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Comparison of Cu Auger electron transitions between the superconductor $YBa_2Cu_3O_{7-x}$ and the oxides of Cu—O system

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Résumé. — Nous avons utilisé la spectrométrie d'électrons Auger pour étudier la valence du cuivre dans des matériaux supraconducteurs $YBa_2Cu_3O_{7-x}$. La comparaison des spectres Auger de $YBa_2Cu_3O_{7-x}$ avec ceux des oxydes CuO et Cu_2O montre l'existence d'une transition électronique $LM_{45}M_{45}$ pour le cuivre dans le supraconducteur. Un dédoublement très prononcé de la transition $L_3M_{45}M_{45}$ est observé dans le cas de $YBa_2Cu_3O_{7-x}$. Ce résultat peut être attribué approximativement à l'existence de deux états de valence Cu^+ et Cu^{2+}. Une autre interprétation pourrait être de considérer qu'il existe un dédoublement très prononcé dans les niveaux des orbitales 3d du cuivre dans le supraconducteur.

Abstract. — Auger electron spectroscopy (A.E.S.) has been employed to investigate the valence of copper in superconducting $YBa_2Cu_3O_{7-x}$ ceramics. Comparison of A.E.S. spectra of $YBa_2Cu_3O_{7-x}$ with CuO and Cu_2O oxides shows a very specific $LM_{45}M_{45}$ electronic transition for copper in the superconductor. A very clear doublet splitting of the $L_3M_{45}M_{45}$ transition is observed in $YBa_2Cu_3O_{7-x}$. This result can be attributed approximately to the existence of two valency states Cu^+ and Cu^{2+} for copper. Another interpretation could be to consider the existence of a strong splitting in the 3d orbital level of copper.

Introduction.

The exact chemical bonding of the elements involved in superconductor $YBa_2Cu_3O_{7-x}$ remains incertain. In this paper, we report the results of an investigation on $YBa_2Cu_3O_{7-x}$ superconductor and copper I and II oxides by means of Auger spectrometry (A.E.S.). The employment of this technique, associated with other results obtained by means of other techniques, could contribute to clarify the binding states of the elements, especially copper, in these superconductor ceramics. This work concerns essentially the study of the $LM_{45}M_{45}$ Auger transition of copper at about $_c =$ eV.

Experimental procedure.

High purity materials were used for Auger electron analysis. Cu_2O, CuO and $YBa_2Cu_3O_{7-x}$ samples were pressed and sintered pellets.

Pressed pellets of CuO were obtained by oxidization of Cu_2O pellets which were heated in Al_2O_3 crucibles at 490 °C under a pressure of 100 atm of oxygen for 3 hours. Two kinds of $YBa_2Cu_3O_{7-x}$ materials were obtained by calcining and sintering pressed pellets of Cu_2O, Y_2O_3 and $BaCO_3$ powder mixtures. Sample 1 was first sintered at 940 °C for 24 h in oxygen and cooled slowly. The obtained pellets were regrounded, pressed into pellets and sintered for 4 h at 950 °C, cooled slowly (2 h) to 500 °C and held at that temperature for 2 h, and then rapidly cooled to room temperature.

Sample 2 was prepared at the laboratory L.P.M. C.N.R.S. Meudon (France). Detailed informations concerning the sample 2 and preparation procedure may be found elsewhere in this journal [1]. The surface of the sample 2 which was analysed by Auger

Auger spectrometer with an energy-dispersive analyser was used for Auger analysis of the samples. This spectrometer allows to obtain Auger spectra with constant resolution in all energy range.

Results and discussions.

