Responses to Allegations of Data Misrepresentation

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Introduction

Recently, several allegations have been circulated to the scientific community, both verbally and through e-mail, that would appear to imply data fabrication, falsification or manipulation. We have asked that if anyone has issues with any of our work that they please inform us directly so that we may respond in a professional manner. The only direct communication received was sent at the request of *Nature*, a copy of a Brief Communication Arising submitted following publication of a Corrigendum to a 1993 *Nature* paper [1]. Rumors about our scientific integrity were circulated to our colleagues and spread to journalists, who sought to cast us as perpetrators of scientific fraud and to link us with actual cases of scientific fraud. An article in this style appeared in the Boston Globe on the opening day of the 2006 MRS Fall meeting in Boston.

Some of this material is similar to allegations of scientific misconduct initially forwarded to us by Mr. Karl Ziemelis, Physical Sciences Editor at *Nature* and Dr. May Chiao, Associate Editor at *Nature Physics* in May 2006. In accordance with Federal guidelines these allegations were investigated by an independent committee, who found errors of judgment in data presentation, but no evidence for research misconduct. A statement from the committee is available [2].

EELS studies of YBCO/LCMO superlattices

One of the circulated PowerPoint files concerns issues Muller has with a preprint posted on the cond-mat preprint server [3]. Muller states:

"The measurements are at room temperature. In the 2 cond-mat papers, ***the authors claim to have repeated the measurements at 100K and obtained the same results, even though the microscope described in the paper is capable only of room temperature operation.*** *Had they done the low temperature measurements, why did they not show the data as this is a very difficult experiment?"*

While this statement avoids any direct charge of misconduct, its implication is clear. It is of course true that the ORNL 100 keV VG Microscopes HB501UX does not go to low temperature, but coauthors from Dr. Nigel Browning's group at the University of Illinois at Chicago (UIC) were included because the low-temperature data were recorded on the JEOL2010 in Chicago. Dr. Maria Varela went to Chicago April 28-30, 2003. Figures 1-2 are copies of some of the travel documents on record at ORNL, the boarding pass and hotel receipt, and Fig. 3 is a screenshot of some of the data files obtained at UIC.

PASSENGER TICKET AND BAGGAGE CHECK
SUBJECT TO CONDITIONS OF CONTRACT
ISSUED BY AmericanAirlines

BOARDING PASS
DATE OF ISSUE 30APR03 ISSUING OFFICE CODE US
SS. AGENT ID. 05R /ORD PLACE OF ISSUE CHICAGO OHARE
NAME OF PASSENGER (NOT TRANSFERABLE) VARELADELARCO/MARIA
FROM CHICAGO OHARE
TO KNOXVILLE
CARR. FLIGHT CLASS DATE TIME STATUS NOT VALID BEFORE NOT VALID AFTER
AA 4251 Q 30APR113P
REVALIDATION
ENDORSEMENTS/RESTRICTIONS
PNR CODE FLJGJK /AA
ORIGINAL ISSUE
ISSUED IN EXCHANGE FOR
BOARDING PASS
FARE CALCULATION
GROUP 4
SEAT 6C
FARE EQUIV. FARE PAID FORM OF PAYMENT
TAX
TOTAL
STOCK CONTROL NUMBER TK
00108467300391
COUPON AIRLINE FORM SERIAL NO. CK
ELECTRONIC
2 001 7245941584 3

AmericanAirlines
BOARDING PASS
NAME OF PASSENGER VARELADELARCO/MARIA
FROM CHICAGO OHARE
TO KNOXVILLE
AMERICAN EAGLE
CARRIER FLIGHT CLASS DATE TIME
AA 4251 Q 30APR113P
REVALIDATION
GATE BOARDING TIME SEAT SMOKING
G14 1243P 6C NO
ADDITIONAL SEAT INFORMATION
GROUP 4
BAGGAGE TO ARR.
COUPON AIRLINE FORM SERIAL NO. CK
05R /ORD

Fig. 1: Copy of the boarding pass from Varela's trip in Chicago, in 2003, when she visited the University of Illinois at Chicago.

CHICAGO CITY CENTRE
A Holiday Inn Hotel
300 EAST OHIO STREET CHICAGO, ILLINOIS 60611
312 787 6100 • FAX 312 787 5259

GUEST FOLIO

Arrival	Folio Number
MON 28APR,03	018316
Departure	Balance
WED 30APR,03	.00

MARIA VARELADELARCO
OAK RIDGE NATIONAL LABORR
WIGNER FELLOW ELE MICRO
GRUOP SOLID STATE DIVSION
OAK RIDGE, TN 37831

Nights	Date	Time
2	30APR,03	8:45a

Guaranteed by

Adults	Children
1	

	Date	Room	Description	Reference	Amount	
001	28APR	1 /1418	TELEPHONE	525-7978 L	1.25+	
002	28APR	1 /1418	TELEPHONE	252-0271 L	1.25+	
003	28APR	1 /1418	GUEST ROOM	Rm 1418	136.00+	SH
004	28APR	1 /1418	ROOM TAX	Rm 1418	20.27+	SH
005	29APR	1 /1418	TELEPHONE	252-0271 L	1.25+	
006	29APR	1 /1418	GUEST ROOM	Rm 1418	136.00+	SH
007	29APR	1 /1418	ROOM TAX	Rm 1418	20.27+	SH
008	30APR	1 /1418	VISA	4798264031246051	316.29-	AE

Fig. 2: Copy of the hotel receipt from Varela's stay in Chicago, April 28-30, 2003.

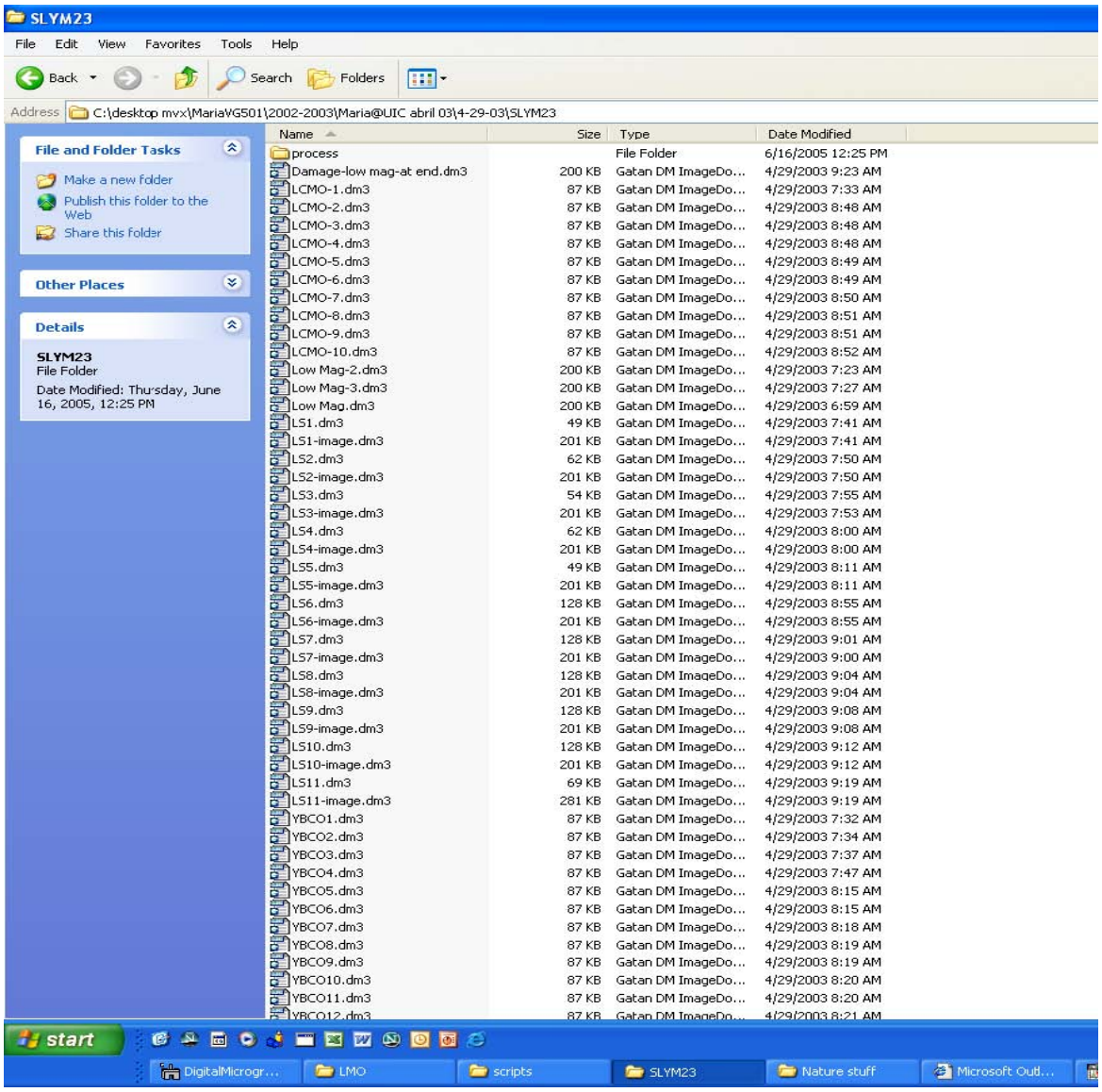
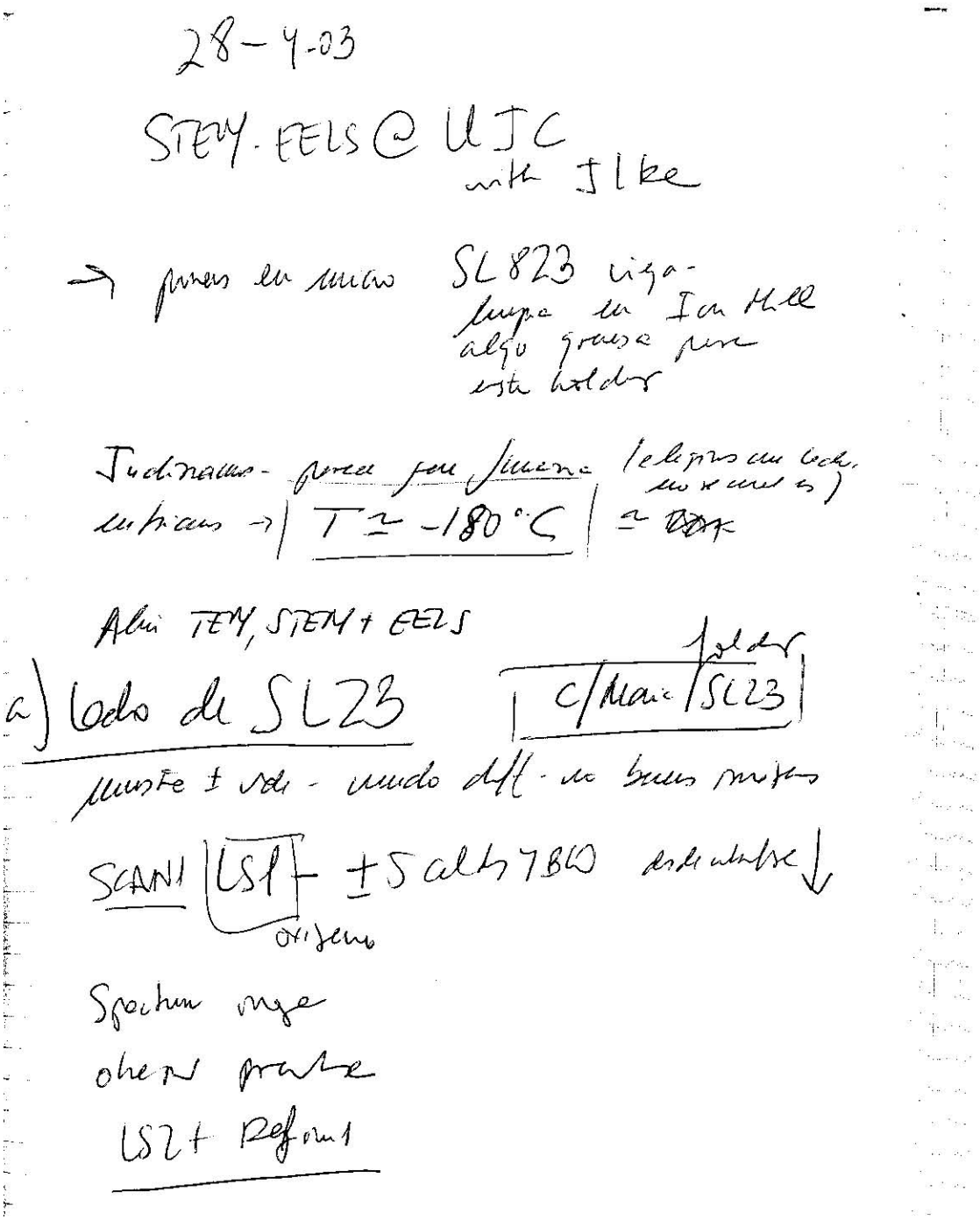


Fig. 3: A screenshot of some of the data files obtained at UIC, with file creation dates in accordance with the travel documents.

