Electron-energy-loss spectra of the high-T_c superconductors Y-Ba-Cu-O and La-Sr-Cu-O

M. G. Ramsey and F. P. Netzer
Institut für Physikalische Chemie, Universität Innsbruck, A-6020 Innsbruck, Austria

J. A. D. Matthew
Department of Physics, University of York, Heslington, York, YO1 5DD, England

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Electronic excitations of Y-Ba-Cu-O in superconducting and nonsuperconducting form and of La-Sr-Cu-O have been investigated by electron-energy-loss spectroscopy (EELS) in the valence and shallow core region, both in dN/dE and $N(E)$ form. The importance of quasiatomic resonances in the loss region 15 eV $\leq \Delta E \leq$ 50 eV are emphasized, while the differences observed between superconducting and nonsuperconducting Y-Ba-Cu-O are ascribed to differences in the Cu-O stoichiometry. The temperature-induced decomposition of Y-Ba-Cu-O leads to a BaO-type surface layer; EELS from this layer corroborates the present loss assignments. The influence of electron-beam irradiation of La-Sr-Cu-O is discussed.

Although we do not expect that electron spectroscopy will solve the riddles of high-T_c superconductivity, discovered by Bednorz and Müller,[1] it is nevertheless important to characterize these very complex multicomponent systems as well as possible. In this area, electron spectroscopic techniques are very useful. In the present Brief Report we report a comparative study of the electronic excitation spectra, as measured by electron-energy-loss spectroscopy (EELS), of $YBa_2Cu_3O_{7-x}$ [in superconducting (SC) and nonsuperconducting (NSC) form] and of $La_{1.85}Sr_{0.15}CuO_4$. EELS of high-T_c superconductors is interesting because low-energy plasmon and exciton-mediated mechanisms have been proposed to explain superconductivity.[2-4] The first EELS data on Y-Ba-Cu-O have been reported by Chang *et al.*[5] in d^2N/dE^2 form. In the present investigation the spectra were recorded in both $N(E)$ and dN/dE form. The comparative aspects of this study together with a wide variation of the electron primary energy and the consideration of thermal decomposition behavior leads to an interpretation of the loss spectra distinctly different from that inferred in previously reported d^2N/dE^2 spectra.[5]

Two samples of nominal $YBa_2Cu_3O_{7-x}$ stoichiometry and one of $La_{1.85}Sr_{0.15}CuO_4$ were investigated here.[6] ac magnetic-susceptibility measurements of the La-Sr-Cu-O and Y-Ba-Cu-O I samples showed them to be superconducting with transition-temperature onsets of 36 and 90 K, respectively, and transition widths of a few degrees. Sample Y-Ba-Cu-O II was nonsuperconducting and investigated here for the purpose of comparison. The samples were attached to a UHV manipulator where they could be cooled to 80 K and heated indirectly to $\approx$ 800 K. EELS spectra were recorded in a VG ADES 400 electron spectrometer[7] using electron primary energies E_p = 10–2000 eV. The base pressure of the system after bakeout to only 75 °C (to prevent oxygen loss) was $\approx 5\times10^{-11}$ mbar. The total-energy resolution in EELS as measured on the elastically reflected primary peak [full width at half maximum (FWHM)] was 0.5–0.6 eV. In order to obtain clean surfaces characteristic of the bulk composition, the sample surfaces were scraped repeatedly in UHV with a corundum file.

Figure 1 shows EELS of Y-Ba-Cu-O I and II and of La-Sr-Cu-O in integral $N(E)$ and differentiated $N'(E)$ form excited with E_p = 150 eV. For Y-Ba-Cu-O I, a spectrum recorded with E_p = 500 eV is also shown. Ten loss features, marked A–J, are observed for each of the sam-