Figure 1 shows the $dN(E)/dE$ Auger spectrum of the sample 2. This feature shows the presence of Y, Ba, C, O and Cu elements on the surface of this sample. This analysis has been performed on the

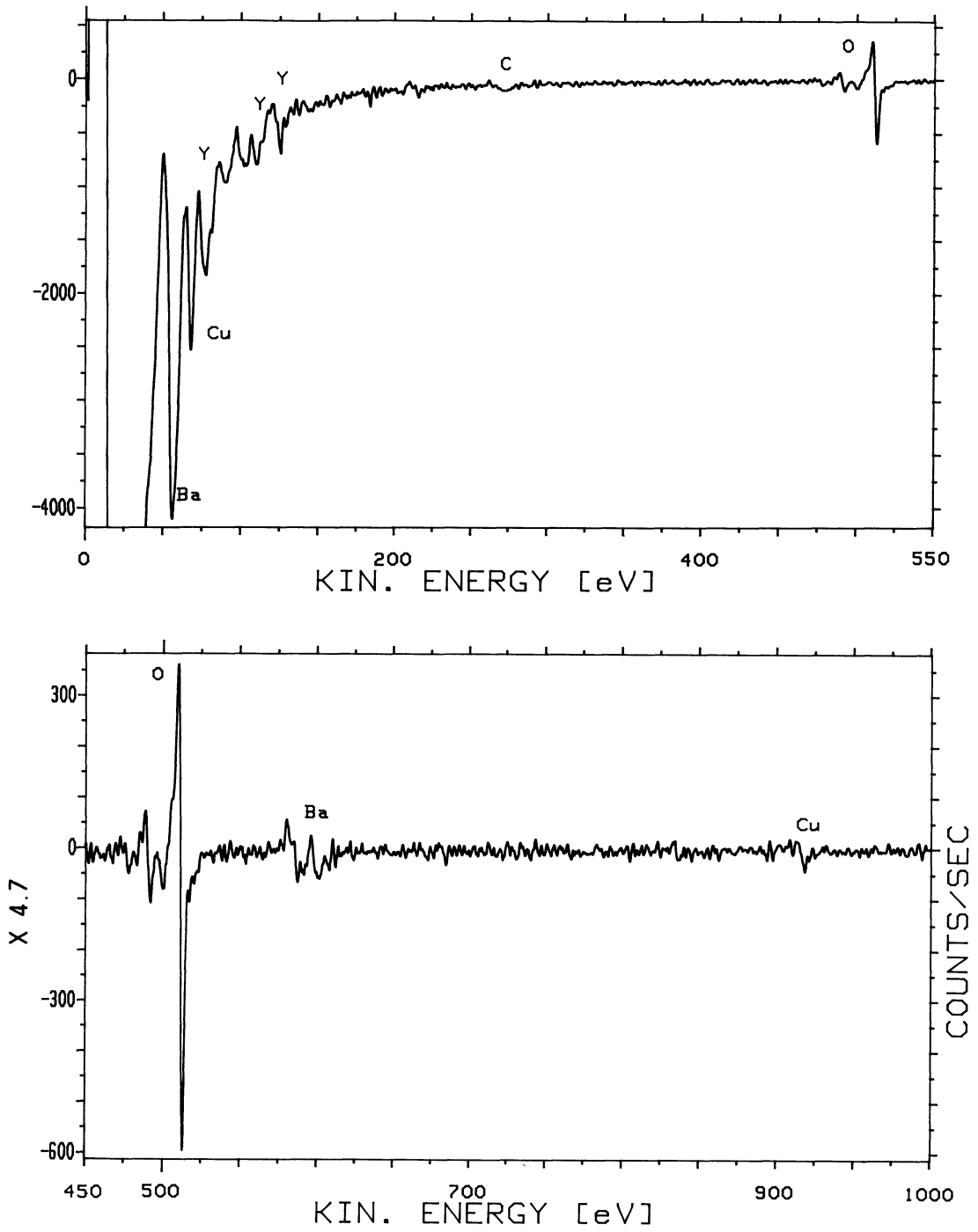

Fig. 1. — Auger spectra of $YBa_2Cu_3O_{7-x}$ (sample 2) in derivated mode $dN(E)/dE$ in the kinetic energy ranges 0-550 eV and 450-1 000 eV.

surface of sample 2, after cleaning this surface by low energy (800 V) argon ion sputtering for 30 mn. Composition of this area cannot be calculated using standard Auger sensitivity factors which are presumably not appropriate for this compound, and which cannot be used with our analyser signals which have a constant resolution in all the energy range. This figure shows that it would be difficult to study the low energy Auger MVV transition of copper because the shapes of these transition can be affected by the NVV transition of Barium, which are very near. Consequently, we examinated the Auger emissions of copper in the range 800-950 eV because the transitions which are in this range cannot be affected by Auger emission of other elements.