Note the file creation dates match the time that Varela was in Chicago. In total there are over 17 Mbytes of data. Figure 4 presents a scan from Varela's logbook that records the temperature obtained on sample SL823, a single cross section TEM specimen comprising a sandwich of two superlattices, SL8 a nominal [$YBCO_1/LCMO_{15}$] superlattice and SL23, a nominal [$YBCO_{10}/LCMO_{15}$] superlattice. The record shows a temperature of 180˚C was obtained. Several pages later, the logbook records shows moving to the SL8 side of the sandwich, as shown in Fig. 5. The next day, April 29, the logbook shows another superlattice sample, SLYM23 was examined, and reached a temperature of 179.5˚C. Logbook records for the growth of these samples also exist in J. Santamaria's laboratory in Spain.



28-4-03

STEM-EELS @ UIC
with Ilke

→ pinces en micro SL823 viga-
limpia en Ion Mill
algo gruesa para
este holder

Indicamos - parece que funciona (elegimos un lado, no se cual es)
entonces → | T ≃ -180°C | ≃ [illegible]

Ahí TEM, STEM + EELS

a) lado de SL23 | C/Maria/SL23 | holder

muestra ± vida - mucho diff - no buenos motivos

SCAN1 | LSF | - ±5 celdas YBCO desde [illegible] ↓
oxígeno

Spectrum image
ohem prueba
LS2 + Refine1

Fig. 4: A scan from Varela's logbook dated 28/04/2003, her first day in Chicago, that records a temperature of -180˚C obtained on sample SL823, a TEM cross section comprising two superlattices, SL8 a nominal [$YBCO_1/LCMO_{15}$] superlattice and SL23, a nominal [$YBCO_{10}/LCMO_{15}$] superlattice.

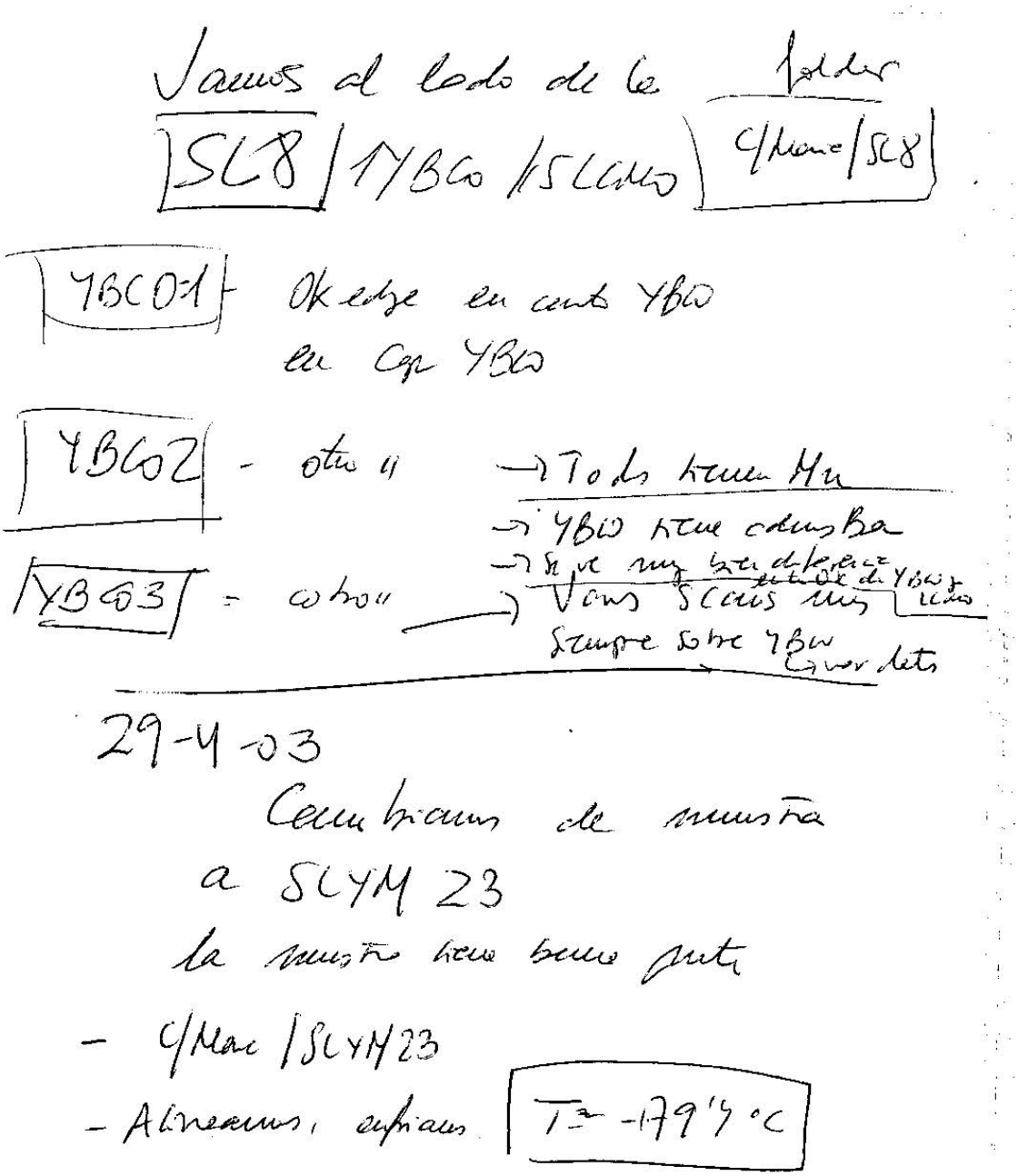


Fig. 5: A scan from Varela's logbook dated 29/04/2003 showing data recorded for sample SL8, a nominal [$YBCO_1/LCMO_{15}$] superlattice, on April 28th. The next day sample SLYM23 was loaded and a temperature of -179.5˚C was recorded.

The data obtained in Chicago were in fact incorporated into an early draft of the paper, as shown in Fig. 6. However, the 100K data showed no significant difference from the room temperature data, and were therefore removed from the first submission of this work, which was made to *Physical Review Letters* in August 2004.

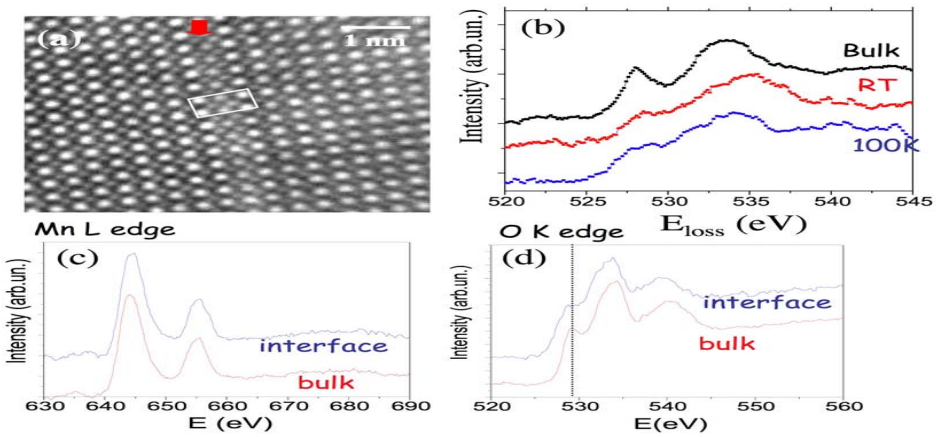


Figure 2

Fig. 6: Part of a figure from an early draft showing the 100K data obtained in Chicago for the [$YBCO_1/LCMO_{15}$] superlattice, which was later removed in the version submitted to *Physical Review Letters*.

It seems unusual to assume that data do not exist simply because they are not shown. With a phone call or email we could have sent the original figure containing the low temperature data.

Muller goes on to question the existence of samples, referring to the [$YBCO_{10}/LCMO_{15}$] superlattice as "*fictional*" in the PowerPoint file. More recently, in a 55-page document, Silcox and Muller say "*At the 2007 Spring MRS Meeting, Varela (both orally and in a slide presented in talk L8.3) claimed measurements at low temperature still needed to be done.*" Figure 7 shows one of the slides presented by Varela at that meeting which shows an image and EELS data for such a supposedly fictional superlattice. This sample is also a nominal [$YBCO_{10}/LCMO_{15}$] superlattice, but originating from a different growth run, sample SLYM139.

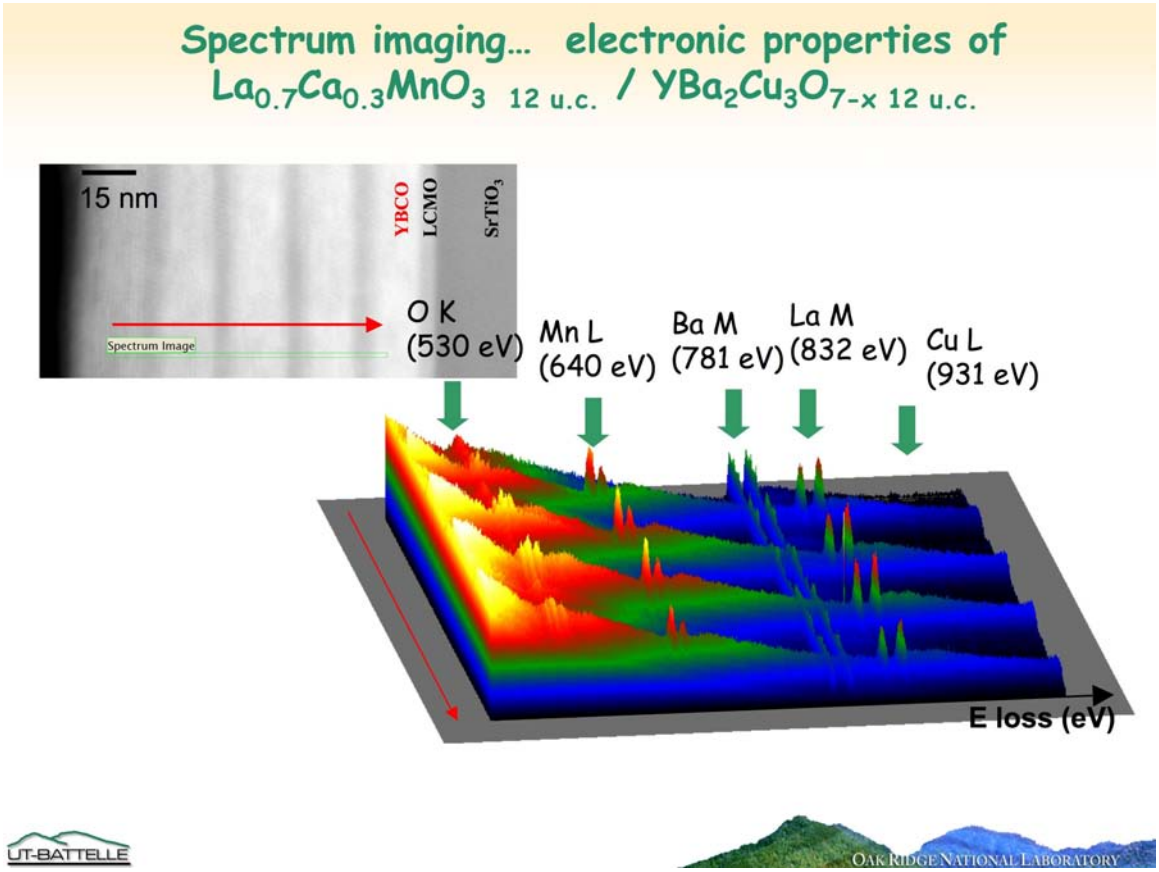


Fig. 7: A slide presented by Varela at the 2007 Spring MRS Meeting showing a superlattice claimed by Muller to be fictional. Upper left is the image recoded in the STEM, and lower right is EELS data recorded in the direction of the red arrow (from the green rectangular region) showing several different peaks.