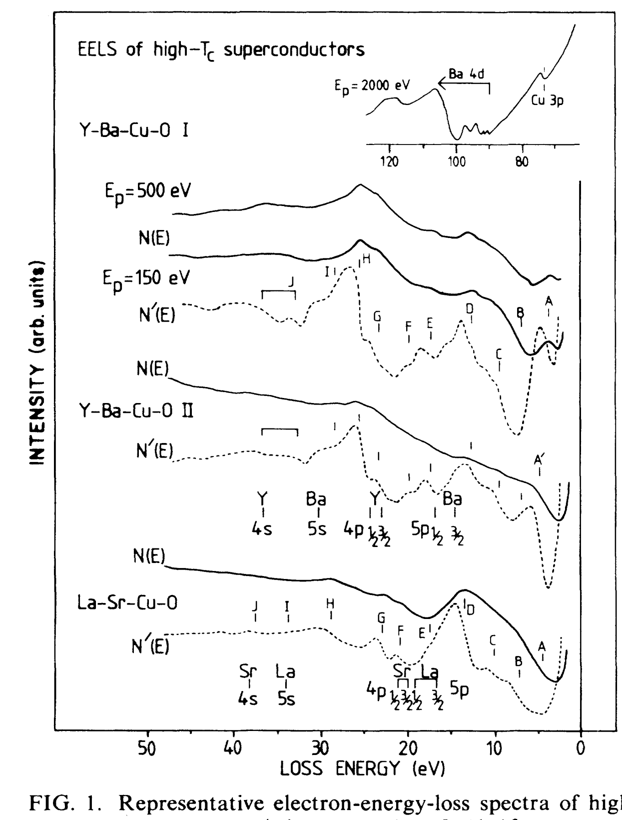

FIG. 1. Representative electron-energy-loss spectra of high-T_c superconductors in $N(E)$ and dN/dE [$N'(E)$] form. Top spectrum E_p = 500 eV, others E_p = 150 eV. Inset shows Cu 3p and Ba 4d core-loss region for Y-Ba-Cu-O I. XPS binding energies for the Ba, Y, La, and Sr shallow core levels are indicated.

TABLE I. Electron energy-loss peaks (energies in eV) of superconducting (SC) and nonsuperconducting (NSC) Y-Ba-Cu-O and of La-Sr-Cu-O and their assignment.

Y-Ba-Cu-O			La-Sr-Cu-O	
I SC	II NSC	Assignment	SC	Assignment
A 3.5		O $2p \rightarrow$ antibonding Cu $3d$-O $2p$	A 4.4	O $2p \rightarrow$ antibonding Cu $3d$-O $2p$
	A' 4.3	O $2p \rightarrow$ modified final states		
B 6.7	6.4	Interband transitions	B 7.2	Interband transitions
C 9.2	9.4	Interband+surface plasmon	C 10.0	Interband+surface plasmon
D 12.5	12.4	Bulk plasmon	D 13.8	Bulk plasmon
E 17.0	17.0	Ba $5p \rightarrow 5d$	E 17.4	La $5p \rightarrow 5d$
F 19.5	19.5	Ba $5p \rightarrow 5d$	F 20	La $5p \rightarrow 5d$; Sr $4p \rightarrow 4d$
G 22	22	Ba $5p \rightarrow 5d$; Y $4p \rightarrow 4d$	G 23	La $5p \rightarrow 5d$; Sr $4p \rightarrow 4d$
H 25	25	Ba $5p \rightarrow 5d$; Y $4p \rightarrow 4d$	H 29	La $5p \rightarrow 5d$; Sr $4p \rightarrow 4d$
I 28	28	Y $4p \rightarrow 4d$; Ba $5s$	I 34	La $5s$
J 33–36	33–36	Y $4p \rightarrow 4d$; Ba $5s$	J 37–39	Sr $4s$

ples, and their respective energy positions are listed in Table I. Nine features were identified in the d^2N/dE^2 loss spectra of Y-Ba-Cu-O by Chang *et al.*[5] up to $\Delta E = 40$ eV. The correspondence in energy positions with the present results is satisfactory apart from deviations at low ΔE, where the influence of sample conditions is most pronounced (see below). Note that not all the loss features are clearly visible at a particular primary energy, but that a careful comparison of different primary energies is necessary to render their identification unambiguous. The SC (I) and NSC (II) Y-Ba-Cu-O samples show very similar EELS profiles for $\Delta E \gtrsim 5$ eV [see particularly the $N'(E)$ spectra], but they differ markedly in the low-energy-loss region of peaks A and A'. The losses of La-Sr-Cu-O are similar in shape and energy positions to Y-Ba-Cu-O I in the region 5–15 eV, where typical "oxide-like" behavior with a broad hump peaking around 12–14 eV and some fine structure at the leading edge is exhibited.[8–10] At low ($\Delta E < 5$ eV) and higher ($\Delta E > 15$ eV) loss energies the excitations of La-Sr-Cu-O are clearly different from those of Y-Ba-Cu-O as expected from the differences in structure and constituents of this compound.