Figure 2 shows a comparison between the Auger emissions in the range 800-950 eV of Cu metal and Cu in $YBa_2Cu_3O_{7-x}$ (sample 2). These two Auger emission features were obtained in the same experimental conditions : a primary electron beams volt-

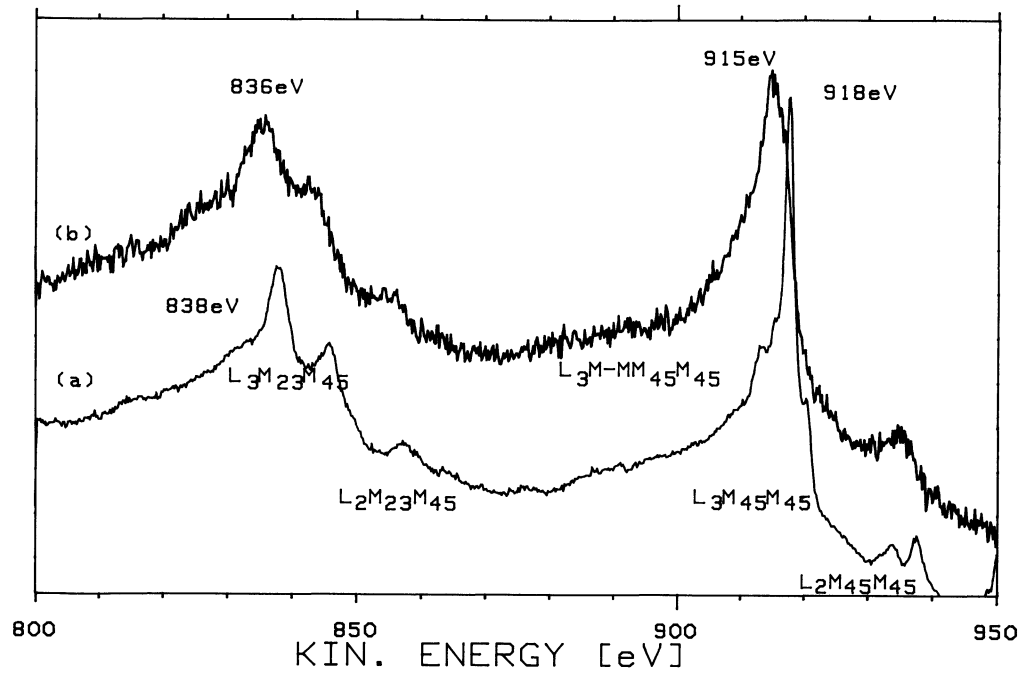

Fig. 2. — Auger copper transitions in the range 900-950 eV (a) - transitions for Cu metal (b) - transitions for $YBa_2Cu_3O_{7-x}$.

age of 5 kV, a beam current of 0.5 μA and a beam diameter of about 5 μm. The energy resolution is $\Delta E = 1$ eV.

The spectra presented in figure 2 are obtained after secondary electron background subtraction. The comparison between $YBa_2Cu_3O_{7-x}$ and Cu spectra shows essentially a width increase of the $LM_{45}M_{45}$ and $LM_{23}M_{45}$ transitions in $YBa_2Cu_3O_{7-x}$. An energy shift of about 2-3 eV is observed for all the copper Auger emissions arising in this energy range. The shifts and the width increase which are observed on the Auger emissions of $YBa_2Cu_3O_{7-x}$ can be attributed to transfer of valence electrons and consequently a change in screening energy for Auger relaxation, or to the existence of various valence states of copper.