In the slide the superlattice is labeled LCMO $_{12\ u.c}$/YBCO $_{12\ u.c.}$. In the slide, the *actual* average superlattice periodicity was quoted, as determined from Z-contrast images. In the previous preprints we referred to the *nominal* periodicity expected from the deposition times during sputter deposition, as usually done in the absence of better microstructural evidence, which was LCMO $_{15\ u.c}$ /YBCO $_{10\ u.c.}$.

Muller claims Varela admitted at the MRS meeting that measurements at low temperature still needed to be done. This is partially true, the Chicago data for this sample was not ideal because the sample was drifting too much. Therefore, the intended context of Varela's comment was **further** measurements at low temperature still needed to be done.

Damage threshold for Hi Tc superconductors

In a *Nature Materials* News and Views article [4], it is stated that spectroscopy data from superconductors in a recent *Nature* paper [5] involved "*electron doses that exceed by tenfold the damage threshold.*" As Muller understands, it is the oxygen pre-peak that is used to quantify holes in superconductors. Exceeding the damage threshold by 10 times would result in no

quantifiable prepeaks at all, so therefore the accusation amounts to one of data fabrication.

Below we present the raw data, free from damage artifacts, along with the extensive tests carried out to ensure the data were collected below the damage threshold.

Figure 8 presents page 226 from Varela's logbook (mostly in Spanish) with blue outlined comments translated, showing that R. Klie's sample with Ca was loaded into the microscope on June 7th, 2004, dates that coincide with a visit to ORNL by R. Klie. Figure 9 shows page 229 from Varela's logbook, containing comments on acquiring EELS from several dislocation cores with a static beam, and an explicit test for damage by increasing the beam current using the gun lens. The conclusion was the cores damage very slowly but the next page (Fig. 10) shows the beam current was restored to the prior (lower) level in order not "to burn the sample." The record shows that Varela was perfectly aware of the beam damage issue and checked to be sure there was no significant damage.

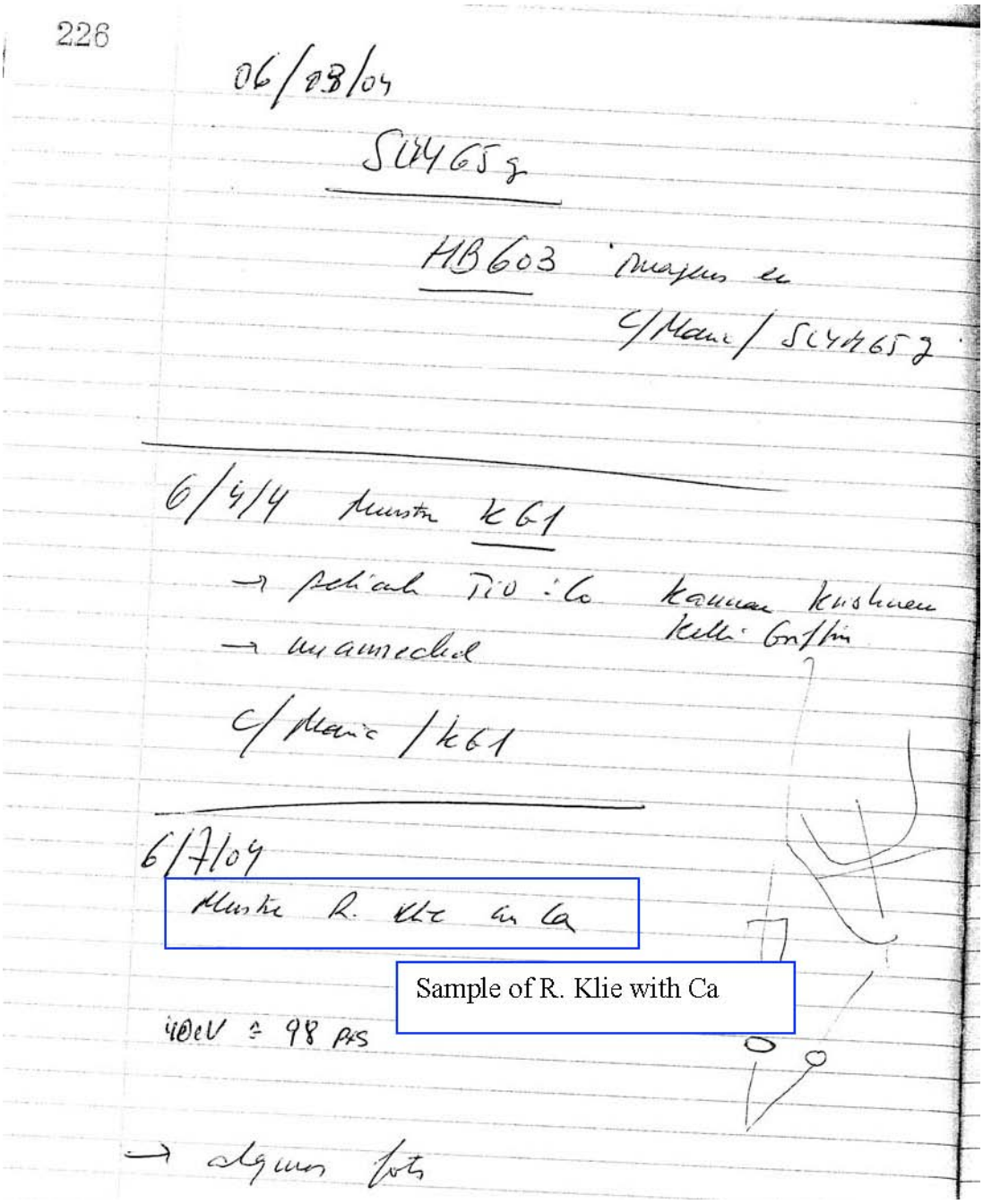
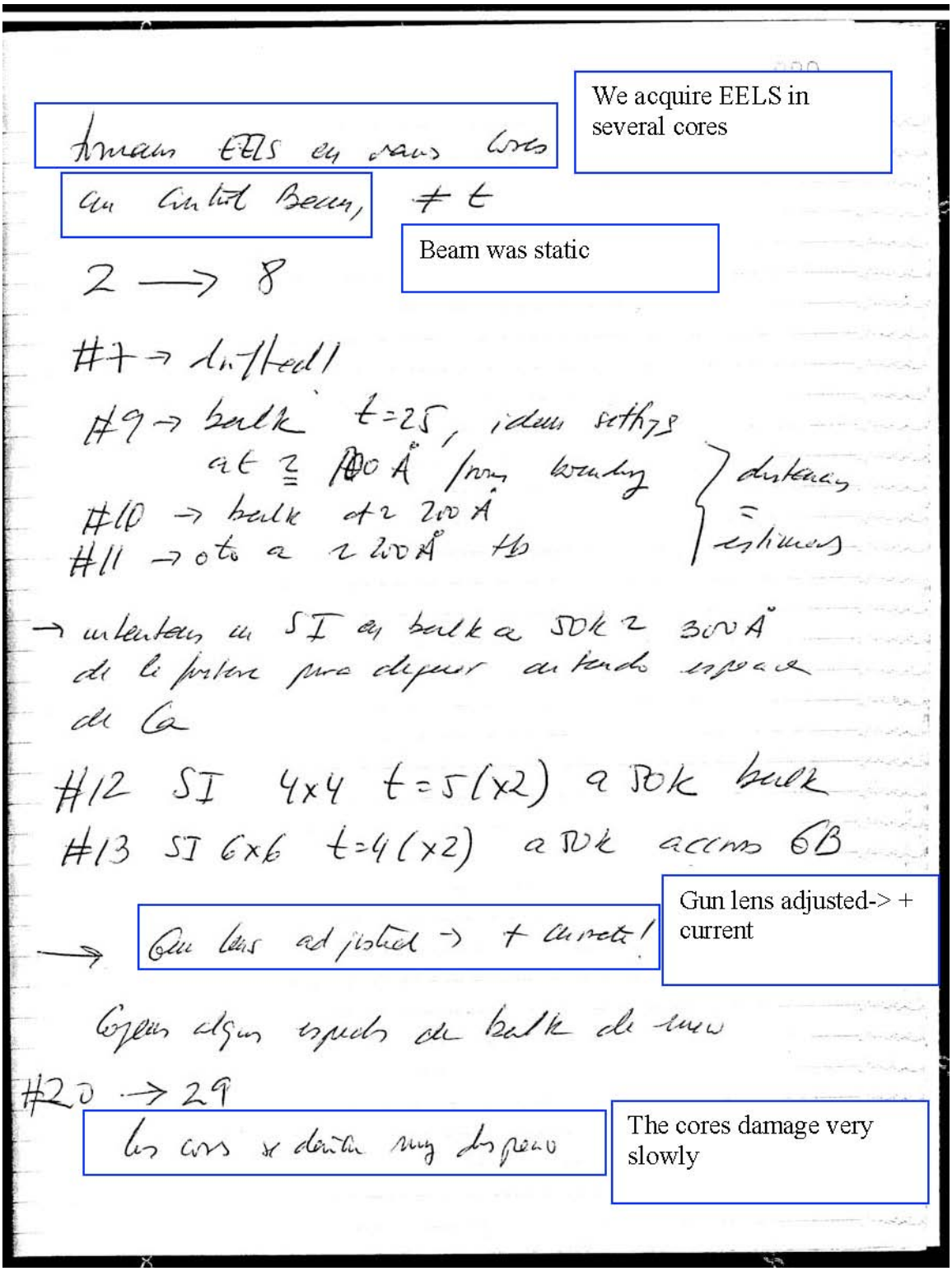


Fig. 8: Page 226 from Varela's logbook (in Spanish) with blue outlined comments translated, showing that R. Klie's sample with Ca was loaded into the microscope on June 7th, 2004.



We acquire EELS in several cores

Beam was static

Gun lens adjusted-> + current

The cores damage very slowly

Fig. 9: Page 229 from Varela's logbook, containing an explicit test for beam damage by increasing the beam current using the gun lens. The conclusion was the cores damage very slowly.

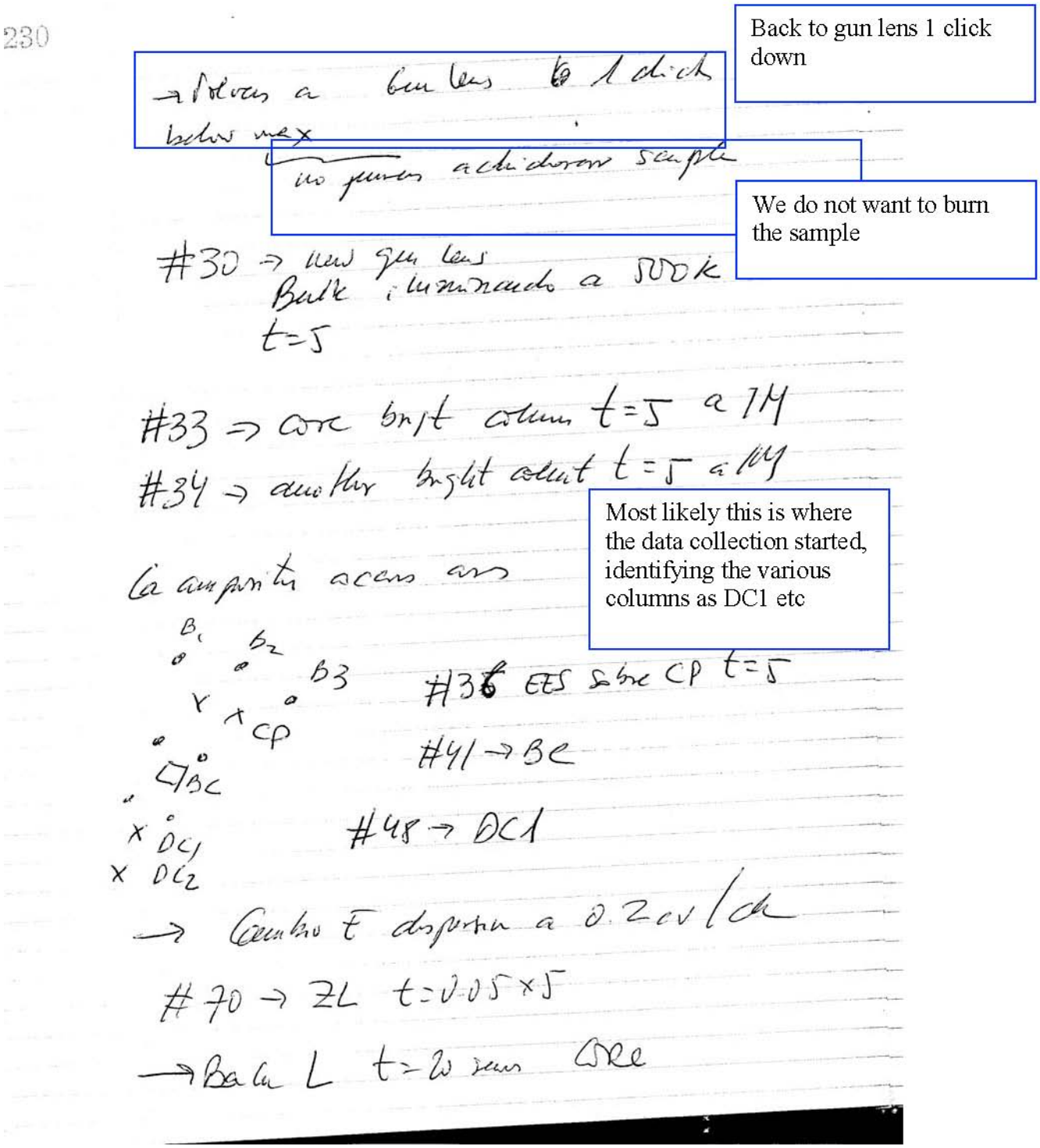


Fig. 10: The beam current was restored to the prior (lower) level in order not "to burn the sample."

