WE REPLY TO YAMAMOTO:

A cuprate superconductor with unconventional features

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We report studies on the Ba2CuO4+δ superconductor (1) with features including compressed local coordination and extreme over-doping level, etc.; while such behaviors are not favorable for superconductivity in previous cuprates (2), Yamamoto (3) raises an inquiry on one of these features: The compressed local octahedron. We have solid evidence to show that what we discussed in our paper has nothing to do with his speculation.

There are 2 types of “214” structures with a CuO2 plane, i.e., the T phase based on La2CuO4 and the T’ phase based on Nd2CuO4 due to the different charge reservoir substructures, the rock-salt type for the former and the fluorite type for the latter. The relative strong Coulomb attraction interaction in the rock-salt layer over the fluorite layer makes the a lattice parameter in La2CuO4 (a ~ 3.80 Å) shorter (4) than that (3.95 Å) for Nd2CuO4 (5). Hence the T phase is more favorable to compression than the T’ phase. It was indeed observed pressure-induced phase transition from the fluorite type to the rock-salt type charge reservoir for a very similar layered perovskite compound (figure 1 b and c in ref. 6). We actually tried to refine diffraction patterns of our high-pressure synthesized Ba2CuO4+δ samples with both T and T’ phase while preparing the manuscript. The refinements with T-type phase get automatic convergence with the Rwp factor ~3%, indicating that La2CuO4 is a highly reliable structure model. On the other hand the refinement with T’-type phase is divergent due to the unsuitable atomic position in the fluorite-type Ba–O layer. Both X-ray measurements and neutron diffraction (performed at NIST) lead to the same conclusion. Hence the T’-type structure can be easily excluded from the candidate structural modes either simply from volume-wise change at high pressure or from real refinements of the sample. Further evidence comes from X-ray absorption (XAS) measurements. The spectroscopic behavior in the O–K edge between the 2 systems is very different (7). It is well known that the doped carriers occur in the valence band in T-type La2CuO4 leading to the preedge peak at a photon energy well below the upper Hubbard band (UHB) in the O–K edge (528.5 eV); while in contrast there is no pre-edge peak in the T’-type Nd2CuO4 whereas the spectral weight of the UHB at 529.1 eV increases upon carrier doping. In our Ba2CuO4+δ system, we have indeed observed the preedge peak in the O–K XAS spectrum as shown in figure 4 in ref. 1. This experimental observation firmly demonstrates the equivalence to La2CuO4.

It should be pointed that the lattice parameter of our Ba2CuO4+δ sample (y ~ 0.8) cannot be simply extrapolated from (Sr,Ba)2CuO4+δ (y ~ 0.6) (8) since their oxygen contents are quite different and will change the bond length and consequently the lattice parameters. The materials reported by Yamamoto et al. (references 13 and 14 in ref. 1 or reference 7 in ref. 3) are different from what we studied here. Their structure is the normal La2CuO4 type with very long apical oxygen distance to the CuO2 plane. It has a “conventional” elongated octahedron as they apparently summarized (reference 14 in ref. 1).
8 W. B. Gao et al., Out-of-plane effect on the superconductivity of Sr$_x$Ba$_{2-x}$CuO$_{3+\delta}$ with $T_c$ up to 98 K. Phys. Rev. B Condens. Matter Mater. Phys. 80, 94523 (2009).