

Substitution sites of Pb and Y in $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{8+\delta}$: X-ray photoelectron diffraction as fingerprinting tool

Th. Pillo,^{a)} J. Hayoz, and P. Schwaller
Institut de Physique, Université de Fribourg, CH-1700 Fribourg, Switzerland

H. Berger
Institut de Physique Appliquée, EPF, CH-1015 Lausanne, Switzerland

P. Aebi and L. Schlapbach
Institut de Physique, Université de Fribourg, CH-1700 Fribourg, Switzerland

The substitution site of Y and Pb in the cuprate-type high temperature superconductor $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{8+\delta}$ is determined in a very direct and unambiguous way by means of angle-scanned x-ray photoelectron diffraction (XPD). Using XPD as a fingerprinting tool, we conclude that Y occupies the Ca sites and Pb the Bi sites, respectively. Furthermore, low-energy electron diffraction data unequivocally show the presence of the incommensurate lattice modulation which is known for pure Bi2212, but not for sufficiently Pb doped Bi2212. We can, therefore, attribute the reappearance of the modulation directly to the Y doping.

Many studies have been done since the discovery of high temperature superconductors in order to investigate particularities of their geometrical structure. In the case of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_{8+\delta}$ (Bi2212) many different materials have been used to dope the pure Bi2212 either to influence the charge around the Cu-O planes believed to be responsible for superconductivity or to modify the structure. Special attention has been given to the incommensurate lattice modulation in Bi2212 both at the surface¹⁻³ and in the bulk⁴⁻⁶ using various techniques.

The question about the influence of dopants on the modulation has been examined. In particular, Pb substitution of Bi has led to many studies.⁷⁻⁹ It appears that sufficient Pb doping inhibits the modulation. Here we further expand the considerations onto the effect of Y doping of Pb-Bi2212.

In all these questions it is very important to know what site the dopant atom is occupying and whether it is distributed homogeneously substituting mainly one element of the host compound or clustering together. Using chemical intuition it is often possible to strongly suggest the occupation of one or the other site. However, it is difficult to prove, and in many cases uncertainty remains.

X-ray photoelectron diffraction (XPD) now allows for a very direct and simple identification of the dopant site using the experimental pattern as a fingerprint for a specific site.^{7,10} We want to stress that the method may, of course, also be applied to other compounds, e.g., minerals.

As a result of our study of Y-Pb-Bi2212 we find unequivocally that Pb and Y occupy the Bi and Ca sites of the host material, respectively. Furthermore, low energy electron diffraction (LEED) shows that the lattice modulation is present again for Y-Pb-Bi2212 although it is absent in Pb-Bi2212 for similar Pb contents.

The samples were grown from nonstoichiometric sys-

tems consisting of solute and flux which form a high temperature solution.¹¹ The near surface composition of the Pb-Y-Bi2212 crystals was carefully determined with x-ray photoelectron spectroscopy (XPS). We obtained values of 0.27 and 0.38 for the Pb:Bi and Y:Ca ratios, respectively. The Pb:Bi ratio is well above the critical value of about 0.25 for removing the modulation.^{8,9}

The single crystals have been cut to small rectangles with dimensions of about $3 \times 4 \text{ mm}^2$ with a thickness of $\approx 0.5 \text{ mm}$ and mounted onto the sample holder with silver epoxy. For the measurements the crystals were cleaved *in situ* at a pressure of better than $1 \times 10^{-10} \text{ mbar}$, yielding clean mirrorlike surfaces with (001) orientation.

The measurements were performed in a modified VG ESCALAB Mk II spectrometer equipped with a two-axis sample goniometer enabling sequential computer-controlled sample rotation.^{12,13} For XPS and XPD a twin anode was used delivering either Mg- $K\alpha$ (1253.6 eV) or Si- $K\alpha$ (1740 eV) radiation. The angular resolution was better than 1° full cone acceptance. Due to its chemical sensitivity and the sensitivity to local order XPD is a powerful technique for surface structural investigations.¹⁴ It has been shown that full hemispherical XPD patterns (diffractograms) provide very direct information about the near surface structure.^{15,16} At electron energies above about 500 eV, the strongly anisotropic scattering of photoelectrons by the ion cores leads to a forward focusing of electron flux along the emitter-scatterer axis. Prominent intensity maxima in diffractograms can, therefore, often be immediately identified with near-neighbor directions. The photoelectron angular distribution therefore is, to a first approximation, a forward-projected image of the atomic structure around the photoemitters. For a XPD diffractogram we typically measured about 5500 angle settings $[(\theta, \phi)$, photoelectron emission angles θ (polar) and ϕ (azimuthal)], each displaying the angular dependent intensity of the selected core level. The obtained intensities are plotted in

