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Authors

Vurens, G.H.
Strongin, D.R.
Salmeron, M.

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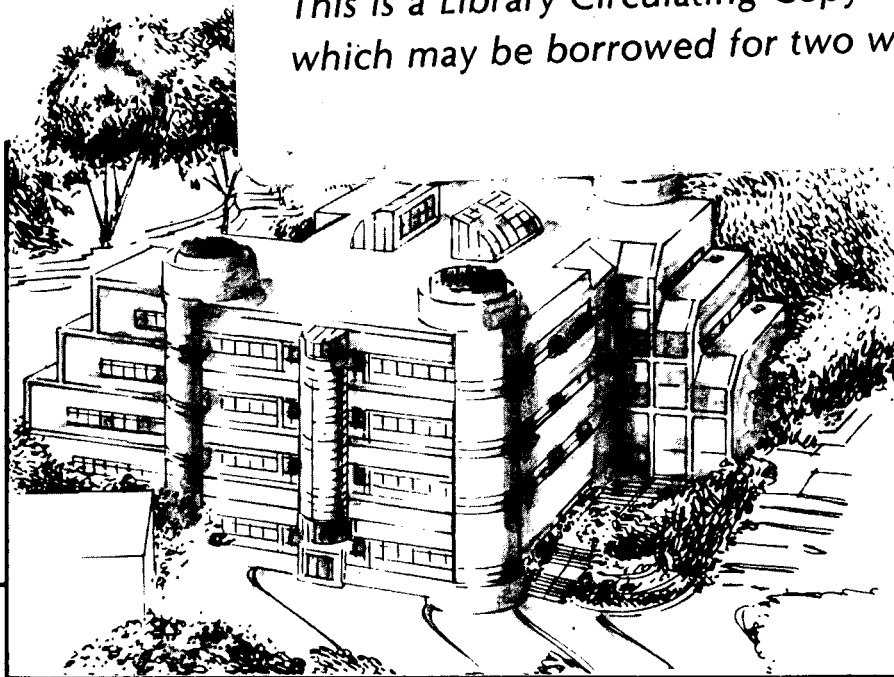
An ISS and AES Study of Alkali Induced Sintering of an Iron Oxide Monolayer Adsorbed on Pt(111)

G.H. Vurens, D.R. Strongin, M. Salmeron, and G.A. Somorjai

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An ISS and AES Study of Alkali Induced
Sintering of an Iron Oxide Monolayer Adsorbed
on Pt(111)

G. H. Vurens, D. R. Strongin, M. Salmeron, and G. A. Somorjai

Department of Chemistry

University of California

Berkeley, California 94720

and

Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory

Berkeley, California 94720

Abstract

An iron oxide monolayer adsorbed on Pt(111) is used as a model system for studying sintering of transition metal oxides. At 1 monolayer (ML) iron oxide coverage only iron and oxygen peaks are observed by ion scattering spectroscopy (ISS). This persists up to 1050 K at which time the iron oxide monolayer decomposes and platinum appears in the ISS spectrum. When 4 ML of sodium oxide, lithium oxide, or potassium oxide are deposited on the iron oxide, only alkali peaks are observed by ISS indicating that the alkali resides in the outermost layer. Heating the sodium oxide covered surface to 850 K induces sintering of the iron oxide monolayer, evidenced by the appearance of a platinum peak in the ISS experiment. Lithium oxide or potassium oxide sinters the iron oxide to a lesser extent than sodium oxide. One monolayer of sodium oxide is found not to induce sintering of the iron oxide adsorbed on Pt(111). A model is proposed in which sintering requires dissolution of iron oxide in an alkali phase.

An ISS and AES Study of Alkali Induced Sintering of an Iron Oxide Monolayer Adsorbed on Pt(111)

Introduction

This letter reports on a unique method, utilizing ion scattering spectroscopy(ISS) and Auger electron spectroscopy(AES), for studying the sintering of transition metal oxides as a function of temperature and additive concentration. Iron oxide has been chosen as the model system since it has important catalytic properties[1,2] and has been shown previously, in our laboratory[3], to grow ordered for the first monolayer on the Pt(111) surface. Hence, at one monolayer coverage iron oxide has a dispersion of unity in contrast to three dimensional growth where the dispersion would be lower.

