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**The Gold/High Temperature Superconductor Interface; Metallicity of the
Near Surface Region and a Search for the Proximity Effect**

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ABSTRACT

We have used high resolution photoemission spectroscopy to probe the electronic structure of a wide variety of gold/high temperature superconductor interfaces, the majority of which were formed by low-temperature (20K) gold evaporations on cleaved high quality single crystals. For c-axis interfaces formed on the 123 family of superconductors, we find that the gold deposition essentially destroys the metallicity of the superconducting substrate in the near surface region ($\sim 5\text{\AA}$), while the near surface region of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ remains metallic. We have also used photoemission spectroscopy to search for a proximity-effect superconducting gap in gold overlayers on c-axis single crystals and a-axis thin films, though no such effect was found.

Introduction

A key requirement in both utilizing and understanding the high temperature superconductors is the fabrication of very high quality materials. With the advent of high quality single crystals and films, this requirement is at least now partly fulfilled. One very important next step is a knowledge of the properties of interfaces of these materials with others. Photoemission spectroscopy is a natural tool to probe the interfacial region because of its surface sensitivity (in the range of 3 to 100 $\text{\AA}$) and ability to detect changes in the local chemical environment of an atom. It has already been very successfully applied to the study of the interfacial chemistry of a wide variety of adatoms on the different types of high T_c substrates¹⁻⁴. Typically, the effects of the adatoms on the Cu 2p and O 1s line shapes were emphasized most strongly, since the Cu-O planes are thought to be crucial to the superconductivity. In particular, a single O 1s peak centered at a binding energy of around -529 eV and a strong Cu 2p satellite/main line intensity ratio are thought to be especially important. Higher binding energy O 1s components are usually associated with the formation of some oxide while the disappearance of the Cu 2p satellite signals a decrease of the Cu valency from 2+ to 1+. These earlier experiments showed that gold formed the cleanest interfaces with each of the cuprate superconductors; it goes down smoothly with

no evidence for islanding and does not adversely affect the Cu 2p or O 1s lineshapes^{1,2}. Other noble metals such as Ag, Pd and Cu did not tend to fare as well^{3,4}.

This paper addresses primarily the states at the Fermi level, and how they are affected by the application of gold adatoms. This is a more sensitive and direct test of the interfacial region than the core level line shape studies for a number of reasons. Firstly, we are considering those states that are directly responsible for the superconductivity. Secondly, we have used higher resolution than is possible with XPS (X-ray Photoemission Spectroscopy) core level studies, and, since the photoelectron kinetic energies are lower, we are more surface sensitive (escape depths on the order of 3-10 Å as opposed to 5-50 Å for XPS)⁵. This surface sensitivity is actually very crucial because of the very short superconducting coherence lengths of these materials, particularly along the c axis ($\sim 3\text{Å}$)⁶.

We first will present the results of our investigations of the effect of low temperature gold evaporations on the metallicity of the near surface region of the superconducting substrates. In particular, we have studied c-axis junctions of gold with high quality cleaved single crystals of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ and found that the metallicity of the $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ substrate in the near surface region ($\sim 5\text{Å}$) is essentially destroyed by the gold deposition, while the near surface region of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ remains metallic. This has potentially wide ranging consequences for the applicability of the different types of superconductors in real devices.

We will then present preliminary results of our search for a proximity effect induced gap in the gold overlayers of the gold/High T_c interface. We have searched for this effect in c-axis junctions of gold/ $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$, where the interface is very clean but the superconducting coherence length is unfortunately very short, and in a-axis junctions of gold/ $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ where the coherence length is much longer but the interface is unfortunately not quite so clean. Our studies do not show any evidence for a proximity effect induced gap in the gold overlayers. We have done some model calculations, and in particular place an upper limit of approximately 2 meV for the gap in the gold overlayer on our a-axis gold/ $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ junctions.

