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Combined HRTEM, X-ray microchemical and EELS fine structure analysis of planar defects in $YBa_2Cu_3O_{7-\delta}$

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High temperature superconductors in the systems $YBa_2Cu_3O_{7-\delta}$ (123) and decomposed $YBa_2Cu_4O_{7-\delta}$ (124) often contain planar faults with (001) as the nominal fault plane. Such planar defects have been analyzed using a unique combination of high resolution TEM (HRTEM) imaging and high resolution analytical electron microscopy (HRAEM). HRTEM confirmed that these planar faults are stacking faults with double or multiple insertion of crystal planes parallel to the c-plane of the crystal, most probably Cu-O planes. X-ray microanalysis clearly showed enrichment of copper associated with these defects. EELS fine structure of Cu-L_{23} edge from the fault regions resembled that of pure CuO. The combined results indicate that the planar defects are in fact insertions of extra Cu-O planes in an otherwise regular 123 crystal unit cell.

1. Introduction

With the realization that $YBa_2Cu_3O_{7-\delta}$ (123) superconductors usually lack the necessary transport current at lower temperatures, even in moderate magnetic fields, immense activity concerning flux pinning by lattice defects is currently underway [1,2]. It is expected that crystal defects with dimensions approaching the coherence length may participate in flux pinning [3] and hence enhance the critical transport current density, J_c. In view of the potential of crystal defects as possible flux pinning sites, it is necessary to obtain structural, chemical and electronic structural information about crystal defects in the superconducting matrix.

Planar faults are ubiquitous in 123 superconductors [4]. They are especially profuse in quench-melt-grown 123 and decomposed 124 [5,6]. Such defects have been a subject of many experimental studies. HRTEM provided crucial information pertaining to such defects and there is a general consensus that these defects can be described as stacking faults with the insertion of extra double or multiple planes normal to the c-axis, which are in fact chemical stacking faults [5-7]. However, there has been no direct confirmation of the chemistry and electronic structure of these defects at the scale of their dimension. In this communication, we present our combined HRTEM, X-ray analysis and EELS results of isolated planar defects in 123 superconductors which unequivocally show that these defects can be simply described as insertions of extra Cu-O layers in an otherwise regular 123 unit cell.

2. Experimental

The specimens used in the study were provided by Dr. Balu Balachandran of Argonne National Laboratory. The specimens were quench-melt-grown 123 using the time-temperature cycle described previously [8]. Specimens for TEM were prepared by conventional polishing and ion beam thinning method as well as by crushing the bulk specimens and floating thin fragments on holey carbon films. Results from both of these specimens were identical.

Transmission electron microscopy (TEM) was performed, using the Hitachi HF-2000, 200 kV cold field emission gun (FEG) TEM equipped with an ultra thin window (UTW) Link X-ray detector and