The inset of Fig. 1 displays the region of the Cu $3p$ and Ba $4d$ core excitations of Y-Ba-Cu-O I in $N(E)$, for $E_p = 2000$ eV. The Ba^{2+} $4d \rightarrow 4f$ resonance excitations in the Y-Ba-Cu-O's, however, are prominent and will be discussed in detail elsewhere.[11] The La $4d \rightarrow 4f$ excitation profiles in La-Sr-Cu-O (not displayed here) show similar fine structure as in La metal,[12] consistent with the atomiclike nature and the insensitivity to chemical environment of these transitions.

In Fig. 2, EELS of Y-Ba-Cu-O I and La-Sr-Cu-O are shown at $E_p = 11$ and 20 eV, respectively. These experiments were performed to emphasize low-energy excitations in the region $\Delta E \approx 0.5$–3 eV. As in Fig. 1 we observe the loss features A and B, but no prominent lower-energy excitations (down to the resolution-limited value of $\Delta E \approx 0.5$ eV) can be detected. Cooling of Y-Ba-Cu-O I to below T_c introduces no changes in the EELS curves as evident from Fig. 2.

The interpretation of the electron losses is summarized in Table I. The losses beyond the $5p$ thresholds of Ba and La are dominated by the $5p \rightarrow 5d$ resonance excitations. As it has been demonstrated for the rare-earth metals[13] these resonances may be understood in atomic terms, and they result from the strong Coulomb interaction between the $5p$ and $5d$ subshells.[14] The large $5p$-$5d$ exchange interaction drives the dominant multiplet terms high up into the continuum, and very intense structures, up to 10 eV

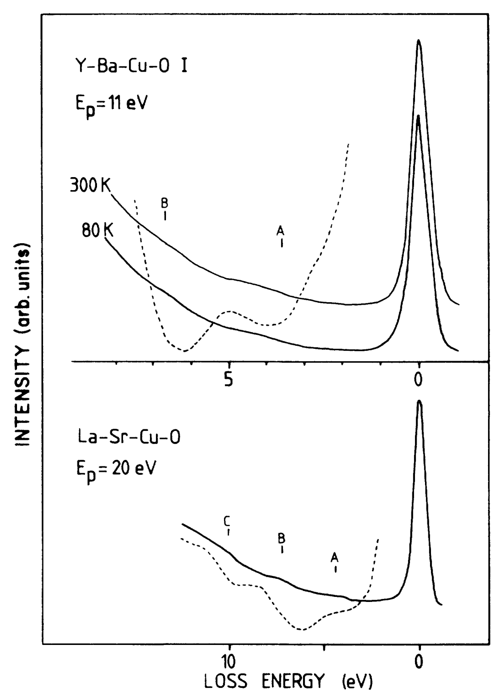

FIG. 2. EELS at low E_p of superconducting Y-Ba-Cu-O, above and below T_c, and La-Sr-Cu-O in $N(E)$ (solid curves) and $N'(E)$ (dashed curves).