Ion scattering is an extremely surface sensitive technique[4], and at monolayer coverage of iron oxide on Pt(111) only iron and oxygen is visible by the technique under our conditions(500eV He⁺ ions). Thus, any decrease in the iron oxide dispersion will be reflected in the appearance of a Pt substrate signal in the ISS experiment. It is shown in this letter that the high dispersion of clean iron oxide on Pt(111) is maintained up to 1050 K. The coadsorption of 4 monolayers(ML) of sodium is found to induce sintering of the iron oxide at much lower temperatures. Adding 4 monolayers(ML) of potassium or lithium to the iron oxide monolayer causes iron oxide to sinter also, but to a smaller extent than sodium. We propose a sintering mechanism whereby iron oxide dissolves in the alkali phase. These surface science results are in excellent agreement with work which has been performed on iron ammonia synthesis catalysts where 1 -3% by weight of sodium fused together with Fe₃O₄ - Al₂O₃ produces an active catalyst, upon reduction, with a smaller surface area than iron catalysts where either lithium or potassium were used instead[5].

Experimental

The ultra-high vacuum (UHV) studies were performed in a standard system with a base pressure of 1×10^{-10} Torr ($1 \text{ Torr} = 133 \frac{N}{m^2}$). AES and ISS experiments were carried out with a double pass cylindrical mirror analyzer (CMA), and for ISS it was operated in constant pass energy and pulse counting mode. Helium ions with 500 eV kinetic energy, E_0 , were used and the approximate scattering angle of the ions was 150° .

The preparation of the monolayer iron oxide consisted of repeated evaporation of submonolayer amounts of Fe, by resistively heating a 0.76mm diameter tungsten wire wrapped with 0.38mm diameter iron wire, followed by oxidation in 5×10^{-7} Torr oxygen at 830 K. The evaporation of iron was repeated until the one monolayer coverage was achieved[3]. The sodium and potassium was deposited from commercial SAES Getters sources, while lithium was deposited from a source consisting of a 0.51mm diameter tantalum coil that had been coated with lithium hydroxide. After the alkali deposition, oxygen was admitted into the chamber for one minute at a pressure of 5×10^{-7} Torr. An increase in the oxygen 510eV AES, with respect to the monolayer iron oxide 510eV oxygen peak, showed that the alkali was being oxidized. The amount of alkali was determined by monitoring the attenuation of the Fe(651eV) peak. One-third attenuation of this peak corresponds to 4 to 5 monolayers of alkali oxide[6]. Samples were heated to the temperatures, quoted in the paper(300 K to 1050 K), at a constant rate(≈ 40 K/sec). The samples were then cooled to room temperature at which time AES and ISS were performed.

Results and Discussion

Figure 1a shows an ISS spectrum for a clean iron oxide monolayer on Pt(111). Helium ions are only being scattered by iron and oxygen at this coverage. Heating the iron oxide to 850 K or 950K produces no change in the ISS or AES spectra. Only

at temperatures at or above 1050 K does the platinum substrate become accessible to the helium ions. In this temperature range the iron oxide monolayer disappears from the surface, and only Pt is detectable by ISS and AES.

The addition of approximately 4ML of oxidized sodium, lithium, or potassium to the iron oxide monolayer, at 300 K, produces the ISS spectra shown in figure 1. In both the potassium and sodium case, only the alkali metal is observed by ISS while the only visible feature in the lithium spectrum is a rising background at low E/E_0 values. This is because helium ions which scatter from the lithium atoms emerge from the surface with low energies, and they are masked by sputtered ions from the surface. Auger electron spectroscopy exhibits, in all three cases, alkali, iron, oxygen, and platinum peaks. Thus, ISS detects atoms only in the topmost surface layer, while AES monitors the presence of all the species in the top six layers. The fact that oxygen is observed in AES and not in ISS, in all cases, indicates that the alkali resides in the outermost surface layer. The presence of a small amount of oxygen in the outermost layer, in the sodium and potassium cases, can not be ruled out, since both sodium and potassium exhibit broad peaks due to multiple scattering[4] of the He^+ ions, which might obscure the oxygen peak in the ISS spectrum.