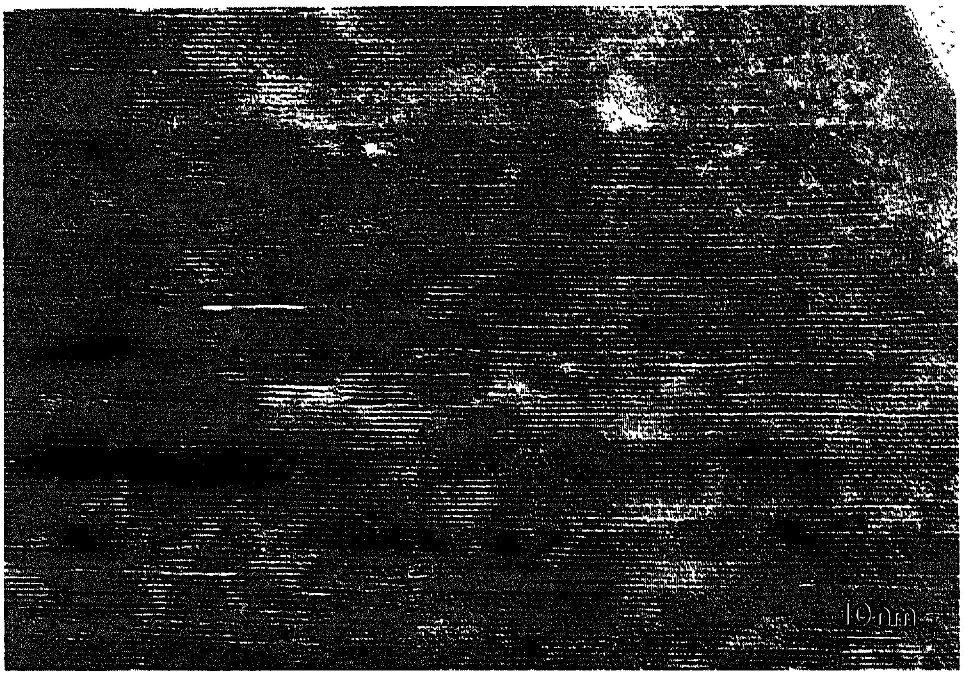

Fig. 1. Low magnification HRTEM image of a melt-quench-grown 1 2 3 specimen exhibiting profuse faulting. The coarser faults are CuO precipitates.

a Gatan parallel EELS spectrometer run on a Mac II fx. HRTEM was performed using axial illumination along [100] (or [010]) where the faults are edge-on to the electron beam. A probe size of little less than 1 nm in nominal diameter was used for analytical studies. During analytical experiments, the

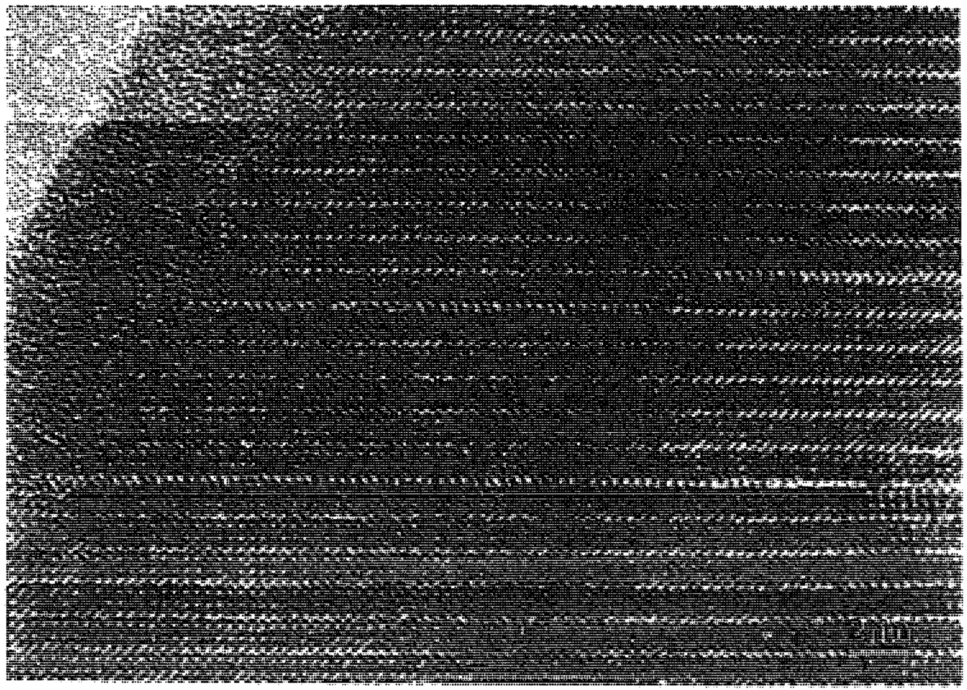

Fig. 2. A high magnification HRTEM image showing a couple of planar defects with a double layer at the core of the fault.

crystal was tilted off the zone axis to avoid anomalous X-ray/EELS effects. Several EELS and EDS spectra were simultaneously obtained by focusing the probe on the edge-on planar faults. In a few cases, planar channeling conditions along the planar fault were made use of to reduce delocalization of X-ray and EELS signals.