It was not until June 10th that the published data were collected. Figure 11 presents screenshots of the folders containing the High Tc data, 183 Mbytes of it, and the folder "Ca-doped 06-10-04" that contains the files corresponding to the increase and decrease of the gun lens.

Name	Date Modified	Size	Kind
Ca doped	Dec 14, 2007, 12:25 PM	--	Folder
Ca doped 06-10-04	Dec 14, 2007, 12:25 PM	--	Folder
YBCO4	Dec 14, 2007, 12:24 PM	--	Folder
YBCO4 07-14-04	Dec 14, 2007, 12:24 PM	--	Folder
1_HAADF_1M_general.dm3	Jul 14, 2004, 10:32 AM	2.1 MB	DM3 File
1_LAADF_1M_general.dm3	Jul 14, 2004, 10:33 AM	2.1 MB	DM3 File
2_HAADF_1M_general.dm3	Jul 14, 2004, 10:44 AM	2.1 MB	DM3 File
2_LAADF_1M_general.dm3	Jul 14, 2004, 10:45 AM	2.1 MB	DM3 File
3_HAADF_2M_general.dm3	Jul 14, 2004, 10:45 AM	664 KB	DM3 File
3_LAADF_2M_general.dm3	Jul 14, 2004, 10:46 AM	664 KB	DM3 File
4_HAADF_2M_general.dm3	Jul 14, 2004, 10:48 AM	664 KB	DM3 File
4_LAADF_2M_general.dm3	Jul 14, 2004, 10:48 AM	664 KB	DM3 File
5_HAADF_1M_big mask.dm3	Jul 14, 2004, 10:50 AM	664 KB	DM3 File
5_HAADF_1M_general.dm3	Jul 14, 2004, 10:50 AM	664 KB	DM3 File
5_LAADF_1M_big mask.dm3	Jul 14, 2004, 10:50 AM	664 KB	DM3 File
6_HAADF_2M_big mask.dm3	Jul 14, 2004, 10:51 AM	664 KB	DM3 File
6_LAADF_2M_big mask.dm3	Jul 14, 2004, 10:51 AM	664 KB	DM3 File
7_HAADF_50k_big mask.dm3	Jul 14, 2004, 10:53 AM	2.1 MB	DM3 File

Name	Date Modified	Size	Kind
57_EELS_core_BC_t=5_1M.dm3	Jun 10, 2004, 4:02 PM	92 KB	DM3 File
53_EELS_core_DC2_t=5_1M.dm3	Jun 10, 2004, 3:51 PM	92 KB	DM3 File
51_EELS_core_DC1good_t=5_1M.dm3	Jun 10, 2004, 3:51 PM	92 KB	DM3 File
52_EELS_core_DC2_t=5_1M.dm3	Jun 10, 2004, 3:51 PM	92 KB	DM3 File
49_EELS_core_DC1_t=5_1M.dm3	Jun 10, 2004, 3:45 PM	92 KB	DM3 File
50_EELS_core_DC1_t=5_1M.dm3	Jun 10, 2004, 3:44 PM	92 KB	DM3 File
40_EELS_core_CP_t=5_1M.dm3	Jun 10, 2004, 3:42 PM	92 KB	DM3 File
43_EELS_core_BC_t=5_1M.dm3	Jun 10, 2004, 3:42 PM	92 KB	DM3 File
41_EELS_core_CPgood_t=5_1M.dm3	Jun 10, 2004, 3:42 PM	92 KB	DM3 File
45_EELS_core_BC_t=5_1M.dm3	Jun 10, 2004, 3:42 PM	92 KB	DM3 File
46_EELS_core_BC_t=5_1M.dm3	Jun 10, 2004, 3:42 PM	92 KB	DM3 File
48_EELS_core_DC1_t=5_1M.dm3	Jun 10, 2004, 3:42 PM	92 KB	DM3 File
47_EELS_core_BCgood_t=5_1M.dm3	Jun 10, 2004, 3:39 PM	92 KB	DM3 File
44_EELS_core_BC_t=5_1M.dm3	Jun 10, 2004, 3:36 PM	92 KB	DM3 File
42_EELS_core_BC_t=5_1M.dm3	Jun 10, 2004, 3:35 PM	92 KB	DM3 File
39_EELS_core_BC_t=5_1M.dm3	Jun 10, 2004, 3:29 PM	92 KB	DM3 File
38_EELS_core_CP_t=5_1M.dm3	Jun 10, 2004, 3:27 PM	92 KB	DM3 File
37_EELS_core_CP_t=5_1M.dm3	Jun 10, 2004, 3:25 PM	92 KB	DM3 File
36_EELS_core_CP_t=51M.dm3	Jun 10, 2004, 3:25 PM	92 KB	DM3 File
35_EELS_SI_500k_t=4.dm3	Jun 10, 2004, 3:23 PM	360 KB	DM3 File
35_HAADF_SI_500k_t=4.dm3	Jun 10, 2004, 3:01 PM	1.2 MB	DM3 File
34_HAADF_SI_500k_t=4.dm3	Jun 10, 2004, 2:57 PM	1.2 MB	DM3 File
34_EELS_core bright colum_bulk_1M_t=5.dm3	Jun 10, 2004, 2:56 PM	92 KB	DM3 File
32_EELS_1M_core_t=5.dm3	Jun 10, 2004, 2:43 PM	92 KB	DM3 File
33_EELS_core bright colum_bulk_1M_t=5.dm3	Jun 10, 2004, 2:42 PM	92 KB	DM3 File
32_EELS_another gun lens_bulk_1M_t=5.dm3	Jun 10, 2004, 2:36 PM	92 KB	DM3 File
31_EELS_another gun lens_bulk_500K_t=5.dm3	Jun 10, 2004, 2:31 PM	92 KB	DM3 File
30_EELS_core bright columr_500K_t=3.dm3	Jun 10, 2004, 2:21 PM	92 KB	DM3 File
29_EELS_core bright columr_500K_t=3.dm3	Jun 10, 2004, 2:10 PM	144 KB	DM3 File
28_EELS_core_500K_t=3.dm3	Jun 10, 2004, 2:09 PM	92 KB	DM3 File
25_EELS_core_500K_t=5.dm3	Jun 10, 2004, 2:00 PM	92 KB	DM3 File
27_EELS_core_500K_t=3.dm3	Jun 10, 2004, 2:00 PM	92 KB	DM3 File
26_EELS_core_500K_t=5.dm3	Jun 10, 2004, 2:00 PM	92 KB	DM3 File
24_EELS_bulk_avg500K_t=5.dm3	Jun 10, 2004, 1:55 PM	92 KB	DM3 File
21_EELS_new gun lens_bulk_t=5.dm3	Jun 10, 2004, 1:53 PM	92 KB	DM3 File
23_EELS_bulk_avg50K_t=10.dm3	Jun 10, 2004, 1:53 PM	92 KB	DM3 File
22_EELS_new gun lens_bulk_t=5.dm3	Jun 10, 2004, 1:51 PM	92 KB	DM3 File
20_EELS_new gun lens_bulk_t=5.dm3	Jun 10, 2004, 1:46 PM	92 KB	DM3 File
12_HAADF_SI bulk at 400A_50k_t=10.dm3	Jun 10, 2004, 11:28 AM	1.2 MB	DM3 File

Fig. 11: Screenshots showing the High Tc data. The upper image shows four folders and the lower image shows the contents of the folder "Ca-doped 06-10-04" with the files corresponding to the increase and decrease of the gun lens.

Figure 12 presents two sample spectra from dislocation cores. The oxygen pre-peak is clearly seen in both (arrowed) showing that significant damage had not occurred. The beam currents did not exceed the damage threshold.

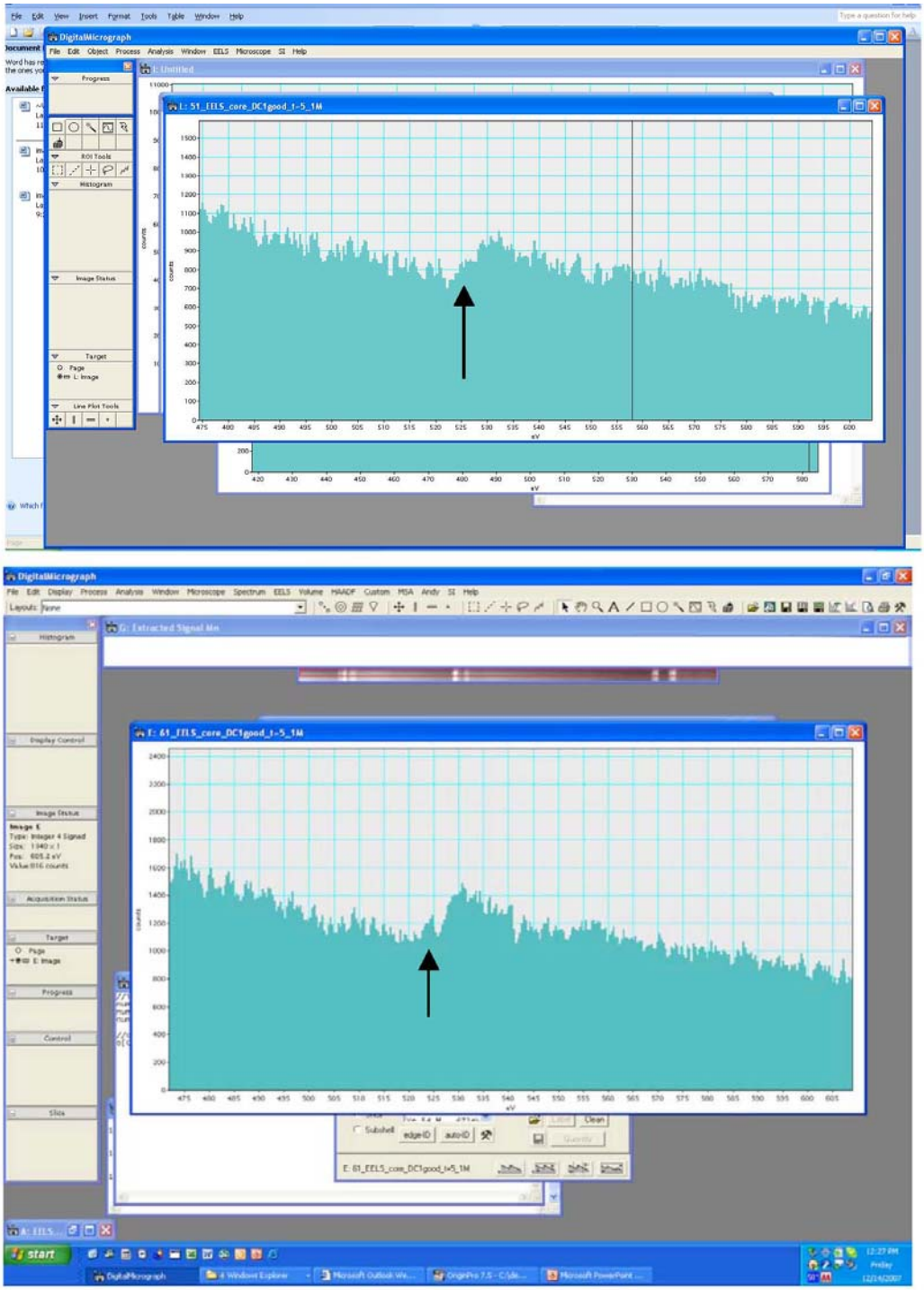


Fig. 12: Two sample spectra from dislocation cores. The oxygen pre-peak is clearly seen in both (arrowed) showing that significant damage did not occur.