^{a)}Electronic mail: thorsten.pillo@unifr.ch

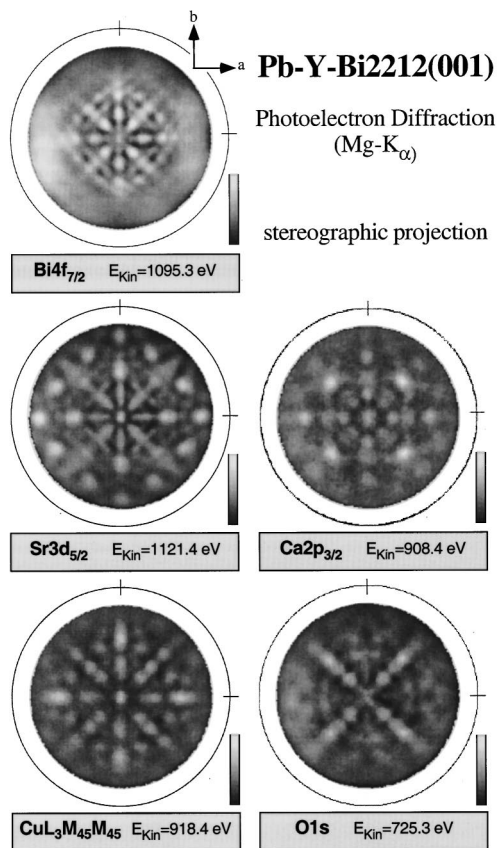


FIG. 1. A set of XPD patterns of Pb-Y-Bi2212. Shown are measurements on the core levels (Auger line for Cu) of elements present in pure Bi2212, i.e., Bi $4f_{7/2}$, Sr $3d_{5/2}$, Ca $2p_{3/2}$, Cu $L_3M_{45}M_{45}$, and O $1s$. Measurements have been performed with Mg- $K\alpha$ radiation (1253.6 eV) and raw data is shown as a linear gray scale plot in stereographic projection.

a linear gray scale image in stereographic projection.

In Fig. 1 we present a set of XPD patterns for Pb-Y-Bi2212. Displayed are the experiments for those atom types occurring also in pure Bi2212. In the diffractograms, the outer circle corresponds to grazing emission ($\theta=90^\circ$) and the center denotes normal emission ($\theta=0^\circ$), respectively. For each polar angle from $\theta=78^\circ$ to normal emission, we plot the azimuthal intensity distribution of the selected core level.

One observes a clear fourfold symmetry of all patterns. This is in contrast to previous work of Osterwalder *et al.*¹⁷ where the strong modulation along the b axis in pure Bi2212 causes a considerable deviation from the fourfold symmetry, i.e., the XPD diffractograms become twofold symmetric, clearly distinguishing between the crystals a and b axis. The overall fine structure in the images, however, remains identical.

The structure of these diffractograms is quite complicated but, most importantly, the images are distinctly different from each other. Therefore, instead of trying to understand the very details of the fine structure due to interference and forward focusing we can take the individual patterns as a *fingerprint* for the respective local real-space environment of the corresponding element, i.e., for the crystallographic site. It is very clear then, that in order to determine the site of the dopant we simply have to measure its diffractograms. A comparison with the fingerprints then directly leads to the identification of the site.

Pb-Y-Bi2212(001)

Photoelectron Diffraction
Mg- $K\alpha$
stereographic projection

Fingerprinting:

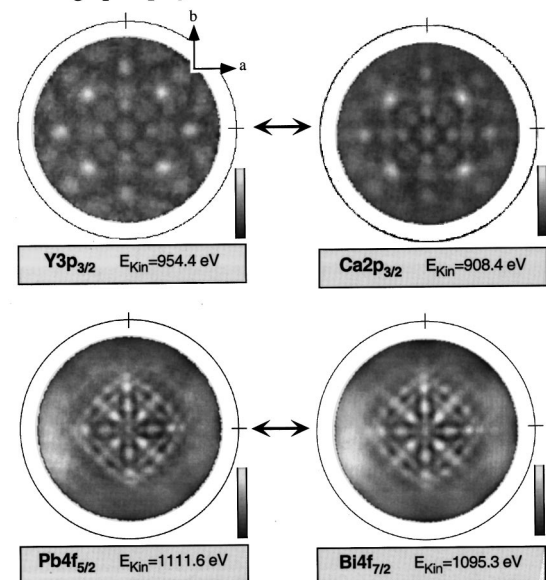


FIG. 2. Fingerprinting: Direct comparison of the XPD patterns of Y $3p_{3/2}$ and Pb $4f_{5/2}$ with Ca $2p_{3/2}$ and Bi $4f_{7/2}$, respectively.