3. Results and discussions

Figure 1 is a low magnification HRTEM image of a quench-melt-grown 123 crystal. Many planar faults of varying lateral dimension are clearly visible in this image. Coarser scale faults (> 2 nm in width) were clearly identified as CuO precipitates by X-ray microanalysis. Special attention was then given to the narrower faults of the type shown in fig. 2. The HRTEM image clearly shows a double layer at the core of the defect with a partial dislocation termination visible in the image. Such faults have been previously identified [5–7] as stacking faults with extra planes normal to the c-direction of the unit cell.

Figure 3 is a montage of EDS scans and EELS Cu-

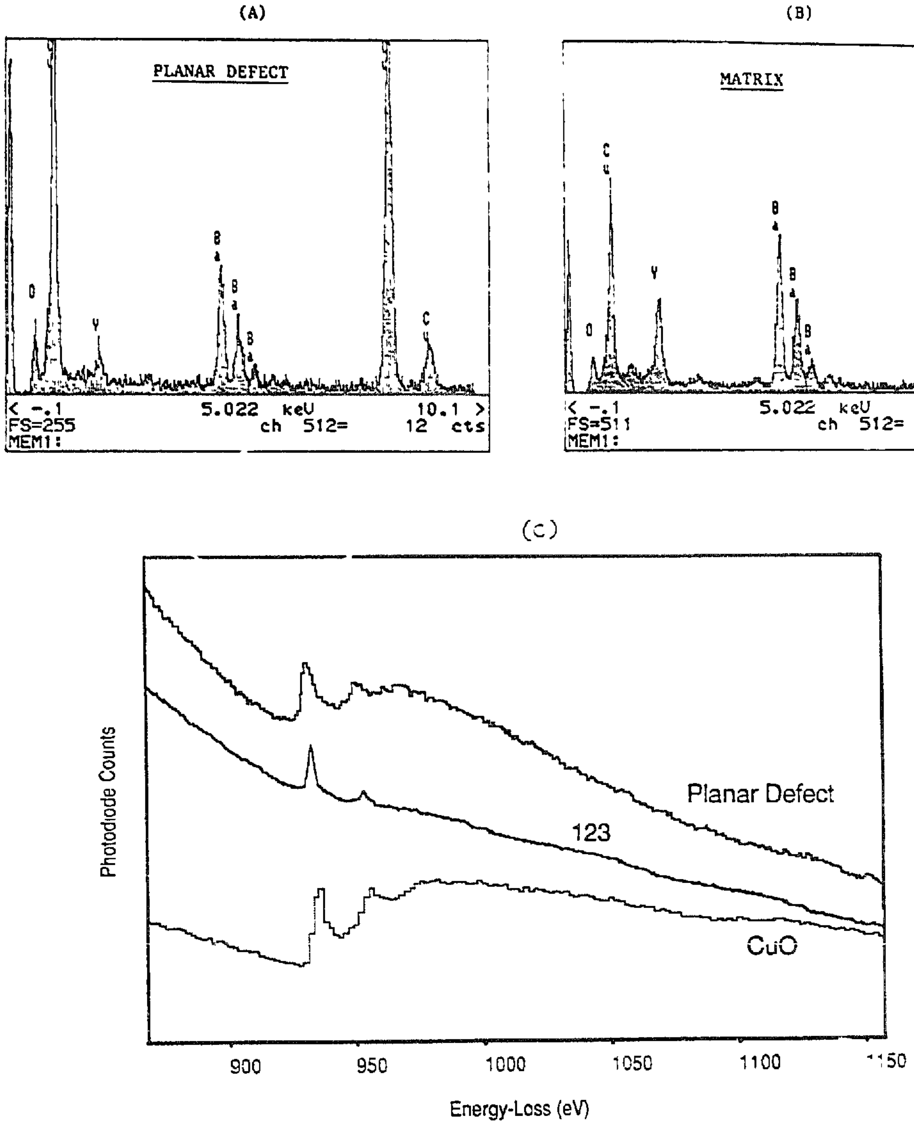

Fig. 3 X-ray spectra from the planar defect with < 1 nm probe (A), and the adjacent 1 2 3 matrix using a bigger probe (B). (C) EELS Cu-L_{23} edge from the fault region along with Cu-L_{23} edges of the adjacent 1 2 3 matrix and a CuO external standard.