If the iron oxide monolayer, which has been covered with 4ML of sodium, is heated to 850 K, and then cooled to 300 K, the ISS exhibits a strong platinum peak, along with a sodium peak as shown in figure 2. The resulting AES spectrum shows an increase in the intensity of the Pt and iron LMM peaks, and a factor of two decrease in the sodium peak indicating that about 2ML of the alkali is now present on the surface. Thus, both ISS and AES show that the sintering of iron oxide has occurred leading towards a less than unity dispersion as shown by the presence of the platinum substrate peak in the ISS spectrum. Further heating to 950 K leaves only about 1ML of sodium(as seen by AES) and ISS shows no bare Pt. Hence, 1ML of sodium is not enough to keep the iron oxide sintered, so the iron oxide spreads back over the Pt(111) substrate. If the surface is now heated back to 850 K there is no evidence of sintering by both ISS and AES.

Heating the iron oxide monolayer coadsorbed with 4ML of lithium to 850 K

(temperature at which sintering occurred in the presence of sodium) produces no change in the ISS spectrum, but the platinum, iron, and oxygen peaks in AES become more intense implying that lithium is being lost from the surface. After heating the surface to 950 K the ISS spectrum (fig. 3a) shows a small Pt peak along with a rising background. This observation indicates that lithium sinters the iron oxide, but to a much lesser degree than sodium. Continued heating at 950 K removes more lithium, and at the point where AES indicates that only about 1ML of the alkali is left, ISS shows only a rising background with no Pt peaks. The iron oxide coadsorbed with a monolayer of lithium has now become redispersed over the Pt(111) surface (with the lithium in the outermost layer), again indicating that 1ML of alkali will not sinter iron oxide.

The coadsorption of four monolayers of potassium with the iron oxide on Pt(111), like lithium, does not sinter iron oxide as well as sodium. There is no sign of Pt peaks, when the surface is heated to 850 K, in the ISS experiment and when the potassium covered iron oxide is heated to 950 K (fig. 3b) the only change in the ISS spectrum is the appearance of a small oxygen peak (probably resulting from the decomposition of the potassium oxide overlayer). If a small amount of sintering has occurred, it can not be determined, since a small Pt peak would not be resolvable from the broad potassium peak.

In conclusion, our experiments reveal two significant results. First, in all experiments the alkali metal is located in the outermost layer. Strong evidence for this is that ISS exhibits only helium ion scattering from alkali metal when 1 or 4 ML of oxidized Na, K, or Li are present. The second result is that the addition of 4 ML of oxidized sodium or lithium, induces sintering of the iron oxide on Pt(111), whereas in the potassium case, sintering can not be clearly determined in our experiments. It is also found that sodium induces sintering, at a lower temperature, and to a greater degree than either lithium or potassium.

The experimental results give some insight into the sintering of the iron oxide. The observation that a coverage of one alkali monolayer does not induce sintering, but that this occurs when the concentration of alkali is larger, suggests that a liquid

like alkali phase can form which dissolves or increases the mobility of the iron oxide, thus inducing sintering of the iron oxide. Further heating to 950 K, in the case of sodium, removes all but about one monolayer of sodium on top of the iron oxide. The dissolution of the iron oxide in the alkali is now not possible and the iron oxide spreads back over the Pt(111) surface.

It is not discernable from the experiments whether the iron oxide sinters immediately, at room temperature, when the alkali is deposited or at temperatures lower than 850 K where the ISS experiment finds bare Pt. This is because alkali might be covering Pt at low temperatures, where sintering of iron oxide might have already occurred, and only after higher temperatures (≈ 850 K) have been obtained, does the excess alkali desorb, exposing Pt to ISS.

Experiments are being planned to probe the mechanism in more detail, but it is clear from this work that surface science can add much insight to sintering phenomena.