Effect on the Metallicity of the Near Surface Region of the Superconducting Substrate

This group of experiments used photoemission spectroscopy to carefully monitor the effect of the gold evaporations on the superconductor-derived density of states at the Fermi level. The experiments were performed at the Mark II grasshopper monochromator at the Synchrotron Radiation Center in Stoughton, WI in an angle resolved Vacuum Science Workshop (VSW) chamber with base pressure in the 10^{-11} torr regime. During the gold evaporations, the chamber pressure never rose above 2×10^{-10} torr. All experiments were performed at normal emission, though we will interpret the spectra in this paper as if they were essentially angle-integrated. This is because the photon energies are relatively high, which makes the uncertainty in the momentum k high, and because the cleaves of our single crystals were not perfect over a distance the size of the photon beam - about 3 square mm. The incident angle of the photon beam was 75 degrees from normal, and the combined energy resolution of the photon source and spectrometer was held constant at 200 meV.

High quality single crystals of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ and $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$, of transition temperatures of approximately 90K each, were cooled to 20K before being cleaved in the ultra-high vacuum environment, and were maintained at that temperature for the full duration (including the gold deposition) of the experiments. The low temperature is important for a number of reasons. It had been shown to be necessary for getting accurate spectra for the 123's, particularly in the near Fermi surface regime⁷. Though the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ samples appear much more stable at room temperature⁸, and there are recent reports showing high quality spectra from 123's cleaved at room temperature⁹, we elected to perform all of our measurements at low temperature for safety and consistency. The low temperature evaporation is also superior for a number of reasons. Interfacial processes such as chemical reactions and the creation of defects will be greatly inhibited. In addition, the decreased surface mobility of the adatoms at low temperature favors Frank-van der Merwe or layer-by-layer growth, instead of the Volmer-Weber growth mode, where the deposited atoms aggregate to form clusters or islands on the substrate surface. Examination of the spectra shows very uniform exponential decay of the Bi 5d core level intensity with gold coverage, implying true layer-by-layer growth. The very short escape depth of 3Å in the gold layer confirms that no intermixing or alloying of the gold with the substrate surface has occurred.

Figure 1 shows the valence bands and Bi 5d core levels of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ for different gold coverages. As depicted in the figure, the spectra were all normalized to give equal Bi 5d core level intensity. Thus the contribution to the valence band from the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ states should to first order be essentially the same in each of the spectra presented, since the signal from the underlying states should fall off as a simple exponential

with distance, governed by the photoelectron escape depth through the gold. Thus we see that with even as little as 2.0 Å of gold on the surface (approximately one monolayer), the valence band signal is almost completely dominated by the gold states. This is because of the extreme surface sensitivity of the spectroscopy.

The detailed effects that the gold adatoms have on the superconducting substrate are best seen for low gold coverages (below one monolayer). For these coverages, the gold overlayer will not yet have reached its full 'metallicity', which in cases where the substrate is nonmetallic, is easily discernable by the lack of a Fermi edge. Other signals of a film that has not yet reached metallicity are (adatom) corelevels that are broader and at higher binding energy than those of the bulk material. The behavior of our core levels confirms that the 0.5 Å thick gold films are not metallic. Blowups of the valence band and near Fermi level region of just the 0.0 Å and 0.5 Å gold coverages on Bi₂Sr₂CaCu₂O₈ are shown in figures 1b and 1c, with the same normalization as in Figure 1a. A clear Fermi edge is observed for both the clean substrate and the substrate with the 0.5 Å gold overlayer¹⁰. Since the Fermi edges could not have been derived from the gold overlayers, it is clear that the surface of Bi₂Sr₂CaCu₂O₈ remains metallic, which is of course a prerequisite for the superconductivity. Thus we can conclude that there is very little chemical reaction between the gold and the Bi₂Sr₂CaCu₂O₈ substrate, and that the Bi₂Sr₂CaCu₂O₈ derived density of states at the Fermi level is essentially unaltered by the gold deposition, at least within the scale of our energy resolution (approximately 200 meV). Much higher resolution (~35 meV) angle resolved measurements have recently been completed in our lab, and have in fact shown that there is some alteration of the BiO states (in the cleavage plane) at the Fermi level from a deposition of gold. The states which originate from the CuO planes, which are a few angstroms below the surface, are essentially unaltered¹¹.