In Fig. 2 XPD patterns of the Y $3p$ and the Pb $4f$ core levels together with the patterns of Ca $2p$ and Bi $4f$ are presented. One observes a striking coincidence of the Y pattern with the Ca XPD and of the Pb pattern with the one of Bi. Therefore, we can conclude unequivocally, that Y and Pb dopant atoms occupy Ca and Bi sites, respectively. XPD thus represents a unique tool to directly fingerprint substitution sites.

Figures 3(a) and 3(b) give an view of the reconstruction scheme appearing due to the (5×1) modulation present in pure Bi2212. We start in Fig. 3(a) with the comparison of a simple square lattice in real space which represents a plane of metal atoms. The transformation into reciprocal space also leads to a square lattice, as well known from text books. Figure 3(b) illustrates the case of a lattice modulation along the crystal b axis $[010]$. This (5×1) or strictly speaking $(\sqrt{2} \times 5\sqrt{2})R45^\circ$ superstructure leads to additional diffraction spots displayed as the small spots. The intensities of the superstructure spots are also modulated due to the wave character of the real space modulation as already pointed out by Lindberg *et al.*¹ for the case of pure Bi2212. Experimentally, the superstructure can be examined, e.g., by LEED measurements.¹ In Fig. 3(c) a LEED picture of the Pb-Y-Bi2212 crystal is shown, taken with an incident electron energy of 33.9 eV. This pattern clearly shows the modulation induced superlattice spots along the crystal b axis. Therefore, we conclude that in Pb-Y-Bi2212 the modulation is apparent again. We note that in the case of Pb-Bi2212 the modulation spots have totally vanished except for a $c(2 \times 2)$ superstructure which is still seen in the transmission electron microscopy (TEM) pictures.⁷ Therefore, we can assume that the Y doping is responsible for the reappearance of the modulation although the Pb concentration is high enough to prevent it.

This is interesting, in particular because Y does not in-

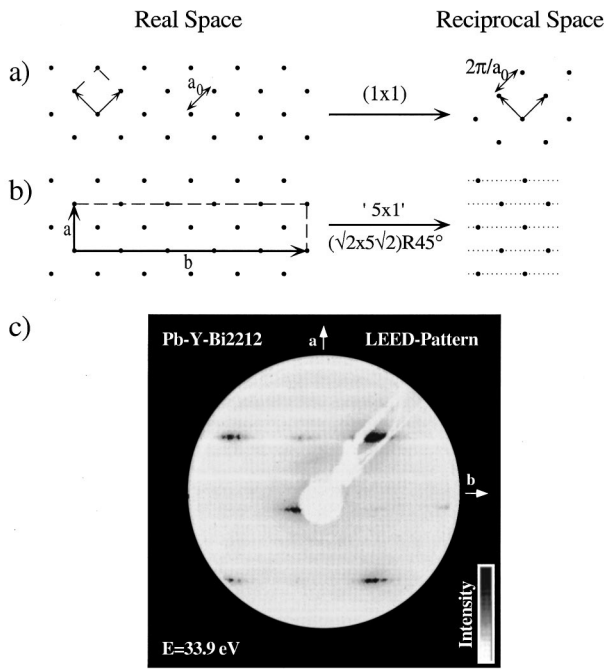


FIG. 3. Real and reciprocal space representation for the Bi-type high temperature superconductor without modulation (a) and with the (5×1) modulation (b). In real space the dots represent metal atoms (oxygen atoms were neglected) and in reciprocal space the dots are identified with diffraction spots. Part (c) shows a low energy electron diffraction experiment of Pb-Y-Bi2212, clearly indicating the reappearance of the modulation.

terfere with Bi planes. If one considers only Pb doping and since Pb doping is able to inhibit the lattice modulation, one may be led to conclude that the Bi-O layers are exclusively responsible for the (5×1) modulation. However, the modulation appears to be *intrinsic* to the Bi2212 crystal structure since it is possible to reintroduce it by Y doping into the Ca planes. As a matter of fact, a more detailed analysis shows¹⁸ that the Y-induced modulation corresponds to a (10×1) or $(\sqrt{2} \times 10\sqrt{2})R45^\circ$ symmetry. Finally, the fact that XPD does not show the influence of the modulation, manifest in a two-fold symmetric pattern as in Ref. 17, whereas LEED clearly exhibits the superspots, is consistent with a smaller modulation amplitude in Pb-Y-Bi2212 than in pure Bi2212.¹⁹

In conclusion, we have shown that XPD represents a powerful and direct tool to determine substitution sites of dopants. For the example of Pb-Y-Bi2212 we revealed Ca and Bi sites as the corresponding sites for Y and Pb, respec-

tively. The overall fourfold symmetry of the XPD patterns together with the electron diffraction results indicate that the lattice modulation along the crystal b axis is present but weaker than in pure Bi2212.