Acknowledgements

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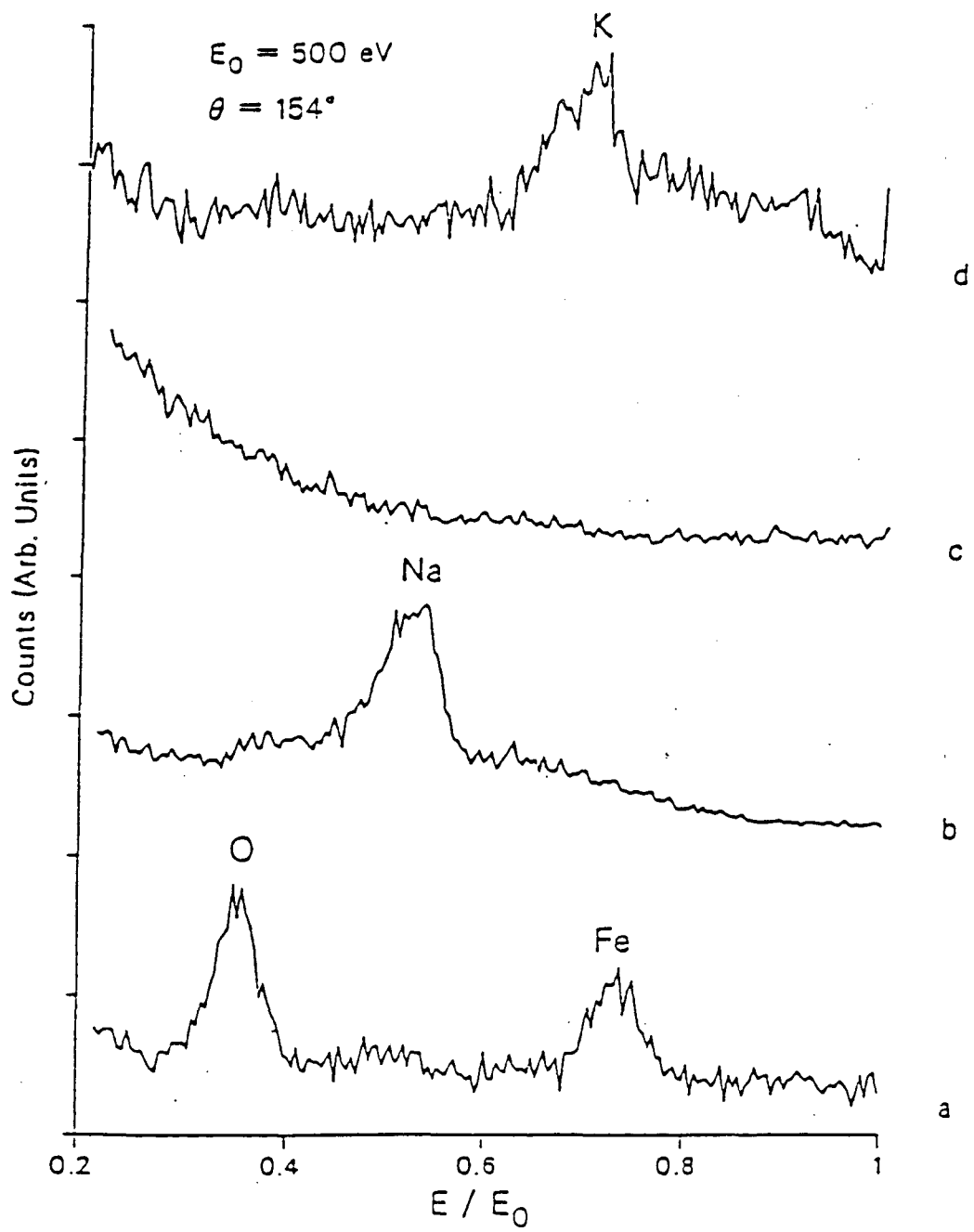
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Figure Captions

Figure 1. ISS spectra of (a) 1 ML of iron oxide on Pt(111). Only iron and oxygen is visible; (b) four monolayers of sodium on iron oxide monolayer. Sodium peaks can be seen with no oxygen; (c) 4 ML of lithium on iron oxide. The only feature visible is a rising background(see text); (d) 4 ML of potassium on the iron oxide monolayer. Like sodium and lithium there is no oxygen present in ISS, indicating that the alkalis reside in the outermost layer with oxygen underneath.