The gold/EuBa₂Cu₃O_{7-δ} interface is unfortunately not quite so nice, as is shown in figure 2, which presents the valence bands of a single cleaved crystal of EuBa₂Cu₃O_{7-δ} for different gold coverages. The normalization was performed in a similar way as done earlier on Bi₂Sr₂CaCu₂O₈, except that the Ba 4d core levels were used instead of the Bi 5d's. The crucial piece of information is obtained from the blow ups of the near Fermi level region in figure 2b. We note a clear Fermi edge for the clean EuBa₂Cu₃O_{7-δ} substrate which disappears with 0.5 Å of gold coverage (There is a sloping density of states that does just cut the Fermi level in the 0.5 Å spectrum, though it is much broader than the system resolution of 200 meV and the midpoint is pushed at least 100 meV below the Fermi energy). As the gold overlayer becomes metallic at larger coverages, a gold-derived Fermi edge appears. Thus we can conclude that the gold deposition alters the states near the Fermi level in the near surface region of the EuBa₂Cu₃O_{7-δ} substrate and

renders it nonmetallic. Since we formed the interface under the ideal conditions of very low temperature and ultrahigh vacuum, with the most inert of overlayers, this is potentially hazardous for any device on these materials (particularly c-axis films) that intends to make use of the proximity or Josephson effects. Better choices may be to make the junctions along the a or b axes, where the superconducting coherence length is much greater⁶, or to use the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ material, which appears to be much less affected by the gold deposition.

To conclude the first section, low temperature evaporations of gold, which should form the cleanest and most abrupt junctions with the high T_c cuprates, appear to alter the near Fermi level states of $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ at the interface enough to render the surface essentially non-metallic, making the feasibility of 123/gold junctions along the c axis questionable at best. The situation with c-axis $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ /gold junctions is much more favorable, as the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ substrate remains metallic in the near surface region.

Search for the Proximity Effect Induced Gap

The proximity effect is a fundamental and important property of the interfaces of metals with pre-High T_c superconductors. In this phenomenon, Cooper pairs will leak from a superconductor to a normal metal if the electrical contact between the two is good. The normal metal will then become a superconductor itself, that is, it will obtain the excitation spectrum of a superconductor, as evidenced by specific heat¹² and tunneling measurements¹³. Interestingly, the "proximity effect" is of comparatively long range: under suitable conditions, a supercurrent can cross a "normal" layer even microns in thickness.¹⁴

The study of the proximity effect between the High T_c superconductors and normal metals has both technological and scientific importance. For device work, a promising route is the construction of SNS proximity effect Josephson devices. From a scientific standpoint, the coupling of the superconductivity to other materials will help us to better understand the nature and hopefully the origin of the superconductivity in the High T_c cuprate superconductors. The proximity effect has not, however, been convincingly demonstrated to exist in metal/High T_c junctions. The best evidence for it to date comes from the observation of a tunneling supercurrent through the normal metal barrier in SNS structures¹⁵⁻¹⁷. However, while the presence of a tunneling supercurrent is a necessary condition for the proximity effect, it is not sufficient, for the supercurrent may have arisen from simple tunneling across the barrier, as would happen in an SIS junction. In addition,

the magnitude of the observed supercurrent is approximately two orders of magnitude lower than expected from the conventional theories.¹⁸

The necessary condition for the existence of the conventional proximity effect between a normal metal and a conventional BCS superconductors is that the superconducting order parameter ψ (ψ^2 = the probability for finding Cooper pairs) must extend into the "normal" metal. If in addition, the electron-phonon interaction energy $V_{\text{el-phonon}}$ is non-zero in the "normal" metal, then the normal metal will obtain the excitation spectrum of a superconductor, with a gap $\Delta = \psi * V_{\text{el-phonon}}$. The analogous relationship (if it exists) for the high temperature superconductors is not yet known.

