## Temperature dependence of the impurity-induced resonant state in Zn-doped $Bi_2Sr_2CaCu_2O_{8+\delta}$ by scanning tunneling spectroscopy

H. Kambara, Y. Niimi, M. Ishikado, S. Uchida, and Hiroshi Fukuyama

Department of Physics, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

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We report on the temperature dependence of the impurity-induced resonant state in Zn-doped  $Bi_2Sr_2CaCu_2O_{8+\delta}$  investigated by scanning tunneling spectroscopy at 30 mK  $\leq T \leq 52$  K. It is known that the Zn impurity induces a sharp resonance peak in the tunneling spectrum at an energy close to the Fermi level. We observed that the resonance peak survives up to 52 K. The peak broadens with increasing temperature, which is explained by the thermal effect. This result provides information for understanding the origin of the resonance peak.

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The scanning tunneling spectroscopy (STS) technique based on the scanning tunneling microscope (STM) enables us to measure the local electronic density of states (LDOS) at the atomic scale. So far, there have been a lot of important studies investigating this key property of high- $T_c$  cuprates by STS.<sup>1–8</sup> Pan *et al.*<sup>4</sup> reported STS imaging of the LDOS around impurity sites at the surface of Zn-doped Bi<sub>2</sub>Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8+ $\delta$ </sub> (Bi2212). On the Zn site, they observed a tunneling spectrum with a sharp peak at an energy (-1.5 meV) slightly below the Fermi level ( $E_F$ ) and crossshaped fourfold quasiparticle spatial distributions. The origin of this near-zero-energy peak (NZEP) is usually considered to be an impurity-scattering resonant state<sup>9–12</sup> because the Zn impurity has a strong scattering potential.<sup>13</sup>

Salkola and co-workers<sup>9</sup> considered quasiparticle scattering from a repulsive  $\delta$ -potential impurity using the *T*-matrix approach and derived a resonant state within the superconducting gap. But it is not straightforward to explain why the LDOS on the impurity site is the largest since the Zn impurity site is a strong scattering center. Martin *et al.*<sup>11</sup> calculated tunneling matrix elements between a STM tip and the Cu-O plane. They claimed that tunneling electrons are "filtered" and consequently the largest intensity is measured on the Zn site. Recently, Tang and Flatté<sup>14</sup> gave a more quantitative explanation for the experimental results<sup>4</sup> by considering spatially extended Zn-impurity potentials on the Cu-O plane.

On the other hand, another competing interpretation exists based on the Kondo effect. The Kondo resonance scenario<sup>15,16</sup> arose after NMR experiments<sup>17–20</sup> which showed that the four nearest-neighbor Cu atoms surrounding a Zn impurity possess local moments. These polarized spins will form a spin-singlet state with quasiparticles. Note that it is not the standard Kondo effect, since the density of states of the quasiparticles vanishes at the Fermi energy due to the *d*-wave superconducting gap structure. In this scenario, the strongest LDOS peak at the Zn site can be naturally explained without considering the filtering effect. However, the scenario assumes unrealistically weak potential scattering, which is not consistent with the transport measurements.<sup>13</sup> The origin of the NZEP is still a matter of debate.

To test these scenarios, measuring the temperature evolution of the NZEP should be one of the key experiments. If the Kondo resonance scenario is correct, the peak weight of the NZEP will increase at  $T < T_K$ . The value of  $T_K$  is estimated as about 15 K (Ref. 15) from the measured peak energy of -1.5 meV.<sup>4</sup> In this Brief Report, we report on the temperature dependence of the NZEP in Zn-doped Bi2212 in the temperature range from 30 mK to 52 K using an ultrahigh-vacuum-compatible STM.<sup>21</sup>

The samples are Bi<sub>2</sub>Sr<sub>2</sub>Ca(Cu<sub>1-x</sub>Zn<sub>x</sub>)<sub>2</sub>O<sub>8+ $\delta$ </sub> single crystals grown by the floating zone method (the superconducting transition temperature  $T_c$ =89 K, nominal x=0.6%). They are cleaved at 100 K below 1×10<sup>-7</sup> Pa and then cooled to 30 mK. The data were taken during subsequent warming up to 52 K. We used an electrochemically etched tungsten wire for the STM tips. The STS measurements were performed by the lock-in technique with a modulation amplitude of 0.50 mV<sub>rms</sub> and a frequency of 411.7 or 511.7 Hz. It takes typically 24 h to obtain a STS image of 128×128 pixels. It was crucial to keep the temperature variations within ±1% at  $T \ge 20$  K to avoid unexpected tip crushes and thermal drifts of the STS data.

In Figs. 1(a)-1(d), we show the STS data for the cleaved surface of Zn-doped Bi2212 obtained at T=30 mK. Figure 1(a) shows a topographic image. The inset is a magnified topographic image but on a different surface where the atomic corrugation and supermodulation of the BiO layer<sup>22</sup> are more clearly seen. Figure 1(b) is a dI/dV image at a bias voltage V=0 mV of the same area as that for the main topographic image in Fig. 1(a). The NZEPs are visible as several bright spots here. The apparent number density of the NZEP spots within this area is about 0.2% which is of the same order as x=0.6%, the nominal doping concentration of Zn. Figure 1(c) is a dI/dV image at V=40 mV. The patch structure of the contrast indicates the inhomogeneous distribution of the superconducting gap structure.<sup>7</sup> In the bright patches of a few nanometers width, the superconducting coherence peak energy would be around 40 meV. In Fig. 1(d), we show a typical tunneling spectrum at a Zn impurity site with the NZEP (solid circles), and the superconducting gap structure obtained far away from the impurities without the NZEP (open circles). The NZEP spectra are characterized by depressed superconducting coherence peaks as well as by sharp peaks near the Fermi energy.