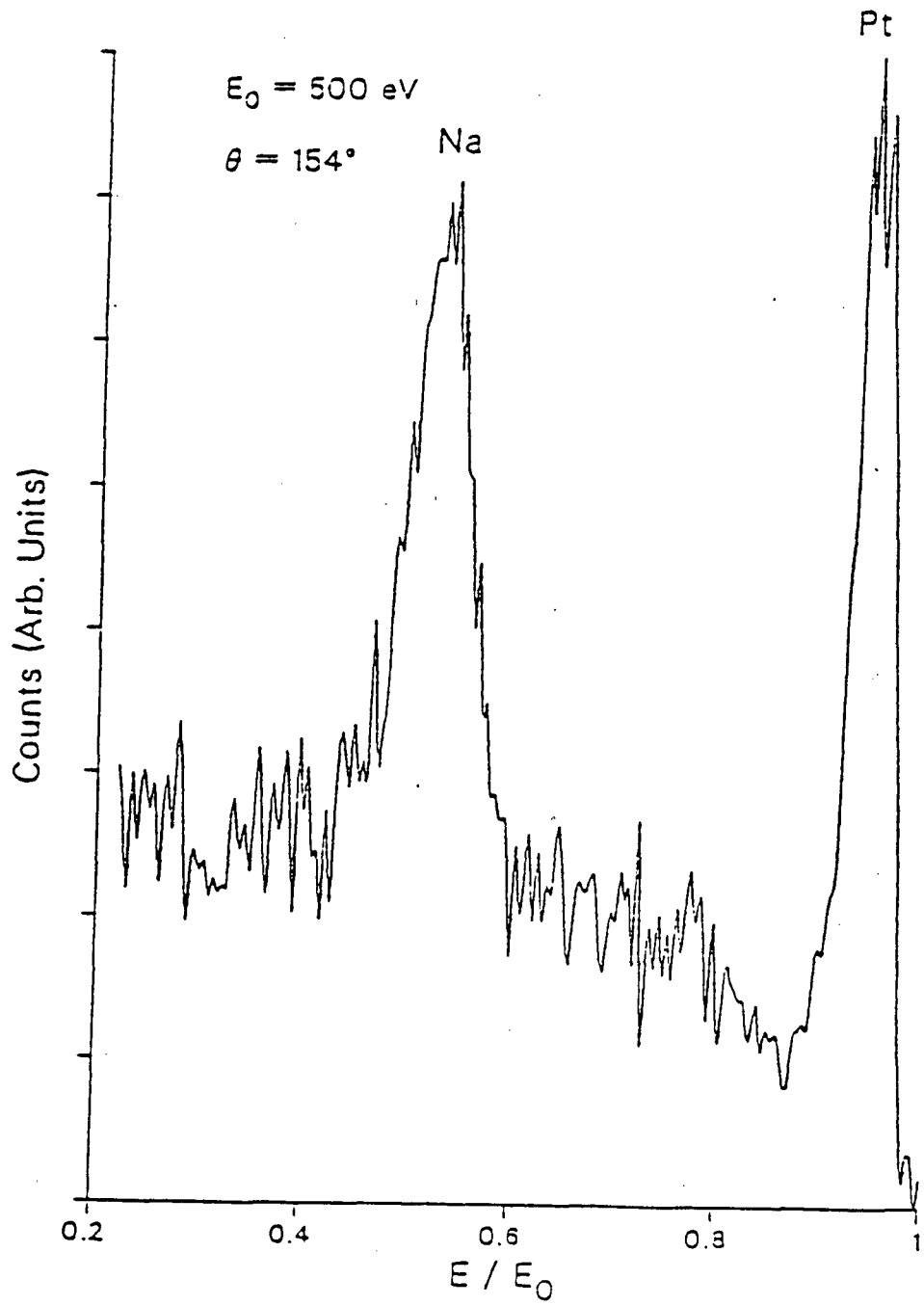
Figure 2. ISS spectra of sodium covered iron oxide surface after heating to 850 K. The presence of an intense Pt peak indicates extensive sintering of the iron oxide monolayer.

Figure 3. ISS spectrum of (a) the lithium coadsorbed with iron oxide surface after heating to 950 K. A small Pt peak is present suggesting that a small amount of sintering has occurred; (b) potassium covered iron oxide surface after heating to 950 K. In this case, a small Pt peak if present, can not be resolved from the broad potassium peak. The Pt signal, if present, is probably smaller than in the sodium and lithium cases indicating that potassium is the least effective iron oxide sintering agent of the three alkalis studied (sintering ability of sodium >> lithium > potassium).