Figure 3 shows the $LM_{45}M_{45}$ Auger emission of CuO, Cu_2O and $YBa_2Cu_3O_{7-x}$ sample 2. CuO and Cu^{2+} in CuO is approximately of 1 eV according to the others authors [2, 3]. The Auger $L_3M_{45}M_{45}$ transition of $YBa_2Cu_3O_{7-x}$ at 917 eV matches the peak observed for CuO at 917 eV. The Auger $L_3M_{45}M_{45}$ transition of $YBa_2Cu_3O_{7-x}$ observed at 915 eV doesn't correspond exactly to any transition observed on Cu_2O and CuO Auger spectra, but it is near the Cu^+ transition. Recently, some authors reported XPS and Auger results which showed evidence for copper ion Cu^+ and Cu^{2+} binding states [5] or in Cu^+, Cu^{2+} and Cu^{3+} binding states [4] in $YBa_2Cu_3O_{7-x}$. Our result could corroborate the Cu^{2+} Cu^+ binding states presence in $YBa_2Cu_3O_{7-x}$ if we consider that the lower energy peak at 915 eV can be attributed to Cu^+. The splitting of the $L_3M_{45}M_{45}$ Auger transition of $YBa_2Cu_3O_{7-x}$ could also be due to a multiplet splitting of the Cu 3d level according to results

an energy of 1 kV. $YBa_2Cu_3O_{7-x}$ sample 2 was cleaned with argon sputtering having a smaller energy of 800 V, for 30 mn. These spectra were obtained with a primary electron energy of 5 kV and an analyser resolution of $\Delta E = 1$ eV. Secondary background substraction, and Shirley background substraction were mathematically performed on these spectra.

The spectra of CuO and Cu_2O are in good agreement with results reported above by others authors [2, 3]. The shift between Cu^+ in Cu_2O and

spectrum, in the range 900-950 eV observed on the sample 1 after cleaning the surface with argon ion having an energy of 800 eV. This spectrum, in which the background were not substracted, is identical to the spectrum of $YBa_2Cu_3O_{7-x}$ sample 2 in figure 3. The figure 5 shows the spectrum of the same sample 1 obtained after argon sputtering for 30 mn with ions having an energy of 3 kV. The comparison of figure 4 and figure 5 shows evidence for ion sputtering damages which can occur on these materials under high vacuum.