While photoemission spectroscopy is not sensitive to the order parameter, it is sensitive to the effects of the superconducting gap Δ on the density of states. However, because of the small energy scale of the superconducting excitations and the difficulty in doing very high energy resolution photoemission experiments, photoemission has only recently become a viable tool for the study of superconductivity. From it we have learnt, in a very short time, a great deal about the physics of the superconducting as well as the normal state of the high temperature superconductors.¹⁹⁻²² It has recently even been proven effective for the study of non High T_c superconductors, where the energy scale of the excitations is a great deal smaller than in the High T_c 's.²³

The effect of the superconductivity in a clean $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ crystal is clearly shown in the temperature dependant photoemission spectra of figure 3, which we have reproduced from Olson et. al. (reference 20). At 90K (above T_c) we observe an approximately flat density of states which is cut off by the Fermi level. As the temperature is lowered below T_c the states which are within Δ (the superconducting energy gap) of E_f are pushed out of the gap region and "pileup" below, to form the peak centered at approximately 40 meV in the figure. The solid curves represent Olson et.al.'s attempt to fit the data with a BCS lineshape. Reasonably good agreement is obtained for a superconducting energy gap of 24 meV.

If the proximity effect is present in a normal metal/High T_c junction, we should expect to observe the same type of photoemission lineshape in the normal metal overlayer as is observed in the clean superconductor, though of course the strength of the signal might be much less, for the size of the proximity effect induced gap could be much smaller than it is in the High T_c 's. Though photoemission has never before been used to study the proximity effect, it is actually very well suited. With it we should be able to watch the evolution of the proximity effect induced gap with the thickness of the "normal" metal overlayer. When the overlayer thickness is on the order of or greater than the photoemission probing depth then the vast majority of the states probed by the

photoemission process will have originated from the overlayer, assuming of course that the normal metal overlayer is uniform in thickness.

We have searched for the proximity effect with High T_c 's in two basic experimental configurations, where we felt the conditions for the existence and observance of the effect were most promising. For both of these we selected gold as the normal metal overlayer. This is because the gold/High T_c interface is very clean (essentially free of chemically reacted species) and the gold covers the substrate very uniformly, at least for the low temperature evaporations that we have employed. These points have been covered in much greater detail in the first portion of this paper and in references 1-4. In addition, gold has been one of the standard (and was in fact the first) "normal" metals used in proximity effect experiments with conventional superconductors.

In the first configuration, we cleaved a high quality single crystal of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ at low temperatures (20K), confirmed the existence of the superconducting gap on the clean surface with photoemission spectroscopy (as in figure 3), and then evaporated small coverages of gold on the surface of the crystal. Temperature dependant photoemission spectra of a 5Å gold overlayer are shown in figure 4. Though the statistics are not as good as one would like, the only clear changes that we observe as the temperature is lowered is a sharpening of the edge, as you would expect if the edge was a Fermi edge for all temperatures. The data does not show any clear indications for a superconducting gap in the gold overlayer, that is, the edge is not pulled away from E_f and a "pileup" is not observed. A gap of a much smaller magnitude than we had resolution or statistics to observe may of course still have existed in the gold overlayer, and so this should not yet be taken as conclusive evidence for the absence of a proximity effect, but should help set a limit on its size.

There is an aspect to the junctions discussed above that is unfavorable for the occurrence of the proximity effect. This has to do with the strong two dimensionality of the cuprate superconductors. It is well accepted that the CuO planes are crucial for the occurrence of the superconductivity, and that the superconducting charge carriers reside primarily in these planes. Thus we observe large anisotropies in the superconducting effective-mass of the carriers²⁴, the resistivity²⁵, and the superconducting coherence length.⁶ This last property is of crucial concern to us, for it determines how far the superconducting order parameter will leak into the metal overlayer. The coherence length in the c direction (normal to the planes) is only on the order of a few Å, and so even though the interface of the junctions of figure 4 was very clean, the coherence length is so short in that direction that it would make the likelihood of a strong proximity effect suspect.