The data are noisy, which was why spectra from each column presented in the *Nature* paper were averaged over five dislocation cores. All dislocation cores had the same structure, and the

averaging was clearly stated in the Methods section of the paper. Furthermore, in the Ca-doped core, hole concentrations were found that were at or near bulk values, which also excludes the possibility of significant damage having occurred at the grain boundary.

It is illuminating how Muller seems to arrive at his damage threshold estimate. He alleges our beam currents "exceed by tenfold the damage threshold reported by Larbalestier et al." when Larbalestier et al. [6] do not even report their beam current. He appears to base his estimate on a reference cited in the paper that quotes 15 pA beam current. But this was the current needed for Z-contrast imaging, not for EELS, which requires higher beam currents. Thus the tenfold estimate is based on lower current than actually used by Larbalestier et al.

It is unfortunate that Muller would make such published statements without checking with both sets of authors regarding the beam currents that were actually used.

A Selectively Altered Line Profile?

Muller claims selective data manipulation in connection with the LCMO/YBCO superlattices reported in the cond-mat preprint [3]. Some of the data were reported earlier, and Muller states "In the earlier work (e.g SSE) the EELS was recorded at a La-terminated interface. In the later papers however the authors note "*the terminating MnO2 planes electronically couple the manganite to the YBCO*" and now images are shown for a Mn-terminated interface, and **the EELS data is selectively altered to show a SHARP, Mn- terminated interface instead**."

But the statement "the EELS was recorded at a La-terminated interface" was **not** what was reported in the earlier Solid State Electronics (SSE) paper [7]. Muller makes a conclusion regarding the interface termination, again without checking with us, and then accuses us of changing it. The interface termination never changed, and the EELS data were never selectively altered. Both papers use the same figure and extract the same conclusion, a sharp interface, with no interdiffusion. No conclusion on interface termination was drawn from this figure or from the EELS data in any version of the paper. We show in detail below how the conclusions were derived.

The 2nd version of the cond-mat paper now references Sol Stat Elec. 47 (2003) p 2245 as the origin for cond-mat Fig2a:

2248 M. Varela et al. / Solid-State Electronics 47 (2003) 2245–2248

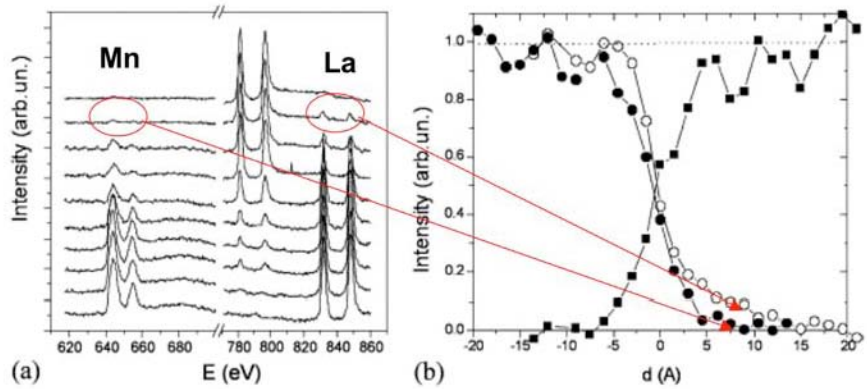


Fig. 4. (a) EEL spectra across the interface showing how the La $M_{4,5}$ edge (840 eV), Ba $M_{4,5}$ (781 eV) and Mn $L_{2,3}$ (642 eV) change across the interface. The spectra were acquired by successive jumps of 2 Å. (b) Integrated intensity, after normalization for La (open circles), Ba (solid squares) and Mn (solid circles) as a function of the distance to the interface.

Open circles in Fig 4b are the integrated La counts.
Solid circles are the integrated Mn counts. The Mn signal decays more quickly than La, consistent with spectra from fig 4a. – i.e a La-terminated interface with La diffusing 15A into the YBCO.

Fig. 13: PowerPoint slide where Muller interprets the traces as indicating a La-terminated interface, contrary to our published assertions.

Figure 13 shows Muller's PowerPoint slide circulated in December 2006 where he says "*The Mn signal decays more quickly than La, consistent with spectra from fig 4a. – i.e a La-terminated interface.*" He appears to be interpreting a small shift (of the order of 1Å) between the La and Mn traces as evidence of the interface termination. But such an interpretation is not valid because the profiles were not obtained in the same scan. The EELS system used for this work had only 385 channels. It was not possible to maintain good energy resolution over the necessary energy range to collect all three edges simultaneously. Two separate scans were used for the profiles, which might have been inferred from the break in the axis in Fig. 4a. The traces were aligned as best as possible, but given the chance of specimen drift it is not scientifically defensible to interpret the small offset between the La and Mn traces as indicative of interface termination, and we hence made no such interpretation.

Figure 2 of the SSE paper does show a Z-contrast image of a La-terminated interface, but the text of the paper clearly states "the most common structure that was found by far was a MnO terminating plane." Furthermore, the caption to Fig. 3 states definitively "the LCMO layer is terminated in a Mn–O plane." The EELS line trace was recorded across a Mn-terminated interface, the dominant, most commonly found interface. Unfortunately, when the SSE data was incorporated into the PRL and cond-mat submissions, a new Ca profile was added, and some of

the symbols were mislabeled in the figure caption. If Muller had contacted us we could have quickly resolved this issue. This was an unintentional error that had no effect on the paper's conclusions.

Instead, as shown in Fig. 14, Muller accuses us of selectively altering the La trace in order to convert the "inconvenient" La termination into Mn.

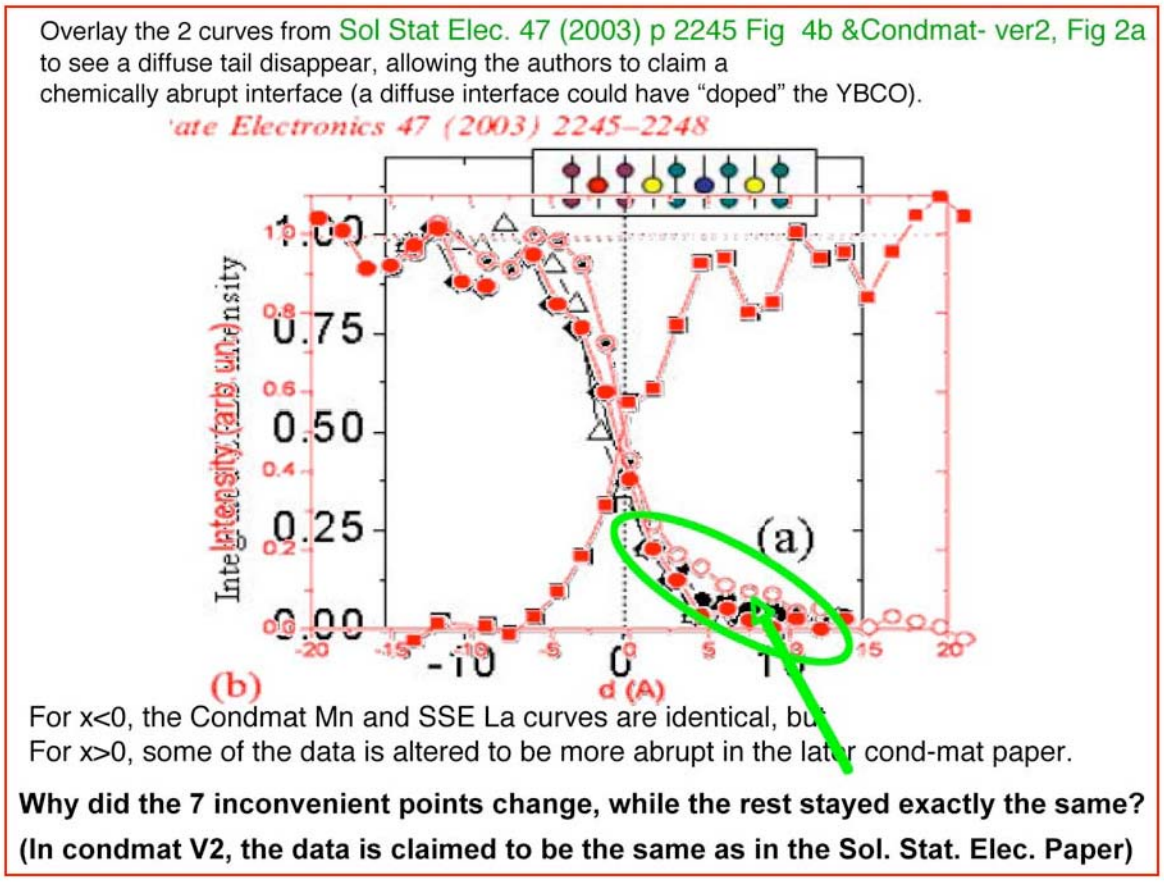


Fig. 14: Slide where seven reanalyzed La concentrations are assumed "inconvenient" to us.

Muller states that a diffuse tail has disappeared in the cond-mat preprint, "*allowing the authors to claim a chemically abrupt interface (a diffuse interface could have "doped" the YBCO). Why did the 7 inconvenient points change while the rest stayed exactly the same?*" The 7 points questioned were not in any way inconvenient. In the text we speculated that the observed charge transfer originated in band bending due to a Fermi level mismatch across the interfaces. We did not attribute the charge transfer to interdiffusion, neither did we rule it out. The subject of the paper was charge transfer, and the conclusions concern charge transfer only, and there are many possible origins.

The data points for La in the YBCO were reanalyzed between the initial Solid State Electronics paper and subsequent submissions using a spatial difference method, a commonly used method, widely accepted in the community. There were two reasons for the reanalysis. First, on the right

hand side of the interface, the YBCO layer, it was not possible to fit an accurate power law in the pre-edge region of the La because of the tail from the large Ba peaks. Second, it was realized that surface La was most likely spurious, arising from ion milling. Therefore the spatial difference method is appropriate and addresses both issues. On the left of the interface, the LCMO, there are no large Ba peaks, and use of a Ba spectrum for background subtraction would not be reasonable.

In the following we show these procedures in more detail. In the YBCO, the small La signals sit on the tail of the large Ba edge, as the one shown Fig. 15. A rough background fit could be obtained using a small energy window, but because the energy window was much smaller than the required extrapolation, the La concentration measurement would have significant error bars. The spatial difference method would provide a much more accurate background subtraction in this situation.

