in the overdoped region, doped holes continuously form charge stripes. In the pristine sample, however, since the charge stripes are highly dynamic, ISC cannot be detected by low-frequency probes. However, spin injection results in carrier localization, which reduces the characteristic frequency of the ISC, and makes it detectable. In the overdoped region of LSCO, a phase separation between the superconducting and normal metallic phases is suggested experimentally [11, 12, 13]. If such the phase separation can result in the saturated $\delta$ but can be suppressed by local Fe-spin injection, one can expect to observe a non-saturating doping dependence of $\delta = p$ in Fe-doped overdoped compounds.

Acknowledgments
We are grateful to K. Kudo for his helpful discussions, and thank K. Nemoto and M. Sakurai for their assistance in neutron experiments at JRR-3 and crystal growth, respectively. This study was carried out under the Common-Use Facility Program of JAEA, and the Quantum Beam Technology Program of JST. The study performed at Tohoku University was supported by a Grant-In-Aid for Science Research C (19540358, 21540350) and B (19340090) from the MEXT.

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