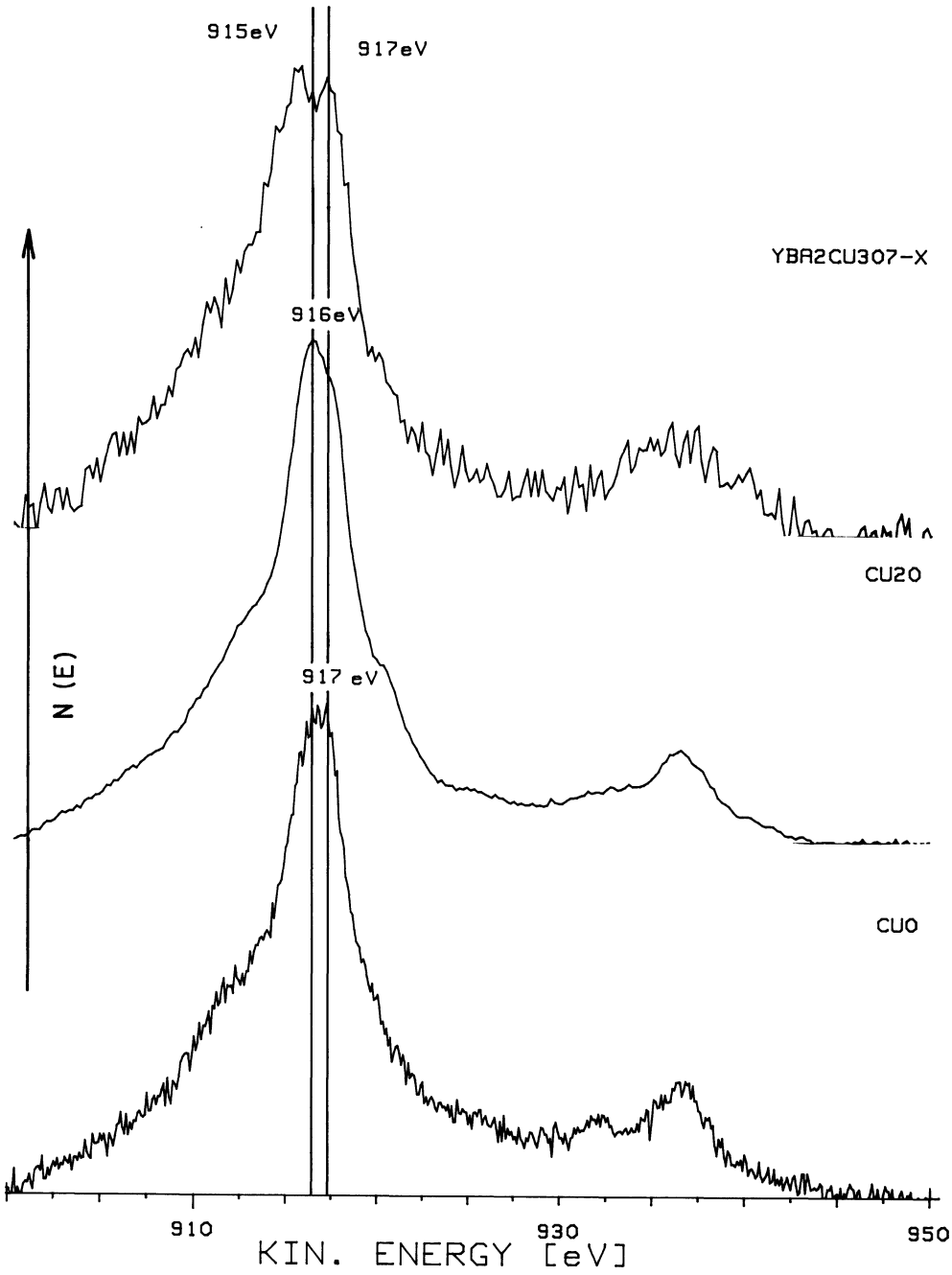

Fig. 3. — Comparison of the Auger $LM_{45}M_{45}$ emissions of copper for CuO, Cu_2O and $YBa_2Cu_3O_{7-x}$ (sample 2). Backgrounds substracted.

Conclusion.

The Auger typical $LM_{45}M_{45}$ transition of copper present in $YBa_2Cu_3O_{7-x}$ seems to be well characterised by the spectrum corresponding to $YBa_2Cu_3O_{7-x}$ in the figure 3.

From this result, we can attribute the transition at $E_c = 917$ eV to Cu in Cu^{2+} binding state. The lower energy transition at $E_c = 915$ eV could be attributed to Cu^+, but it doesn't match very well the Cu_2O Auger transition. The presence of trivalent copper was not detected. The structure of the $L_3M_{45}M_{45}$ transition of copper could also indicate the existence of a strong splitting in the 3d orbitals of copper in $YBa_2Cu_3O_{7-x}$. The unambigous allocation of the $L_3M_{45}M_{45}$ observed transition to specific bonding states requires comparison with other references and a careful study of all the other Auger transitions of copper and oxygen.