above the threshold, are observed in EELS.[13] Thus, the structures E-H with the maximum H at 25 and 29 eV for Y-Ba-Cu-O and La-Sr-Cu-O, respectively, are associated with resonance excitations of the $5p$ shell. The one-to-one correspondence of these features with respective loss structures of BaO (Ref. 8 and see below) and La_2O_3 (Ref. 7) is strongly supportive of this assignment rather than that of a plasmon.[5] The $4p$ threshold of Y is at ≈ 23 eV, and the Y $4p$-Y $4d$ excitations with a delayed maximum around 36 eV in Y_2O_3 (Ref. 15) overlap with the Ba $5p$ excitations; they give rise presumably to the peaks I and J in the Y-Ba-Cu-O spectra. Peak I may also have some contribution from Ba $5s$ excitations, but they are expected to be very weak. Excitations from O $2s$ levels may occur around 22 eV, but again, as a result of the relatively weak oscillator strength for excitations from low-angular momentum states,[16] these transitions should be weak compared to the $5p$ resonance transitions. In La-Sr-Cu-O the Sr $4p \rightarrow 4d$ excitations overlap with the La $5p$ excitations in the region 20–33 eV, as expected; see, for example, EELS of SrO.[8] Overall, the losses in this region are dominated by Coulomb and exchange interaction between the np hole created and the nd-like excited electron: These effects are relatively insensitive to environment, and give no direct information on superconductivity. The results do, however, confirm that intense quasiatomic resonances persist in complex oxide systems.

At electron loss energies, < 15-eV one-electron interband transitions and collective effects are possible. In analogy to other oxide studies[8,15,17] we assign the major peaks D in that region to strongly damped oxide bulk plasmons.[18] Features B and C in both Y-Ba-Cu-O and La-Sr-Cu-O are attributed to interband transitions. There is high density of states (DOS) in both compounds in the Cu $3d$-O $2p$ derived valence bands between 2 and 6 eV below E_F,[19] and a number of empty final states are possible for the transitions. In Y-Ba-Cu-O inverse photoemission experiments place the empty Ba $5d$ and Y $4d$ states at 6 and 8.6 eV above E_F, respectively.[20] Thus, with a suitable electron-hole interaction many transitions can be related to the observed loss peaks, but no more specific assignment is possible. The same is true for La-Sr-Cu-O, where the empty La $5d$ and La $4f$ states were found at 5.8 and 8.7 eV above E_F, respectively.[21,22] In addition to interband transitions some surface-plasmon character is also possible around $\Delta E = 9$–10 eV.

The EELS region of features A ($\Delta E < 5$ eV) is significantly different for the three samples. In SC Y-Ba-Cu-O I a well-resolved peak A is observed, whereas the NSC Y-Ba-Cu-O II sample shows a feature A' at a higher loss energy and not well separated from the broad structure containing features B-D. Loss A in Y-Ba-Cu-O I is associated with transitions from the top of the filled valence band 2.5 eV below E_F of predominantly O $2p$ character[23] to empty Cu-O antibonding bands above the Fermi level. Yarmoff *et al.*[24] found a peak in the empty DOS at ≈ 2 eV above E_F, and their Cu-O character has been identified by calculations.[25,26] We conjecture that the Cu-O derived states above E_F are most sensitive to the oxygen stoichiometry, and that the observed differences in EELS between SC (I) and NSC (II) Y-Ba-Cu-O are a result of differences in the empty antibonding Cu-O bands for the different oxygen stoichiometries. Note that the filled valence-band structure, as observed in ultraviolet photoemission spectroscopy (UPS), is very similar for Y-Ba-Cu-O I and II.[27] Some theoretical support for the above conjecture may be found in the DOS calculations of Herman, Kasowski, and Hsu,[26] where not only the filled, but also the empty, DOS changes as a function of oxygen stoichiometry. The empty DOS is very low up to ≈ 3 eV above E_F for La-Sr-Cu-O,[21,22] and corresponding transitions (A) are very weak in electron loss, in fact only discernible at low E_p (see Fig. 2). The present studies at low E_p and relatively high-energy resolution should reveal differences in low-energy losses inaccessible in the previous loss studies.[5] The absence of discernible features in the 0.5 eV $\leq \Delta E \leq 2$ eV region give no support for the presence of a low-energy plasmon edge suggested in infrared studies,[28,29] but it must be emphasized that the experiments presented here are carried out on rough polycrystalline surfaces with no narrow specular emission. This implies that low-energy losses are not strongly accentuated as in single-crystal studies.[30] EELS experiments in reflection mode on single-crystal samples may show a different pattern as observed by Fink[31] in transmission EELS on such samples. However, there are problems