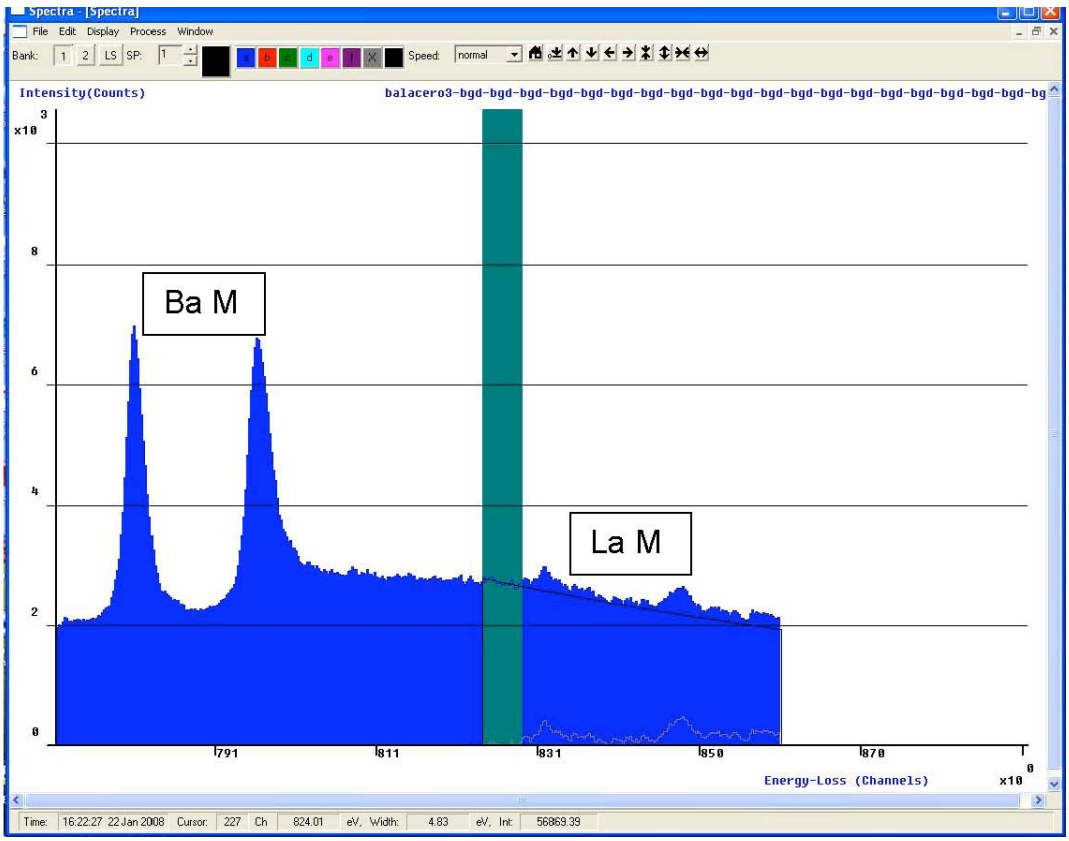
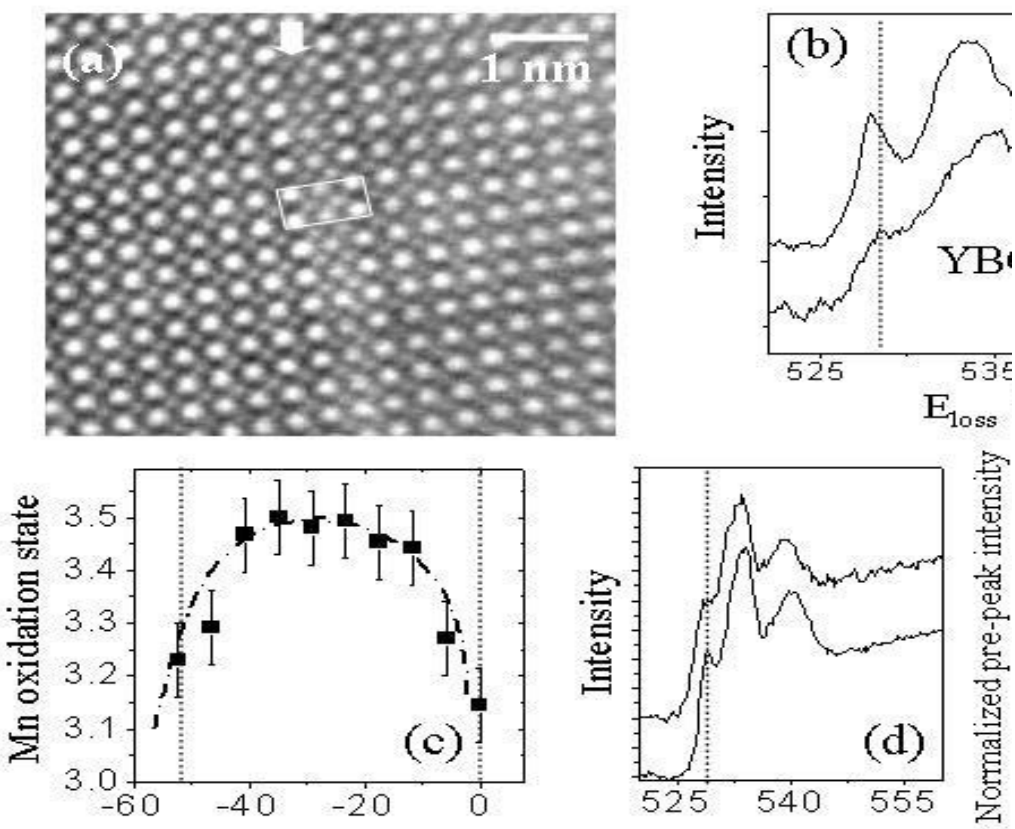


Fig. 15: The La edge sits on the tail of the Ba edge where the spectra cannot be accurately fitted with a power law. Use of a narrow energy window can give a rough measurement, but the spatial difference method would be more accurate.

A second reason for using the spatial difference method was the appreciation that surface debris was in fact a significant problem. When the Gatan Enfina was installed on the 100 kV microscope it did become feasible to perform scans over wide areas, as shown by Fig.
7. In some regions of the sample uniform La and Mn concentrations were found in the center of

the thick YBCO layers, but not in others. Clearly, if this effect were due to real interdiffusion then the same behavior would be found everywhere along an interface, independent of position and specimen thickness. If it were due to surface debris from ion milling it could vary from place to place, which was the behavior found experimentally. For this reason the La signals from the YBCO layer were analyzed using the spatial difference technique, using the La signal from the center of the YBCO as the reference. The La in the LCMO of course was not analyzed this way, since using a Ba reference spectrum for background subtraction would make no sense where there is no Ba, so the usual power law method was used for these points. We did not mention the background subtraction methods in any of the manuscripts; the methods used for the reanalysis were those we believed would give the most accurate concentration profile. There was no attempt or reason to remove any "inconvenient" La.

The interface termination was actually determined from the one unit cell superlattice. In the cond-mat preprint we stated "Figure 3(a) shows a Z-contrast image of a $[YBCO_{1\ u.c.}/LCMO_{15\ u.c.}]_{100nm}$ sample. The incomplete YBCO layer is marked with an arrow. Its structure, as identified from the images and also by atomic plane by atomic plane EELS, shows an atomic plane stacking of MnO_2-BaO-CuO_2-Y-CuO_2-BaO-MnO_2". Figure 16 reproduces Fig 3a from the cond-mat preprint.



Since La and Ba are adjacent in the periodic table it would be difficult to establish the identity of

the cation sequence across the nominal one unit cell YBCO layer. It could be either MnO_2-BaO-CuO_2-Y-CuO_2-BaO-MnO_2 or MnO_2-LaO-CuO_2-Y-CuO_2-LaO-MnO_2. To distinguish the possibilities EELS was used. Placing the beam in the center of the thin YBCO layer showed very little La but a strong signal from Ba. The bright columns in the rectangle were therefore identified positively as Ba, and the Mn termination was therefore assumed for both the 1 unit cell and 10 unit cell superlattices.

Charge transfer in YBCO/LCMO multilayers

In a PowerPoint file Muller makes the following statement concerning the samples studied in the cond-mat preprints :

"Fig 3c&4b shows **identical** data for two **different** systems (pg 2-3)
Fig 4b: A **fictional multilayer structure** with an unphysical symmetry is constructed by mirroring data and digitally altering/cropping an image of a single interface. (pg 4,5,11-13). It is desrcibed as "measured data", both in the figure caption and body of the paper.
In v2 this is replaced by a single interface with different data for the red plot (pg 14). The blue data in V2 is also changed – thus altering the charge transfer at the interface. »

The figure contains measured data, although we acknowledge the data presentation was not clearly described in the first cond-mat preprint and the *Nature Physics* submission. The blue color coding was intended to show that the YBCO data were mirrored left and right. The figure was intended as a concise visual presentation of the *conclusions* of the work, as we show below. It was not "a fictional multilayer structure" made up to *derive* any of the conclusions as implied by Muller. Figure 17 reproduces Fig. 4 of the first cond-mat preprint [3].

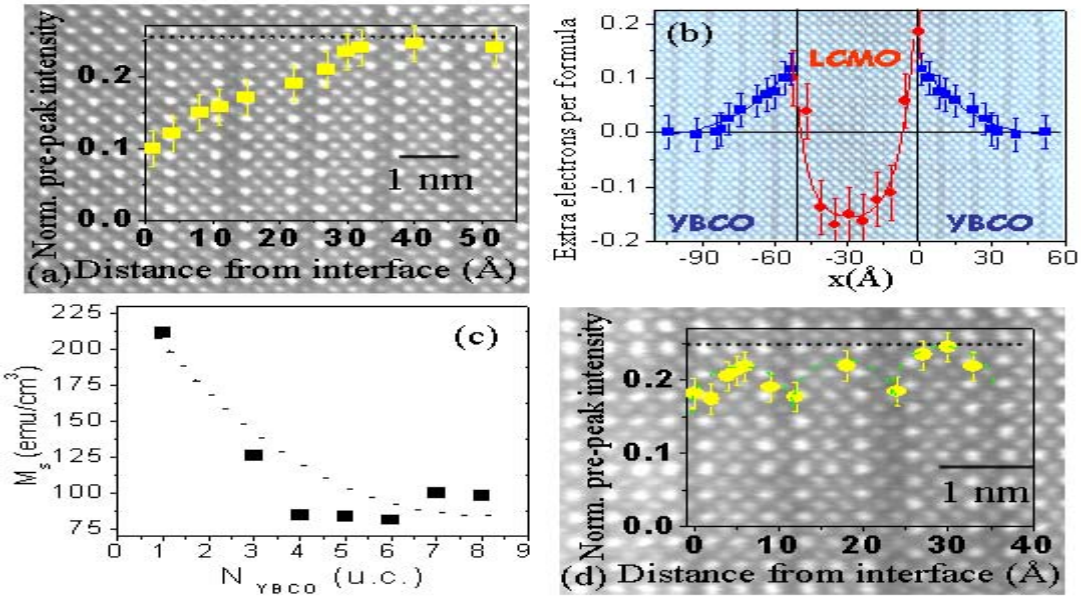


Fig. 17: Figure 4 of the first cond-mat preprint, where the caption read: (Color online) (a) Normalized pre-peak intensity for the O K edge acquired at the YBCO side of a YBCO/LCMO interface, as a function to the distance to the interface. The horizontal dotted line marks the pre-peak intensity in bulk YBCO. (b) Amount of excess (depleted) electrons per formula within the YBCO (LCMO) layers as a function of distance along the growth direction, as measured from EELS. Red and blue lines are a guide to the eye. The vertical black lines represent the interface positions. (c) Saturation magnetization measured at 5K for a set of $[YBCO_{n\ u.c.}/LCMO_{15\ u.c.}]_{100nm}$ superlattices vs. YBCO thickness. The dotted line is a guide to the eye. (d) Normalized pre-peak intensity within the YBCO in a YBCO/PBCO interface, as a function to the distance to the interface. The background images are in real scale in all cases.

The color coding of panel (b) was intended to show the composite nature of the image, the blue regions coming from a quantification of the O K pre-peak intensity presented in panel (a) and the red region coming from a quantification of the Mn $L_{2,3}$ ratio across the LCMO layer. In the *Nature Physics* submission this was made more explicit, as shown in Fig. 18, where the red and blue data sets are shown in panels a and b, and the composite is shown in c.

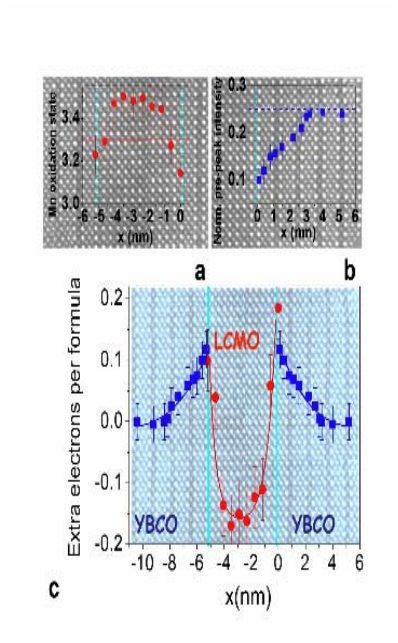
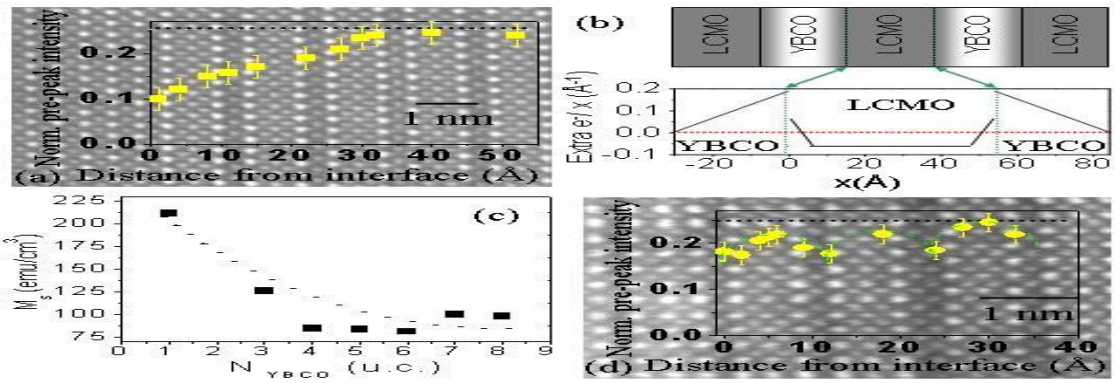


Figure 3
M. Varela et al

Fig. 18: Figure 3 of the Nature Physics submission, where the caption read: Electronic properties of the layers. (a) Mn formal oxidation state across the LCMO layer for the [$YBCO_{10\ u.c.}/LCMO_{15\ u.c.}]_{100nm}$ sample. The data have been averaged over a lateral length of 8 nm**.** Dotted vertical lines mark the interface locations. (b) Normalized pre-peak intensity for the O K edge acquired at the YBCO side of the YBCO/LCMO interface, as a function of the distance to the interface. The horizontal dotted line marks the pre-peak intensity in bulk YBCO. (c) Amount of excess (depleted) electrons per formula unit within the YBCO (LCMO) layers as a function of distance along the growth direction, as measured from EELS. Red and blue lines are a guide to the eye. The vertical light blue lines represent the interface positions, and the images in the background are to scale.