The authors gratefully acknowledge many stimulating and helpful discussions with R. Fasel and R. Agostino. Additionally the authors obtained skillful technical assistance by E. Mooser, O. Raetz, R. Schmid, O. Zosso, C. Neururer, and F. Bourqui. This work has been supported by the Fonds National de la Suisse pour la Recherche Scientifique.

- ¹ P. A. P. Lindberg, Z.-X. Shen, B. O. Wells, D. B. Mitzi, I. Lindau, W. E. Spicer, and A. Kapitulnik, *Appl. Phys. Lett.* **53**, 2563 (1988).
- ² M. D. Kirk, J. Nogami, A. A. Baski, D. B. Mitzi, A. Kapitulnik, T. H. Geballe, and C. F. Quate, *Science* **242**, 1673 (1988).
- ³ C. K. Shih, R. M. Feenstra, J. R. Kirtley, and G. V. Chandrashekhar, *Phys. Rev. B* **40**, 2682 (1989).
- ⁴ S. A. Sunshine, T. Siegrist, L. F. Schneemeyer, D. W. Murphy, R. J. Cava, B. Batlogg, R. B. van Dover, R. M. Fleming, S. H. Glarum, S. Nakahara, R. Farrow, J. J. Krajewski, S. M. Zahurak, J. V. Waszczak, J. H. Marshall, P. Marsh, L. W. Rupp, Jr., and W. F. Peck, *Phys. Rev. B* **38**, 893 (1988).
- ⁵ Y. Le Page, W. R. McKinnon, J.-M. Tarascon, and P. Barboux, *Phys. Rev. B* **40**, 6810 (1989).
- ⁶ A. Yamamoto, M. Onada, E. Takayama-Muromachi, F. Izumi, T. Ishigaki, and H. Asano, *Phys. Rev. B* **42**, 4228 (1990).
- ⁷ P. Schwaller, P. Aebi, H. Berger, C. Beeli, J. Osterwalder, and L. Schlapbach, *J. Electron Spectrosc. Relat. Phenom.* **76**, 127 (1995).
- ⁸ N. Fukushima and M. Yoshiki, *Phys. Rev. B* **50**, 2696 (1994).
- ⁹ N. Fukushima, H. Niu, S. Nakamura, S. Takeno, M. Hayashi, and K. Ando, *Physica C* **159**, 177 (1989).
- ¹⁰ P. Schwaller, P. Aebi, J. Osterwalder, L. Schlapbach, M. Shimoda, T. Mochiku, and K. Kadowaki, *Phys. Rev. B* **48**, 6732 (1993).
- ¹¹ P. Almeras, H. Berger, and G. Margaritondo, *Solid State Commun.* **87**, 425 (1993).
- ¹² J. Osterwalder, T. Greber, A. Stuck, and L. Schlapbach, *Phys. Rev. B* **44**, 13764 (1991).
- ¹³ D. Naumović, A. Stuck, T. Greber, J. Osterwalder, and L. Schlapbach, *Phys. Rev. B* **47**, 7462 (1993).
- ¹⁴ C. S. Fadley, in *Synchrotron Radiation Research: Advances in Surface Science*, edited by R. Z. Bachrach (Plenum, New York, 1990), Vol. 1, pp. 421–518.
- ¹⁵ R. Fasel, P. Aebi, R. G. Agostino, D. Naumović, J. Osterwalder, A. Santaniello, and L. Schlapbach, *Phys. Rev. Lett.* **76**, 4733 (1996).
- ¹⁶ P. Aebi, R. Fasel, D. Naumović, J. Hayoz, Th. Pillo, M. Bovet, R. G. Agostino, L. Patthey, L. Schlapbach, F. P. Gil, H. Berger, T. Kreutz, and J. Osterwalder, *Surf. Sci.* **402–404**, 614 (1998).
- ¹⁷ J. Osterwalder, P. Aebi, P. Schwaller, L. Schlapbach, M. Shimoda, T. Mochiku, and K. Kadowaki, *Appl. Phys. A: Solids Surf.* **60**, 247 (1995).
- ¹⁸ Th. Pillo, J. Hayoz, L. Schlapbach, and P. Aebi (unpublished).
- ¹⁹ For XPD to be sensitive to a lattice modulation the amplitude has to be strong enough to shift forward focusing directions by a few degrees.