The natural solution to the problem is to try to form junctions along the a or b axes, where the coherence length is much greater (on the order of 10 Å). Lee et. al. have made this point clear by the observation of a tunneling supercurrent in (001) and (103) oriented SNS junctions but not on (100) oriented junctions.²⁷ However, from a technical viewpoint, this is much more difficult. Because of their two dimensional nature, single crystals cleave only normal to the planes, and most thin film samples are also grown with their surface normal to the c axis. A number of high quality thin films with their surface normal to the a axis have recently been developed,^{26,27} but the problem of preparing a clean surface for photoemission still remains.²⁸ What we have done to overcome (partially) this problem is to immediately deposit gold *in-situ* on top of a freshly grown a axis YBa₂Cu₃O₇ film.²⁹ The film could then be removed from the growth chamber and introduced into the analytical chamber, where the surface of the gold overlayer was gently sputter cleaned to prepare it for the photoemission experiments. This cleaning procedure should have little effect on the integrity of the gold/YBa₂Cu₃O₇ interface, since it is well protected by the many layers of gold in-between the sputtered surface and the interface region. (The freshly prepared gold/YBa₂Cu₃O₇ interface is of course not expected to be perfect; the point is that the cleaning procedure we have used should not induce any further damage to it.) The gold overlayer was sputtered until its valence band features very closely approximated those of a freshly evaporated gold film, at which point the gold overlayer showed a very clear and sharp Fermi edge. We then began our temperature dependant high resolution photoemission experiments to search for a gap in the gold overlayer.³⁰

Figure 5 shows our high resolution photoemission spectra of a clean 15Å overlayer of gold on a-axis YBa₂Cu₃O₇. As in figure 4, we again see no evidence for a superconducting gap in the gold, although this time the statistics are much better and will allow us to place a more accurate upper limit on the size of the superconducting gap in the gold. If there is in fact no proximity effect, then the gold overlayer must obey Fermi statistics, which we know how to model very accurately. The solid lines represent our attempt to do such a fit, and reproduce the experimental data points very accurately. All that we have done is convolve a flat density of states cut off by a Fermi function of set temperature with a gaussian of width 32 meV (representing the instrumental broadening) and added a background function. The background function used was the "Shirley" type; that is, the background for any particular energy is proportional to the number of states at higher kinetic energies (lower binding energies). Such fits also work excellently on Pt metal reference spectra that we have taken for the purpose of determining the work function of our analyzer. The insert to the figure shows the fits to the two gold spectra superimposed on top of each other to highlight the effects of changing the temperature; all

that is observed is a sharpening of the edge, with no shifting of the edge away from E_f or a "pileup" below E_f as would be expected. We have repeated the above for a number of different thicknesses of the gold overlayer, from the 15 Å layer presented here up to layers approaching 100 Å in thickness. We observed no thickness dependant effects.

It should be quite clear by now that if there is a proximity effect induced gap in the gold overlayers that we have studied, then it must be quite small. We have done some modelling to help us make this more quantitative. We have assumed a BCS density of states (not because we believe that it can very accurately describe the behavior but because it is all that we really have to work with) and convolved it with the 32 meV instrumental broadening that we used for the fits in figure 5. The results of this modelling for BCS gaps between 0 and 20 meV are shown in figure 6. For gap values greater than 5 meV we see very clear departures from the spectra of figure 5. Even the predicted behavior for a 5 meV BCS gap is quite different from the observed behavior of the gold overlayers; while the "pileup" is quite small, it is still large enough that we should have been able to observe it with the statistics that we had. In addition, the 5 meV gap pushes the edge back substantially, so that the spectra crosses that of the normal (0 meV gap) edge high up the slope. The stability of the effective work function of our spectrometer (± 1 meV) was such that we have great confidence in the energy position of our edges, and so we can state with certainty that a shifting of the edge by a magnitude like that predicted by a 5 meV gap is not happening in our gold overlayers. We thus place a firm upper limit of 5 meV for the size of the proximity effect induced gap in the gold overlayers, though we feel quite certain that 2 meV would also be a safe upper limit. This is consistent with earlier tunneling results which found that the $I_c R$ product (which should be proportional to the geometric mean of the gaps of the two superconductors) was much smaller than expected.^{16,17}

