STM measurements of Ni impurity effects in Bi2212

A Nakagawa, T Sakaidani, Y Kiguchi, T Uto and A Matsuda
Department of Physics, Schools of Advanced Science and Engineering, Waseda University, Okubo 3-4-1, Shinjuku, Tokyo 160-8555, Japan

naktme@gmail.com

Abstract. We report on the STS measurements for the temperature dependences of density-of-states for optimally-doped and overdoped samples. In the tunnelling spectra above \( T_C \) in an overdoped sample, we found two types of a pseudogap; the large one, which had a typical pseudogap size and decreased with increasing a temperature, and the small one, which seemed almost temperature independent in our measured temperature range. The large gap seemed to switch to the small one with some overlap region with increasing a temperature. Similar behaviour was found in the optimally doped samples with an enhanced gap size and the temperature range. We identified the large gap as a conventional pseudogap and the small one as a new pseudogap, which is associated with Ni impurity. This shows a peculiarity of Ni impurity, and suggests an unusual interaction between an impurity and the Cu-O electronic system.

1. Introduction
In the high-temperature superconductor, so called a pseudogap state develops in the underdoped region above a superconducting transition temperature \( T_c \). Although its origin has not been identified yet, it is intimately related to the superconducting state, since their gaps are smoothly connected each other at \( T_c \). Recently, they are considered to be mutually competitive. Nevertheless, the origin of the pseudogap thought to be strongly related to the mechanism of high-temperature superconductivity.

We have been studied impurity effects on the pseudogap states, because they discriminate the difference and/or the similarity of the superconducting and the pseudogap states. One of the features of superconducting gap/pseudogap in Bi2212 is that its value continues to increase with increasing a temperature up to the pseudogap opening temperature \( T^* \) in the wide doping levels from the underdoped to the overdoped region. But, in the heavily overdoped region, it decreases with increasing a temperature and disappears at \( T_c \) (Figure 1) [1]. Previously, we reported transport properties and temperature and carrier doping dependences of the density-of-states (DOS) in the pseudogap states of Co-doped Bi2212s. We found that the Co\(^{3+}\) substitution into the Cu\(^{2+}\) sites essentially preserved the \( T_c \) vs carrier density (\( p \)) relation, so-called Tallon’s empirical law, with some doping level shift due to the difference in the valence value. On the other hand, for overdoped samples, the Co impurity significantly enhances pseudogap value and alters the temperature dependence of the pseudogap from that of the pure-Bi2212 samples [2], while its \( T^* \) is unchanged. There is rather strong impurity effect on the pseudogap, in contrast to the common sense that the pseudogap shows a little impurity effect.

It is important to know that these results are universal or not. Here, we report the result of the Ni impurity effect on the pseudogap states. In the case of the Ni substitution, we found somewhat different behavior in the \( T_c \) vs \( p \) relation; (1) in the overdoped region, the \( T_c \) vs \( p \) relation followed
Talon’s law, (2) in the underdoped region, superconductivity was more strongly destroyed by the Ni impurity [3]. These results indicate that there is large impurity species dependence in the impurity effects. However, a little has been known about the electronic state of Ni substituted samples.

In this paper, we concentrate on the impurity effect in the temperature dependence of a pseudogap in the Bi2212 and compare the results of Co and Ni. The DOSs were measured by a scanning tunneling microscope (STM). We will show a new type of a pseudogap specifically associated to Ni impurity.

**Figure 1.** typical temperature dependence of DOS in pure-Bi2212; (a) The excess oxygen $\delta = 0.28$ (upper panel), $\delta = 0.24$ (lower panel), (b) temperature dependence of gap values estimated as positive bias peak position or shoulder position [1]

### 2. Experiments

The Ni substituted Bi2212 ($\text{Bi}_{2-x}\text{Sr}_x\text{Ca}(\text{Cu}_{1-x}\text{Ni}_x)\text{O}_8$; Ni-Bi2212, $x=0.03$) single crystals were grown by the traveling solvent floating zone method. They were annealed under the atmosphere of Ar and O$_2$ gas mixture, with a proper oxygen partial pressure. The excess oxygen $\delta$ was adjusted to 0.25 for optimally doped (OP) samples and 0.27 for overdoped one. The $T_c$ of both samples determined by the DC magnetic susceptibility measurements were 72 K and 71 K, respectively [6].