There was never any intent to imply a single EELS scan had been made. Each blue point in the hole concentration profile was obtained by summing spectra at the same distance from many interfaces in order to obtain the necessary statistics. It is therefore an average profile. In hindsight, the distance scale on the lower axis and the inclusion of the data points and error bars could be taken to imply a single EELS scan had been performed across the entire region, which had not been done, and we regret the error, which was corrected in a second posting to the cond-mat site [8].
However, neither caption for the composite part of the figure referred to any specific specimen. Neither did the text. It was intended as a schematic depiction of the charge transfer scenario. In an earlier draft, black lines were used for the schematic, as shown in Fig. 19.



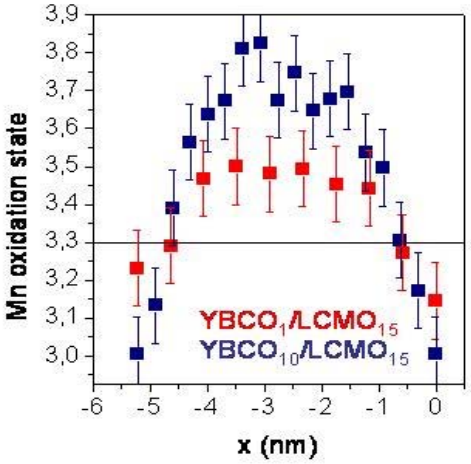
(b) (Top) Sketch of the YBCO/LCMO superlattice. The shaded interface areas within the YBCO layers represent the hole depleted layers as a result of the charge transfer from the ferromagnet. (Bottom) Amount of extra (depleted) electrons per unit length within the YBCO (LCMO) layers as a function of distance along the growth direction, as measured from EELS. The red dotted line represents the average doping of the bulk. Green dotted lines mark the interfaces

In Fig. 19 the purpose of the axes is to set the scale for the charge transfer phenomenon. All YBCO scans showed the same trend; there was no difference between the top and bottom interface with respect to the growth direction. The figure accurately conveyed the central conclusion of the paper. The caption is correct in stating "Amount of extra (depleted) electrons per unit length within the YBCO (LCMO) layers as a function of distance along the growth direction, as measured from EELS." It is clear that this is a schematic depiction of the conclusions of the work. This wording is essentially unchanged in the later versions, but the black lines were replaced with the blue and red data curves which we agree should have been labeled to clearly note that the YBCO data had been mirrored.

The background images were also composites, intended simply for visual clarity, never intended to imply any simultaneous acquisition or the precise location of the EELS data. They were never used to support any of the claims of the paper. No reference is made to background images anywhere in the main text, only in figure captions. The background is intended to help to locate the position of the interfaces and the different layers at a glance, for illustrative purposes only. We never tried to conceal the fact that the image was a composite and therefore the seam is visible to the eye without analyzing the image in detail. The image is actually the one used for Fig. 1(c) in all the submissions, which was rotated and did not fill the space required for the background.

The red data in the *Nature Physics* submission was from the one unit cell sample, whereas it was

intended to be from the 10 unit cell sample, as the figure caption clearly states (reproduced in Fig. 18). This error allowed Muller to allege that the thicker sample never existed. But the text refers to the correct numbers for the ten unit cell sample, which are different to those for the one unit cell sample. The correct LCMO curve actually showed more charge transfer than the single cell data that was shown in the



Throughout the discussion of Figure 4b (page 6 of the main text of the manuscript) we do refer to the correct $YBCO_{10}/LCMO_{15}$ sample. Citing from page 6: "While the overall qualitative behavior of the Mn valence in the LCMO layers in this sample is like that shown in figure 3(c) [the one unit cell sample], the average Mn formal oxidation state was found to increase with increasing YBCO thickness. In this sample [the 10 unit cell sample], its value is +3.5 ± 0.10. If we keep in mind that the nominal chemical doping yields an average Mn valence of +3.3 (the value confirmed by EELS in bulk LCMO samples), around 0.2 electrons per LCMO unit cell are missing." This was the central conclusion of the work.

After the misconduct allegations were received it was realized that the red curve was wrong and a new posting was made to the cond-mat preprint server to correct the data and avoid the duplicated blue curve [8]. In this figure we showed only half of the data for the thick YBCO sample so that the areas under the red and blue curves could again be visually compared, as in the original composite figure. The new figure is reproduced in Fig. 21.

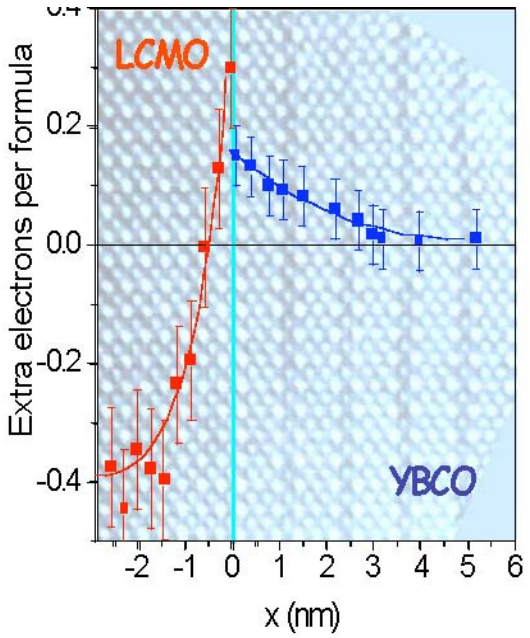


Fig. 21: The new Fig. 4b in the second Cond-mat posting, showing only half the red data set so that the areas under the red and blue curves could be easily compared by eye.

Muller now states: "*The average valence for the LCMO layer is still reported (unchanged) in the paper even though this would require EELS measurements across the whole layer, which is no longer the case.*" As shown in Fig. 20, measurements were taken across the entire LCMO layer.

Valence stripes in mixed-valence manganites

Muller takes issue with more of Varela's valence profiles in another system, the first direct EELS observation of the so-called charge ordering phenomenon in manganites. Again he alleges the data do not support the conclusions and that points have been duplicated to fabricate a chemical shift. Figure 22 shows the first slide from an e-mail circulated by Muller in December 2007.

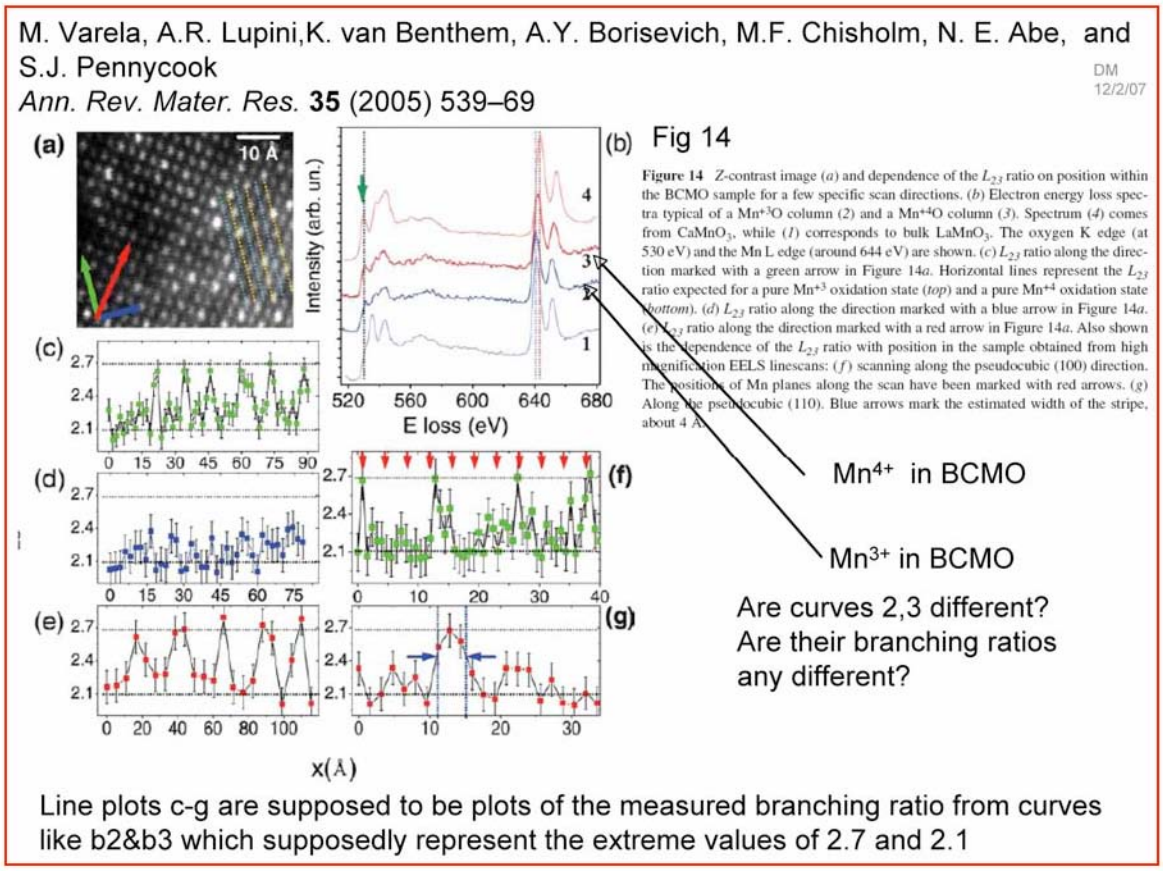


Fig. 22: PowerPoint slide circulated by Muller questioning Varela's observation of valence stripes in a mixed valence manganite.

Muller questions whether curves 2 and 3 are different and states in the next slide "*Varela reports a L23 ratio of 2.1 for Mn^{4+} and 2.7 for Mn^{3+} This means the height of the L2 peak relative to the L3 must change by 28% if the valence is changed from 3+ to 4+ as is claimed for curves 2,3.* But this is not true, it is the ratio of the integrated areas, after background and continuum corrections, that should change by 28%. In the next slide he shows reproductions of the published spectra,

scaled and superimposed. His slide is reproduced in Fig. 23.