L_{23} edges from a typical planar fault. X-ray microanalysis data from the planar fault are shown in fig. 3(A) along with an X-ray spectrum from the adjacent matrix with a larger probe (B). X-ray data from the planar defect clearly show enhancement of the copper signal relative to Y and Ba. The presence of residual Y and Ba peaks can be rationalized in terms of a contribution from the adjacent 123 matrix due to finite beam broadening.

The most convincing result on the identity of these defects was provided by EELS fine structure analysis. Figure 3(c) shows the comparison of the EELS Cu–L_{23} edge from the planar defect, 123 matrix and a CuO standard. EELS near edge structure (ELNES) can be taken as a "finger print" of the environment of the ionized species [9]. The ELNES of Cu–L_{23} from the planar defect is remarkably similar to that of CuO, indicating that the electronic structure, bonding type and coordination of copper within the planar defects are similar, although not identical, to those of the external CuO standard. The subtle difference between the signals from the planar defect and CuO highlights the fact that the nature of the Cu–O bonding and the local coordination are perturbed because the Cu–O layers are inserted in a regular 123 unit cell rather than in CuO.

The planar defects analyzed in this paper are different from those reported by Ourmard et al. [10] Ourmard et al. observed triple-layer defects, where a Y–O layer is sandwiched between two Cu–O layers. These defects correspond to the local stoichiometry of $Y_2Ba_2Cu_4O_{9-\delta}$, whereas the double Cu–O layer defects in this paper correspond to the local stoichiometry of $YBa_2Cu_4O_{9-\delta}$. In a previous study by two of the present authors refs. [4,5], the Cu–O double-layer defect was analyzed using HRTEM imaging and simulations. In this paper we have shown directly, for the first time, the copper enrichment at these defects using X-ray microchemical analysis, whilst EELS fine structure analysis indicates that the double-layer defects exhibit excitations analogous to CuO.

4. Summary

The combined HRTEM, EDS and EELS analysis of planar defects in 123 superconductors is presented. HRTEM revealed the stacking fault nature of these defects and X-ray microanalysis provided evidence for enrichment of copper in the core of these defects. EELS Cu–L_{23} edge structure from the defect region is observed to be remarkably similar to that of CuO, indicating that the coordination, bonding and electronic structure associated with copper in the planar defect region is similar to that of CuO. The combined results on the structure, chemistry and electronic structure strongly suggest that the planar defects observed in 123 oxide superconductors can be described as insertions of Cu–O planes in otherwise regular 123 crystal unit cells.

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References

[1] S. Jin, T.H. Tiefel, S. Nakahara, J E. Graebner, H.M. O'Bryan, R A Fastnacht and G.W. Kammlott, Appl. Phys. Lett. 56 (1990) 1287.
[2] J L Tallon, D M. Pooke, R.G. Buckley, M.R. Presland, N E. Flower, S. Gibson and P.W. Gilberd, Appl. Phys. Lett. 59 (1991) 1239.
[3] T. Matsushita, Cryogenics 30 (1990) 817.
[4] L.D. Marks, D.J. Li, H. Shibahara and J.P Zhang, J. Electron. Micro. Tech. 8 (1988) 297.
[5] D.J. Li, H. Shibahara, J.P. Zhang and L.D. Marks, Physica C 156 (1988) 201.
[6] R. Ramesh, S. Jin, S. Nakahara and T.H. Tiefel, Appl. Phys. Lett. 57 (1990) 1458.
[7] H.W. Zandbergen, R. Gronsky, K. Wang and G. Thomas, Nature 331 (1988) 596.
[8] K. Salama, V. Selvamanickam, L Gao and K. Sum, Appl. Phys Lett. 54 (1989) 2352
[9] R.F. Egerton, EELS in Electron Microscopy (Plenum Press, New York, 1986), see also, J.C.H Spence, Ultramicroscopy 18 (1985) 165.
[10] A Ourmazd, J.A. Rentschler, J.C.H. Spence, M.O. O'Keefe, R J. Graham, D.W Johnson Jr. and W.W. Rhodes, Nature 327 (1987) 308