STM measurements were performed in the temperature range from 79 K to 230 K with an electro-chemically etched W tip under a pressure of $\sim 10^{-10}$ Torr. The Ni-Bi2212 crystals were cleaved under the ultra-high vacuum atmosphere at around 79 K. We acquired I-V characteristics in each 8x8 points of 10x10 nm areas. Then density-of-states were obtained by numerically differenciating the averaged I-V characteristics. The topography of Ni-Bi2212 surface is shown in Figure 2.

**Figure 2.** Topography of Ni-Bi2212 in 10x10 nm$^2$ areas.

**Figure 3.** Temperature dependence of DOS; (a) OP sample and (b) OD sample. The dushed line shows the estimated gap value.
3. Results and Discussions

Figure 3 shows the tunnelling spectra of Ni-Bi2212s. In the optimally doped sample (Fig.3a), we found that the pseudogap value increases with increasing a temperature. However, we see additional structures above 179 K, which was never observed in the pure and Co substituted samples above \( T_c \). We identify this structure as a small pseudogap with a gap value of \( \approx 10 \) mV. Smallness of the signal should be due to a small gap value and a high observing temperature. In the overdoped sample (Fig.3b), the same structure was confirmed at somewhat lower temperatures. Furthermore, the small pseudogap remains open above the pseudogap opening temperature \( T^* \) \( (\approx 160 \) K), which was determined by the c-axis resistivity up-turn (see Fig. 5) [4]. The appearance of the small pseudogap is a new result and discriminate Ni impurity from Co impurity.

We show temperature dependences of these pseudogap values in Fig. 4. The results of the pure-Bi2212 were also shown for the comparison. We adopted the gap value as a shoulder voltage in the DOS. In the optimally doped samples, we see that the pseudogap is enhanced and increasing behaviour with a temperature, similar to the results of the pure sample. In the overdoped samples, the pseudogap value decreases with increasing a temperature. Both tendencies are essentially same as the Co substituted one. We naturally identify the large sized gap as a conventional pseudogap and these characteristic behaviors are universal independent of impurity species. However the existence of small pseudogap is Ni impurity specific. They are temperature independent in our measured temperature range and coexist with a conventional pseudogap above certain temperature but disappear at low temperatures.

In these samples, it is hard to consider that Ni substitution modify the band structure to produce the observed anomaly because the amount of Ni is as small as 3%. However, it is known that the Zn impurity strongly modify surrounding superconducting as well as normal electrons and form the Swiss-cheese-like non-uniform electronic state in the superconducting state [5]. Such a effect has not been examined and reported for Co and Ni impurity. However, our experiments suggest that the Ni impurity locally suppress surrounding density-of-states in the normal state, as Zn did in the superconducting state. Since small pseudogap feature was observed almost uniformly in the measured area, the DOS suppressed area should be larger than 6x6 Cu atoms per Ni impurity.

Finally, Fig. 5 shows a comparison between the c-axis resistivity and the inverse of the density-of-states at a Fermi level. If the c-axis transport is governed by a tunneling process between 2D superconducting layers, it should sensitively reflects opening a gap, and give an upturn at a gap opening temperature. As can be seen in Fig. 5, the upturns in the resistivity and the DOS plots coincide well and they assure the cleaved surface is doped to the same level as a bulk sample. They also provide good \( T^* \) estimations.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig4.png}
\caption{Temperature dependence of gap value in Bi2212 of Fig.2 responsibility, compared between pure and Ni substitution.}
\end{figure}
Figure 5. Comparison between inter-planar resistivity and residual DOS, (a) OP sample and (b) OD sample.

In summary, we reported the results of scanning tunneling spectroscopy measurements on the pseudogap states of Ni3%-Bi2212 samples. We found that Ni impurity induce the new small gap-like feature with weak temperature dependence, as well as the conventional pseudogap. The conventional pseudogap underwent similar impurity effects to the Co doping case, indicating their universal nature. The small gap-like feature is specific to Ni impurity and suggests to its anomalous interaction to the surrounding Cu. They can be related to the steep decrease in $T_c$ in the Ni doping in the underdoped region.

References

[1] A.Matsuda et al., Journal of physics and Chemistry of solids 62, (2001) 65
[2] Yoshinori Numata et al., Physica C 524, (2016) 28
[3] Yuta Kiguchi et al., Physics Procedia 58, (2014) 54
[4] Takao Watanabe et al., Phys. Rev. Lett. 84, (2000) 5848
[5] B. Nachumi et al., Phys. Rev. Lett. 77, (1996) 5421
[6] C. Izutani et al., Journal of Chemical Education 93, (2016) 1667