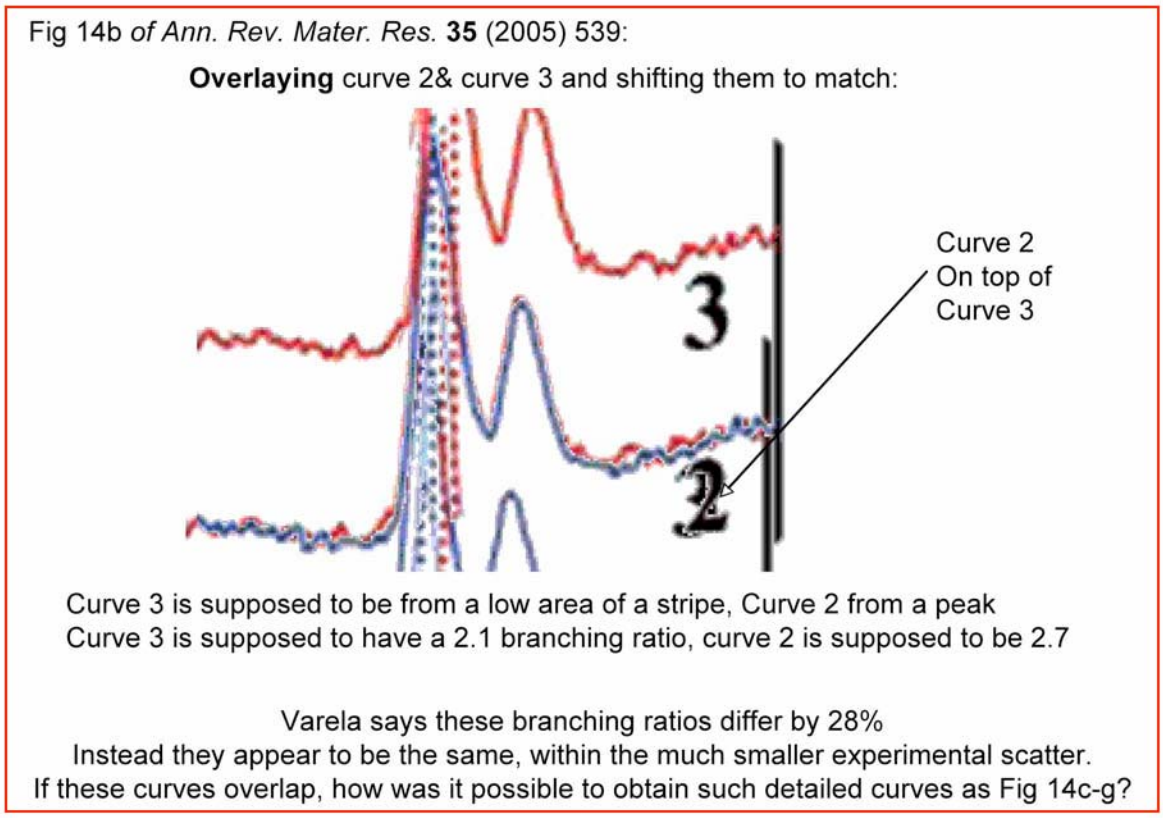


Fig. 23: Muller's slide #3 showing Varela's spectra scaled and overlaid so that the L2 peaks appear to match, but the L3 peak is obscured.

He overlays curves 2 and 3 and we see the L2 peak scaled to match. He appears to imply that the L23 ratios were manufactured. The L23 ratios were obtained by consistent application of an adaptation of the method reported by Wang et al. [9], involving the subtraction of the continuum contribution and integration of the areas. During the ORNL inquiry, Varela was asked to reproduce selected results involving her L23 ratio analysis. The original files were located, the creation dates were appropriate, and reanalysis reproduced the original results. Reanalysis of the two L23 ratios obtained from the two curves reproduced in Fig. 23 are 2.75 and 2.02, in perfect agreement with the values published [10] and quite different from each other. It is not just peak height that changes, but peak shape, and overlaying scanned images is not a scientifically defensible analysis procedure.

The change in valence was also indicated by a chemical shift, which Muller chooses to attribute to the insertion of an extra point in the data, as shown in Fig. 24.

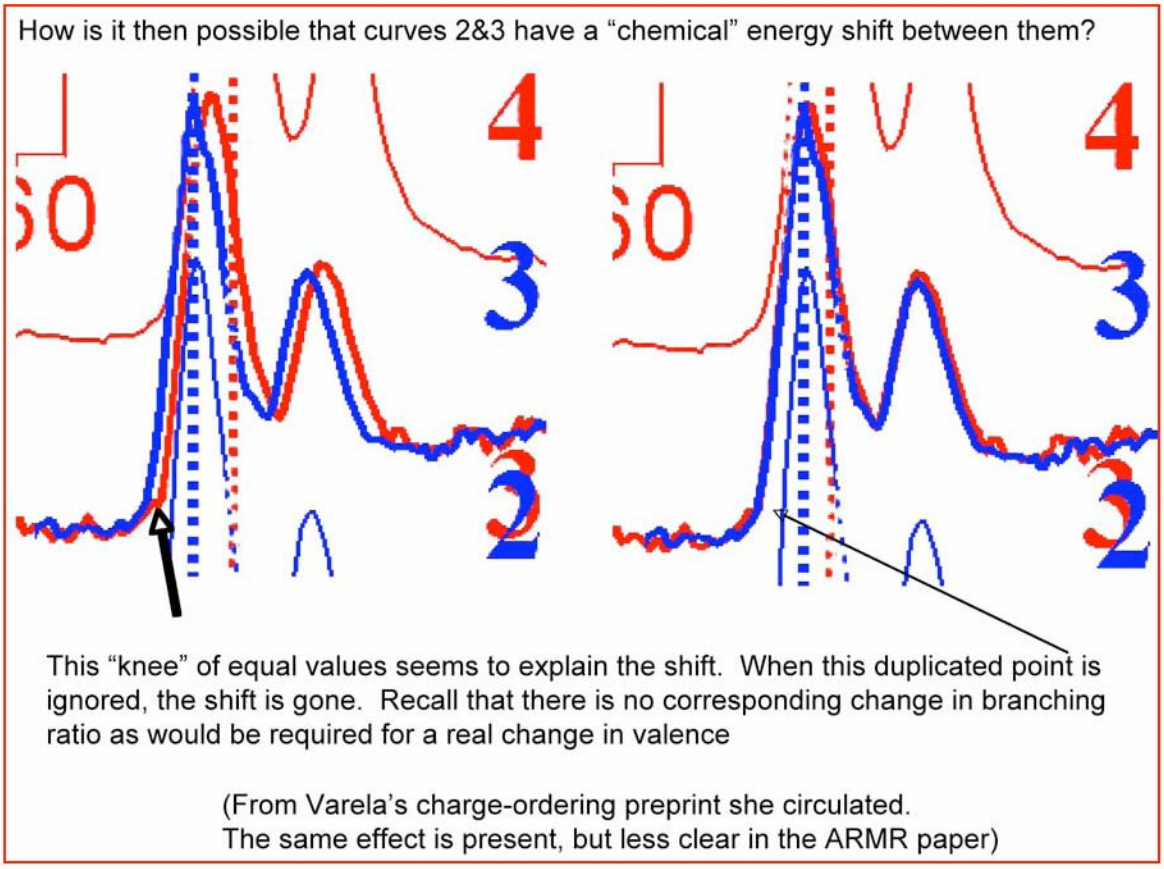


Fig. 24: Muller's slide #6 alleging that an extra point was inserted in the data to create a chemical shift.

The chemical shift is present in the original data, but was not used for quantification purposes.

Same data shifted in different samples?

In the first PowerPoint file sent by *Nature Physics* there are several allegations of the same data reported for allegedly different samples, and an accusation that the "*data were shifted by ~0.3 electrons (necessary to create charge balance, central to their claims*". To this day we do not know the identity of the accuser. Figure 25 shows one slide that alleges different samples, same data.

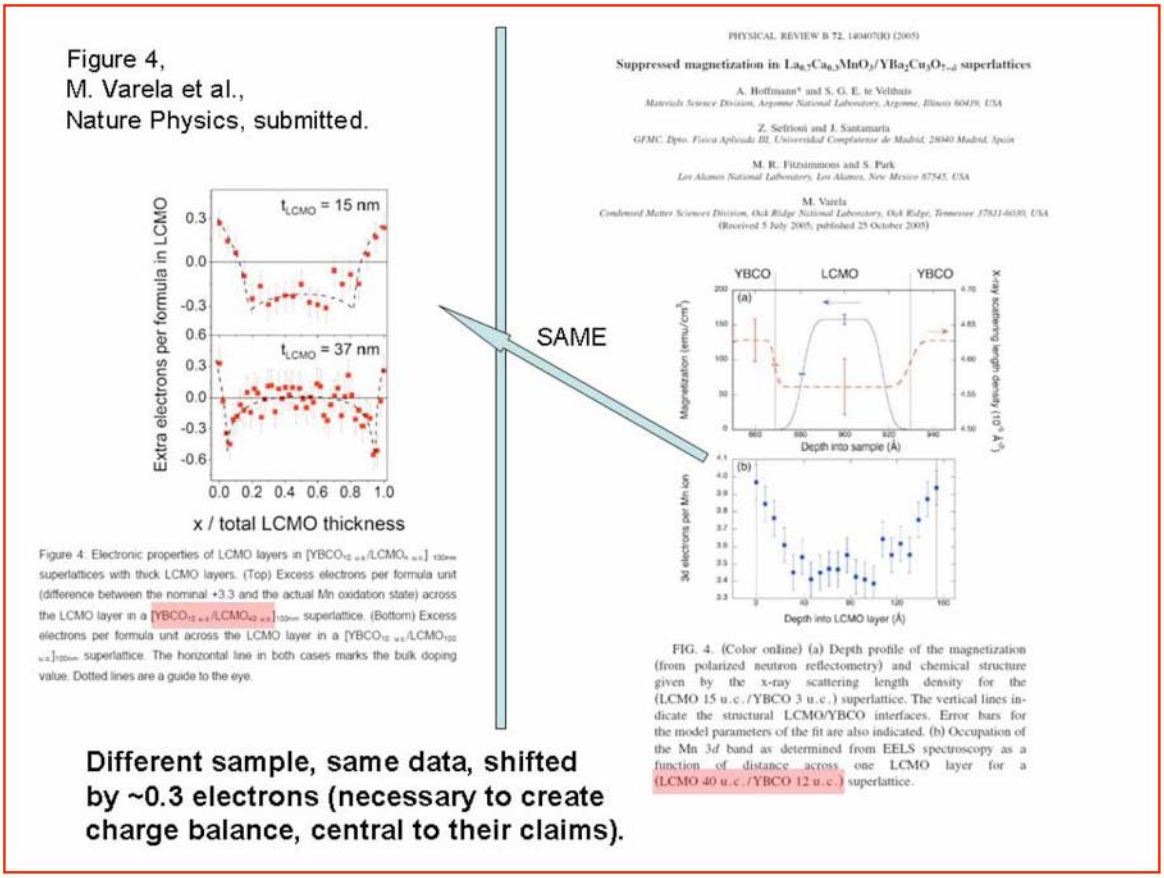


Fig. 25: Slide from the original PowerPoint file sent by Nature Physics to Varela in May 2006 alleging same data used for different samples, but shifted by 0.3 electrons.

We have already discussed the origin of the seemingly different YBCO thicknesses reported in the preprints and subsequent work. The *Nature Physics* submission reported the nominal superlattice periodicity anticipated from the growth times for each layer, while the *Physical Review B* paper [11] reported the thickness estimated from x-ray diffraction analysis. The samples were the same.

The alleged 0.3 electron shift is because the vertical axis of each graph is different. The preprint plotted extra electrons per formula unit whereas the paper published in *Physical Review B* plotted the number of 3d electrons per Mn ion. These quantities differ by 0.3 electrons. The reason is straightforward. A neutral Mn atom has 7 electrons in its outer shells. In $La_{0.7}Ca_{0.3}MnO_3$ La has an oxidation state of +3 and Ca has an oxidation state of +2. For charge neutrality to be preserved a total of 6 electrons are required by the O. The La provides 0.7x3=2.1 and the Ca provides 0.3x2=0.6, leaving 3.3 to be donated by the Mn. The Mn oxidation state is 3.3 and consequently it has 3.7 electrons left in its 3d band. For this material, the excess number of electrons per formula unit is the excess over 3.7, the charge neutrality level, ie.

Excess number of electrons = Measured 3d electrons per Mn – 3.7

The two data sets differ by 3.7. There is no artificial shift.
The accuser alleges that in different papers the same data is presented for samples with different

stoichiometry, one being $La_{0.7}Ca_{0.3}MnO_3$ and the other being $La_{0.67}Ca_{0.33}MnO_3$. These are, in fact, the same samples, since 0.3 is just 0.33 rounded to one decimal place and 0.7 is just 0.67 rounded to one decimal place. The phase diagram in this composition range, generally referred to as the $\mathbf{La_{2/3}Ca_{1/3}}$ portion, is very flat and featureless and no difference would be expected in a 3 percentage point change in stoichiometry. In fact, it would be very difficult to measure stoichiometry to such levels of accuracy in a thin film. Nevertheless, a similar allegation is brought in connection with the caption to Figure 4 of another *Physical Review B* article [12], in which a series of superlattices are referred to as "[LCMO (5 unit cell)/YBCO (N_S unit cell)] with N_S =1,2,3…" The text however only refers to "superlattices with fixed LCMO thickness (15 unit cells) and changing the thickness of the YBCO from 1 to 12 unit cells". The figure caption was a simple typographical error, obvious from the text.

Summary

We admit that mistakes have been made and errors of judgment made in regard to data presentation, which we deeply regret, but never have we fabricated or falsified data. All allegations have a simple explanation, often trivial. In all cases a direct enquiry to the authors could have resolved the issue. We believe it is time to cease unprofessional allegations. Scientific issues should be raised directly with the authors. If issues cannot be resolved directly, they should be raised in the open peer-reviewed scientific literature rather than by circulation of unsubstantiated allegations through PowerPoint files.

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