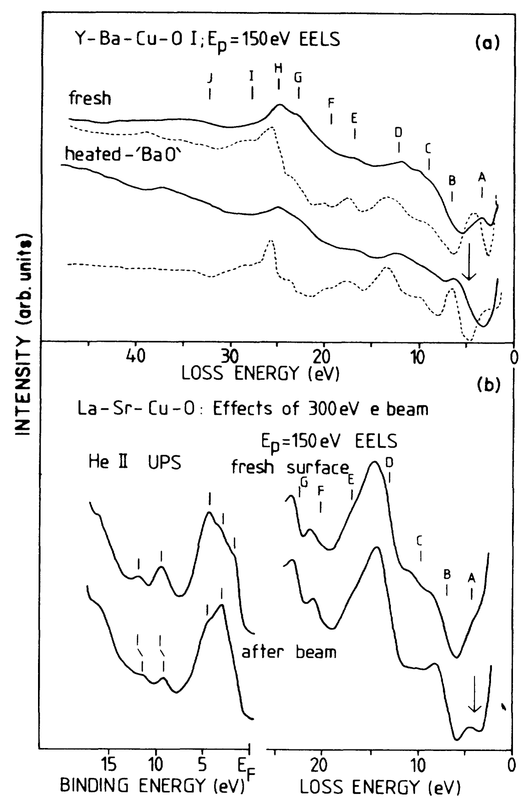

FIG. 3. (a) EELS of freshly scraped and heated (> 800 K) Y-Ba-Cu-O surfaces in $N(E)$ (solid curves) and $N'(E)$ (dashed curves). Arrow indicates the band gap of BaO. (b) He II UPS and corresponding EELS spectra [$N'(E)$ form] of the fresh and electron-beam-irradiated La-Sr-Cu-O surfaces. The arrow emphasizes the appearance of a new loss feature.

with sample preparation which are reflected in the resulting spectra of such studies.[32]

The EELS spectra of Fig. 3 reflect the temperature-induced decomposition of Y-Ba-Cu-O I (a) and the influenece of electron-beam irradiation on La-Sr-Cu-O (b). Y-Ba-Cu-O I had been heated to 700–800 K and oxygen evolution into the vacuum was detected in the mass spectrometer. Auger analysis revealed that all the Cu was driven away from the surface region and that Ba had segregated to the surface, thus forming a Ba oxidelike layer. The loss spectra [Fig. 3(a)] show that the loss region up to 10 eV is strongly modified, consistent with a Cu-O origin in the superconductor, but that beyond the Ba $5p$ threshold very similar excitations profiles are observed for the freshly scraped and the heated sample. This confirms our assignment (Table I) in terms of Ba $5p$ resonance excitations, which dominate the profiles. At low energies a gap of ≈ 5 eV appears to open up in the Ba oxide type, heated layer consistent with the bulk band gap of BaO [arrow in Fig. 3(a), see also Ref. 8].

Figure 3(b) contains EELS in $N'(E)$ form along with He II ($h\nu = 40.8$ eV) photoelectron spectra of freshly scraped La-Sr-Cu-O and after irradiation with 300-eV electrons for ≈ 30 min. The UPS spectra exhibit some changes in the valence-band emission 2–6 eV below E_F and small energy shifts of the two satellites at ≈ 9 eV and ≈ 12 eV (Ref. 27) as a result of electron beam irradiation. The loss spectrum of the irradiated sample shows the appearance of a new structure at 3.8 eV, whose intensity is directly proportional to the irradiation time, and some modification around 10 eV. Gao *et al.*[21] have observed the growth of an inverse photoemission structure under low-energy electron irradiation on La-Sr-Cu-O, and we believe that transitions into these states are observed in the present electron-loss spectra. It is peculiar that a higher-energy electron beam (>1 keV) appears to restore the original surface conditions, as also found by Gao *et al.*[21] Gao *et al.* proposed that the electron-induced inverse photoemission structure might be related to chemisorbed oxygen. In view of the lack of both oxygen in our residual atmosphere and of C in the Auger spectra (as a result of possible CO dissociation), we believe that a more likely interpretation is in terms of oxygen-defect states, created by electrons of intermediate energies (up to approximately several hundred eV). Higher-energy electrons seem to induce healing-out processes, which lead to the disappearance of the defects.

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