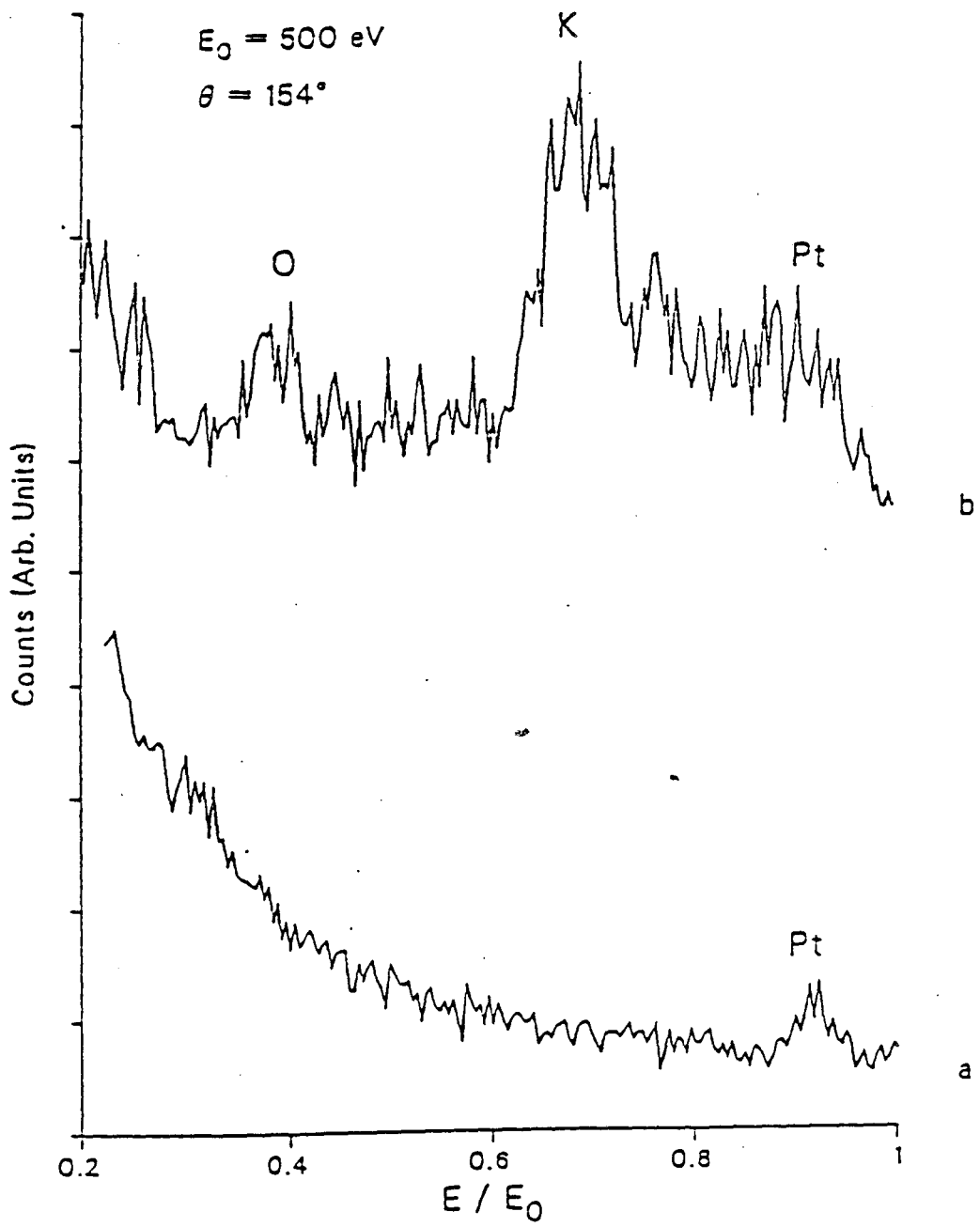
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Fig. 1



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Fig. 2



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Fig. 3

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