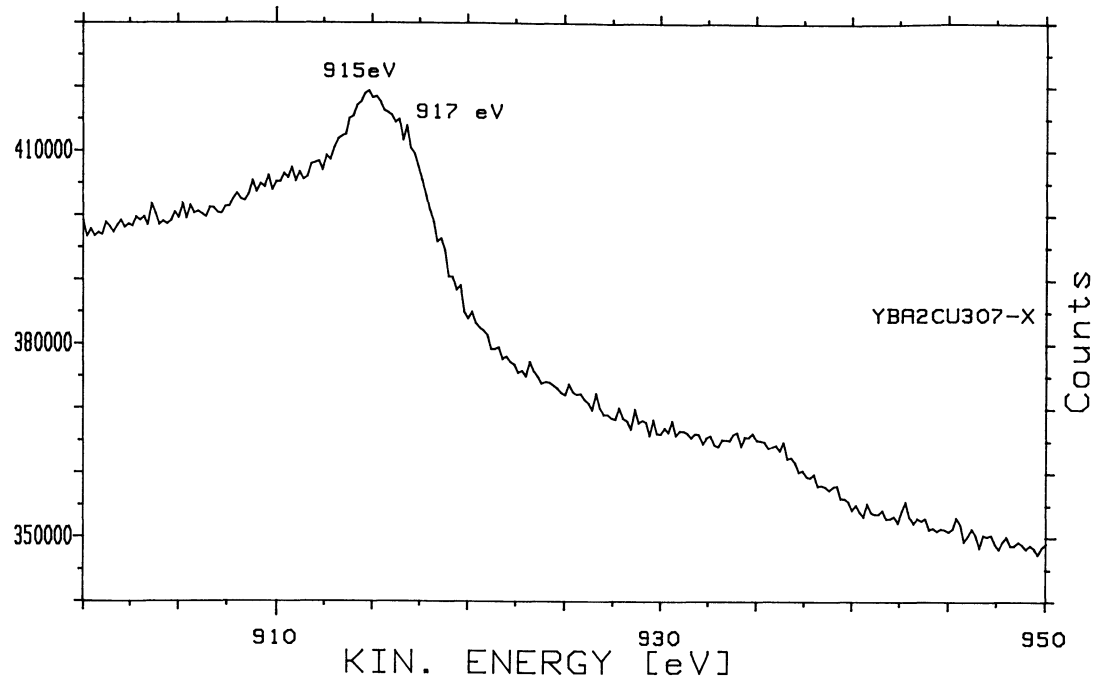

Fig. 4. — Auger $LM_{45}M_{45}$ emission of Cu in $YBa_2Cu_3O_{7-x}$ (sample 1) recently introduced in the high vacuum chamber and cleaned under 800 V argon ion sputtering. Backgrounds are not substracted.

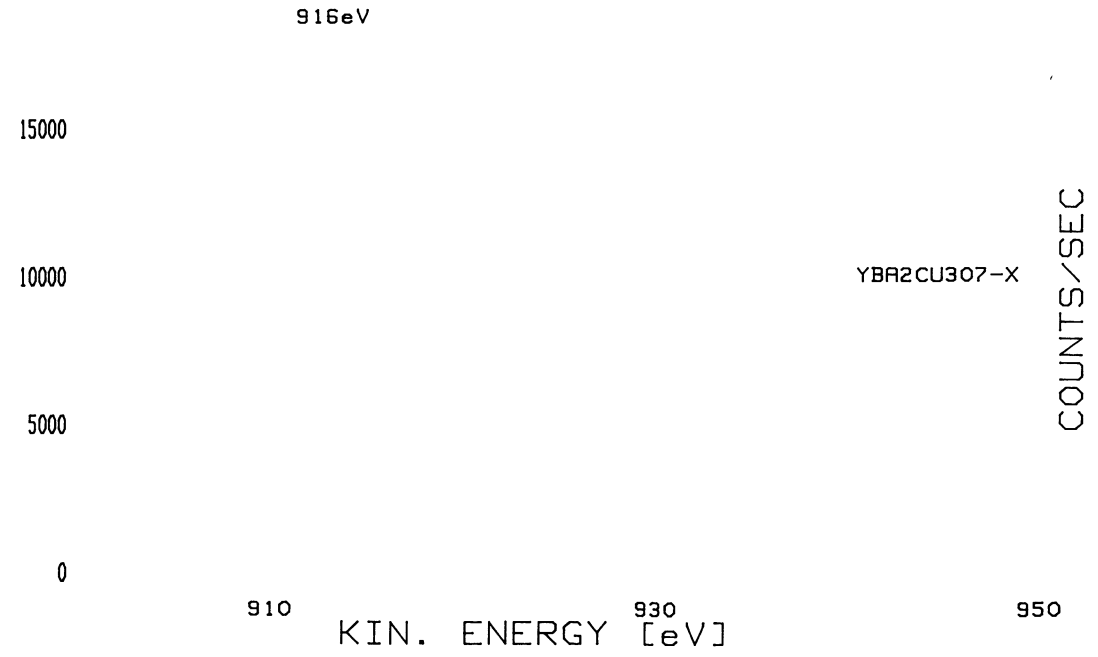

Fig. 5. — Auger $LM_{45}M_{45}$ emission of Cu in $YBa_2Cu_3O_{7-x}$ (sample 1) after 3 kV argon ion sputtering for 30 mn.

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