Plane dimpling and Cu 4s hybridization in YBa$_2$Cu$_3$O$_x$

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Abstract

Oxygen doping dimples the CuO$_2$ planes of YBa$_2$Cu$_3$O$_{6.8}$–6.92 by displacing copper normal to the planes and further towards Ba. The correlated oxygen displacements, however, are constrained to the in-plane axes. This displacement pattern is discussed in terms of doping dependent Cu 4s–3d hybridizations.

Keywords: Electronic structure, superconductivity, YBa$_2$Cu$_3$O$_7$, EXAFS

The atomic positions of the planar copper and oxygen atoms in the high-$T_c$ cuprates exhibit important deviations from the ideal square planar geometry. Most significant are the static displacements normal to the 2D translational axes, the so-called plane buckling or plane dimpling. We discern the LTT-, LTO-type tilts of the rigid CuO$_6$ octahedra in the La 214 family, and the incommensurately modulated tilts of rigid CuO$_5$ pyramids in Bi 2212, from the soft CuO$_4$ squares allowing for “dimples” in e.g. YBa$_2$Cu$_3$O$_x$.

In this short note we address a significant correlation of displacive degrees of freedom in the CuO$_2$ planes of YBa$_2$Cu$_3$O$_x$ upon doping from 6.806 < $x$ < 6.92 = $x_{opt}$. The CuO$_2$ planes of YBa$_2$Cu$_3$O$_x$ are best described as stacks of O2,3 and Cu2 layers with an interlayer distance of $s \simeq 0.24$ Å. The O2,3 layers are located closest to the Y layers, and the Cu2 layers closest to the Ba layers. Y-EXAFS measurements of YBa$_2$Cu$_3$O$_x$ as a function of doping [1] have shown, that doping pulls down the Cu2 atoms towards the Ba layer whereas the spacings between the O2,3 and Y layers remain unaffected. Hence the O2,3–Cu2 interlayer distance increases, in the metallic and superconducting regime relatively up to $\delta s \simeq 0.05$ Å [1,2]. It is important to note that the O2,3–Y interlayer distances do not alter. Thus the reservoir layer accommodates the contraction of the c-axis parameter. From our doping dependent Y-EXAFS the displacements of Cu2 atoms along the c-axis turn out to occur at fixed $R_{Y-Cu2} = 3.202(5)$ Å = const. Phenomenologically this constraint couples the perpendicular displacements of Cu2 (dimples) with the in-plane displacements of the cation sublattices and, most important, with those of the planar oxygens O2,3. Fig. 1 exhibits schematically these correlated displacements by comparing two subcells with differently dimpled CuO$_2$ planes (exaggerated scale). Doping is shown to pull the Cu2 towards the Ba layer and to push thereby the O2,3 horizontally along the dashed line. The latter indicates the projected average in-plane translational axes of the

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Fig. 1. Correlated displacements of the planar Cu2 and O2,3 atoms at different oxygen dopings. See text.

O2,3. Different orthorhombicities, \((b - a)/(b + a)\), are clearly visible in Fig. 1 (top). These correspond to the doping dependencies of the \(a, b\)-axes close to \(x_{opt}\): \(\partial a/\partial x < 0, \partial b/\partial x > 0\), and \(|\partial a/\partial x| > |\partial b/\partial x|\).

The planar dimples are shown by Andersen et al. [3] to have important effects on the single electron structure of YBa\(_2\)Cu\(_3\)O\(_7\) and its Fermi surface, in particular on the dispersion of the dominant Cu 3d\(_{x^2-y^2}\)–O2p\(_{x,y}\) d\(\sigma\) band close to (\(\pi, 0\)), and (0,\(\pi\)). Or the other way round, the single electron structure of the cuprates generically activates atomic displacements perpendicular to the planes affecting thereby also the Fermi surface. In fact hybridizations of the Cu 4s orbital are at heart of all important degrees of freedom normal to the CuO\(_2\) planes. Cu 4s belongs to the minimum set of orbitals describing a realistic single electron structure, and may not be integrated out as the other high energy orbitals. (Cu 3d\(z^2\) hybridization turns out to be a negligible quantum chemical parameter of the electronic structure, both, experimentally and theoretically). Plane dimpling is found to be activated by remote hybridization of the Cu 4s with the Cu 3d\(_{x^2-y^2}\) orbitals. It works via the Cu 3d\(_{xx}\), Cu 3d\(_{yz}\) and their overlap with the O 2p\(_{x,y}\), overlapping with 3d\(_{x^2-y^2}\). As a result perfectly flat CuO\(_2\) planes get intrinsically instable upon doping, but may be stabilized by atomic displacements along the normal axis.

Summarizing we emphasise that doping of the CuO\(_2\) planes in YBa\(_2\)Cu\(_3\)O\(_7\) activates the Cu2 atoms to be displaced normal to the plane, and the planar oxygens to be slaved displacing along the in-plane translational axes. The Cu 4s–3d hybridization seems to be the crucial quantum chemical parameter controlling this correlation of in-and out-of-plane displacements, and possibly also the related interplanar and intraplanar electronic degrees of freedom.

References

[1] J. Röhler et al., in Workshop on High-T\(_c\) Superconductivity 1996: Ten Years after the Discovery, E. Kaldis, E. Liarokapis, K. A. Müller (eds.), NATO ASI Series E343 (Kluwer, Dordrecht, 1997), 469; J. Röhler et al., Physica C 282-287, 182 (1997).

[2] The insulating “background” dimpling of 0.2 Å has to be subtracted. It is most likely due to the unscreened charge contrast between the Y\(^{3+}\) and Ba\(^{2+}\) layers, acting differently on the Cu\(^{2+}\) and O\(^{2-}\) ions as discussed by Deveraux et al., cond-mat/9712128. Electrostatic polarization, however, cannot cause the observed increase of the dimpling at the insulator-metal transition and beyond. The onset of metallic screening in the planes is expected to reduce the dimpling instead of enhancing it. Therefore the electrostatic mechanism is not at the origin of the modified B\(_{1g}\) Raman modes, either. The sd hybridization effects are more likely.

[3] O. K. Andersen et al., J. Phys. Chem. Solids 12, 1573 (1995); O. K. Andersen et al., J. Low Temp. Phys. 105, 286 (1996).