Although we feel that the implications of our results are very important both from a technological and a scientific viewpoint, we again must caution that our data may have been adversely affected by materials problems, particularly at the gold/YBa₂Cu₃O₇ interface which from the first section of the paper we know is not perfect.

In conclusion, we have studied the electronic structure of a wide variety of gold/high temperature superconductor interfaces, the majority of which were formed by low-temperature (20K) gold evaporations on cleaved high quality single crystals. For c-axis interfaces formed on the 123 family of superconductors, we find that the gold deposition essentially destroys the metallicity of the superconducting substrate in the near surface region (~ 5 Å), while the near surface region of Bi₂Sr₂CaCu₂O₈ remains metallic. Using these results as a guide, we have then used photoemission to directly search for a proximity-effect induced superconducting gap in gold overlayers on High T_c

superconducting substrates. We did not observe such an effect, and place an upper limit of 5 meV on its existence.

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Figure Captions

Fig 1. (a) Valence bands and Bi 5d core levels of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ for different gold coverages. Spectra were normalized to give equal Bi 5d core level intensity. Blowups of (b) the valence bands and (c) the near Fermi level region of $\text{Bi}_2\text{Sr}_2\text{CaCu}_3\text{O}_8$ are shown for gold coverages of 0.0 Å and 0.5 Å, with the same normalization as in (a).

Fig 2. (a) Valence bands of $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ for different gold coverages, normalized to the Ba 4d core level intensity. (b) Blowups of the near Fermi level region of $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$.

Fig 3. Temperature dependant photoemission measurements from Olson et. al. (ref 20) of a cleaved single crystal of $\text{Bi}_2\text{Sr}_2\text{CaCu}_3\text{O}_8$ which clearly show the effect of the superconducting gap. The solid lines show a fit to a BCS lineshape with $\Delta = 24$ meV.

Fig 4. Temperature dependant photoemission measurements of a 5 Å gold film on top of a cleaved single crystal of $\text{Bi}_2\text{Sr}_2\text{CaCu}_3\text{O}_8$ which had shown a superconducting gap similar to that of figure 3.

Fig 5. Temperature dependant photoemission measurements of a 15 Å gold film on top of a clean a-axis film of $\text{YBa}_2\text{Cu}_3\text{O}_7$. The solid lines show fits to a Fermi function. The insert shows the fits superimposed on top of each other.

Fig 6. The predicted behavior of a resolution-broadened BCS like gap in the gold overlayer for various sizes of the gap Δ .

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- 28 The problem centers around the fact that photoemission is so surface sensitive and the surfaces of the high temperature superconductors are so fragile. Standard cleaning procedures such as ion milling or high temperature annealing are unacceptable, as they damage the crystal structure and/or promote the outdiffusion of oxygen from the structure, which will render the surface insulating. See for example P.A.P Lindberg et. al. Appl. Phys. Lett. **53**, 529 (1988).
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- 30 While it is true that based on the results of the first section of this paper, the interface should not have been as clean as we would have liked, we felt that the increase in the superconducting coherence length more than made up for this problem.

Gold on $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$

$h\nu = 75 \text{ eV}$

INTENSITY (Arbitrary Units)

Gold on $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$

$h\nu = 75 \text{ eV}$

END

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