At a higher temperature of 52 K (Fig. 2), we obtained a



FIG. 1. (Color online) STS data of Zn-doped Bi2212 at T = 30 mK. (a) Topographic image (V=-0.12 V, I=0.2 nA,  $30 \times 25 \text{ nm}^2$ ). The inset shows a magnified topographic image (V=-0.20 V, I=0.2 nA,  $10 \times 10 \text{ nm}^2$ ). (b) dI/dV image at V=0 mV ( $30 \times 25 \text{ nm}^2$ ) of the same area as that for the main topographic image in (a). The bright spots denote the near-zero-energy peaks caused by the Zn impurities. (c) dI/dV image at V=40 mV ( $30 \times 25 \text{ nm}^2$ ). The bright patches roughly correspond to the regions of the superconducting coherence peak of ~40 meV. (d) Typical tunneling spectra at a Zn impurity site and away from impurity sites, respectively.

similar STS image to that in Fig. 1(b) with several bright spots. This means that the NZEP survives even at this temperature. It is consistent with the fact that broadened NZEPs are observed in the tunneling spectra at three different sites [Fig. 2(b)]. Note that the scan area of Fig. 2(a) is different from that of Fig. 1(b).

The temperature dependence of the tunneling spectra is summarized in Fig. 3(a). The NZEP smears out, i.e., the peak



FIG. 2. (Color online) STS data measured at T=52 K at a different surface position from Fig. 1. (a) dI/dV image at V=0 mV  $(30 \times 30 \text{ nm}^2)$ . The tunneling parameter for stabilization is the same as in Fig. 1 (V=-0.12 V, I=0.2 nA). (b) Tunneling spectra on the three different Zn impurity sites A-C denoted in (a) (solid circles) and that with a regular superconducting gap (open circles) away from the impurity sites. The spectra A-C are offset by 1 unit for clarity.



FIG. 3. (Color online) (a) Temperature dependence of the tunnel spectra. Typical superconducting gap structures (open circles) and near-zero-energy peaks (solid circles) obtained at each temperature. The dashed lines are calculated spectra based on the 1.8 K data, taking into account the thermal broadening effect in the Fermi distribution function. Each curve is shifted by 1 unit for clarity. (b) Temperature dependence of full width at half maximum (*d*) of near-zero-energy peak. The dashed line is a linear fit  $[d \text{ (mV)}=5.0 + 1.2k_BT]$ . Each error bar represents a standard deviation.

height decreases and the peak width increases with increasing temperature up to 52 K. The peak energy is determined as  $-0.8 \pm 2.4$  meV at all the temperatures we studied. There is a large amount of scatter from impurity to impurity, presumably due to different scattering potentials. It is difficult to determine the peak height precisely since we averaged the spectra over 6-18 positions around the impurity, although it is very sensitive to the exact tip location with respect to the impurity site. These curves are not obtained on the same Zn impurity atom. Nevertheless, we emphasize that the NZEPs certainly exist even at high temperatures.<sup>23</sup> The decrease of the NZEP height with increasing temperature seems to be well explained by the thermal broadening effect as seen in Fig. 3(a). Here the dashed lines are calculated spectra based on the 1.8 K data, taking account of the thermal broadening effect in the Fermi distribution function.

Figure 3(b) shows the temperature dependence of the full width at half maximum of the NZEP (d). The peak width is insensitive to averaging around the same impurity. The increase of d at higher temperatures above 20 K shows the thermal broadening effect since the dashed line  $[d \text{ (mV)} = 5.0+1.2k_BT]$  represents the experimental data fairly well. The intrinsic width ( $d_0=5.0 \text{ mV}$ ) below 2 K is similar to that obtained by Pan *et al.*<sup>4</sup>

We carried out STS measurements in a magnetic field of 6 T at T=2 K. We observed a similar width (~6 mV) of the NZEP to that obtained in zero field. Pan *et al.* also reported no significant field dependence of  $d_0$  between 0 and 7 T.<sup>24</sup> The Zeeman splitting energy should be about 0.4 meV at *B* =6 T.<sup>25</sup> This is hard to detect in our measurement since it is much smaller than  $d_0$ . We also note that the field of 6 T is too low to break up the Kondo singlet.<sup>26</sup>

Let us now discuss the origin of the NZEP. First, according to the Kondo resonance scenario, it is predicted that the

broadened Kondo peak still survives almost up to  $T_c$  even though  $T_K < T_c$ .<sup>27</sup> The temperature dependence of the peak weight becomes weaker above  $T_K$ . Thus, just the existence of the NZEP at  $T > T_K$  does not necessarily indicate the relevance of the Kondo resonance scenario. Next, let us consider the impurity-scattering resonance scenario further from the viewpoint of whether or not superconductivity is crucial. According to the calculations by Kruis *et al.*<sup>10</sup> and Balatsky *et al.*,<sup>12</sup> superconductivity is unnecessary to form an impurity-induced resonant state. Thus, they claim that the NZEP will be observed even in the pseudogap region (T $>T_c$ ). On the other hand, there are arguments that the Andreev resonance in unconventional superconductors is the origin of the NZEP. Quasiparticle scattering with a sign change of the pair potential results in the resonance state.<sup>28–30</sup> This is observed in the tunnel junction experiments, for example, by Iguchi et al.<sup>31</sup> Multiple Andreev scat-

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tering around a surface impurity will form the NZEP. Future STS experiments on the pseudogap phase in the underdoped regime would discriminate between these two possibilities.

In summary, we measured the temperature dependence of the near-zero-energy peak in Zn-doped  $Bi_2Sr_2CaCu_2O_{8+\delta}$ . The NZEPs are clearly observed up to 52 K with thermal broadening. This result provides an important hint toward understanding the origin of the NZEP.

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