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ION SCATTERING STUDIES OF SOME ACTINIDE MATERIALS*

by

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ABSTRACT

Surfaces of polycrystalline U, Th, and single crystalline $\text{UO}_2(111)$ have been examined with He^+ , Ne^+ , and Ar^+ at incident beam energies $E_i \leq 650$ eV. For this study we used a double-pass cylindrical mirror analyzer in a custom vacuum system intended primarily for UPS. Our approach was to determine if the instrument could serve in a complementary ISS capacity and, if so, what the ion scattering conditions are for detecting surface oxygen and the actinides. Data are presented illustrating positive results. But severe limitations in resolution are evident, the energies do not correspond exactly to a simple binary-collision model, and with He^+ the scattering intensities are quite low by comparison with a Au reference.

* Work performed under the auspices of the U.S. Energy Research and Development Administration.

INTRODUCTION

At the "Third International Symposium on Physics and Chemistry of Surfaces" of the Dutch Vacuum Society in 1974 were two papers of special interest in ion scattering spectroscopy, (ISS). In the first, Brongersma^{1,2} reviewed the subject and described some then recent progress in distinguishing among possible Ni(100) + O₂ overlayer structures. In the second, Niehus and Bauer³ described the use of a single-pass cylindrical mirror analyzer, (CMA), in ISS. Since we were in the process at that time of assembling a custom vacuum system for high-resolution ultraviolet photoelectron spectroscopy, (UPS), with a double-pass CMA, the intriguing possibility arose of our using that instrument in a dual capacity with some actinide materials of continuing interest to us.^{4,5} Of particular concern was the presence or absence of oxygen in the outermost atomic layer. Low-energy ISS promised to answer that question.^{1,6} Our studies are now complete, and in this article we summarize some of the more prominent ISS features we have observed with the double-pass CMA. Structural aspects of UO₂(111) will be presented later.

In principle the use of a double-pass CMA for energy analysis of ions in ISS is straightforward, as seen in Fig. 1. An ion gun at 90° to the analyzer axis directs a collimated beam of He⁺, Ne⁺ or Ar⁺ onto the target and a portion of the scattered ions are collected by the 42 ± 6° acceptance cone of the CMA.

As discussed by Niehus and Bauer,³ the large acceptance angle of the unmasked analyzer, indicated by the donut ring of Fig. 1, introduces a spread in the detected energies but may be acceptable under restrictive circumstances. Figure 2 illustrates the spread expected for uranium and oxygen target atoms

with incident He^+ . An incident ion of mass m_i and energy E_i is scattered by a target atom of mass m_t into the analyzer cone at angle θ . The inset of Fig. 2 indicates the instrumental slit function and the graph transfers this feature into the spread in detected energy, E_d , versus E_i of He^+ according to the binary-collision relation.¹

$$E_d = \left[\frac{\cos \theta + (r^2 - \sin^2 \theta)^{1/2}}{r + 1} \right]^2 E_i, \quad (1)$$

where $r = m_t/m_i \geq 1$.

The hypothetical profiles in Fig. 2 will be observed only for isotropic scattering and as will be seen do not necessarily correspond to observation because of anisotropy. And, deviations from the simple binary-collision model are expected.¹ But the graph of Fig. 2 does suggest that U with atomic mass 238 should be separable from O with mass 16 even with an unmodified CMA.

EXPERIMENTAL

The heart of the system as shown in Fig. 1 is a double-pass cylindrical mirror analyzer, Physical Electronics Industries Model PHI 15-250, intended for high-resolution UPS. To detect positive ions only two very simple modifications are needed. 1) First, the negative output of the ramp generator, $-V_r$, is biased positively with 1200 V by means of batteries placed in series. For permanent ISS capability, a built-in reversible ramp polarity would be more convenient. In this limited study for which modifications were kept to a minimum, the batteries were acceptable but did require frequent calibration, i.e., every 30' or so. 2) Second, a -900 V acceleration was applied to the 1st stage of the electron multiplier to provide pulses from the positive ions while rejecting stray electrons. For some of the following measurements it was necessary to mask the entrance aperture with one of four different slit configurations. The remainder of the data collection/display system remains the same as in electron energy analysis and is not described here. Data are collected as counts/channel versus analyzer voltage, V_a , in the normal, non-retarding, pulse counting mode. Because of the + bias in obtaining V_a , in the following illustrations of data, as taken, the energy axis appears reversed.

After bakeout, the custom vacuum system reached a base pressure in the mid- 10^{-10} torr, (10^{-8} Pa), range. The ion gun is Varian Model 981-2043 with a few volts high frequency ripple. In normal ISS operation rare-gas was leaked continuously into the chamber, pumped by a turbomolecular roughing pump through a throttled valve, and held at 3×10^{-5} torr, (4×10^{-3} Pa). Gas renewal was ca. every 10^4 . Primary beam current, I_0 , was in the range

of 2-10 μA spread over 10 mm^2 depending upon the ion identity. To reduce surface contamination from residual gases in future studies of reactive metals, the need of a differentially pumped, ripple-free ion source is indicated. The beam was focussed and collimated by increasing the gas pressure a factor of 10, and making adjustments while observing the luminous ion-beam column and the fluorescent spot under the ion beam on the samples.

Materials and their preparation are described in refs. 4 and 5. The samples were mounted onto an indirectly heated 300-series stainless steel holder which in turn was mounted onto a variable position manipulator that allowed smooth variations in both azimuthal and polar angles. The sample and ion beams were positioned for optimum signal at $\gamma \sim 45^\circ$. With Ne^+ and Ar^+ , the signal intensities were sharply dependent upon sample position relative to the analyzer; e.g., a change of 3 mm would extinguish the signals but changes in the scattered energies were too small to measure. With He^+ , the acceptance zone was much larger and energy shifts were detectable but do not modify the discussions/conclusions that follow.

RESULTS AND DISCUSSION

In Fig. 3 are data for 300 eV He^+ scattered from Au using an unmasked CMA aperture indicated by the open ring of 'a', and a masked aperture with $\theta = 90 \pm 7^\circ$ in 'b' (line 3 of Figs. 1 and 2). In normal operation for He^+ at $I_0 \sim 3 \mu\text{A}$, curve 'a' would have several thousands of counts at maximum in a single sweep of 5", but was reduced here for comparison with the weaker signals in 'b' and 'c'. As expected, the aperture sharpens the peak and as seen in 'c' with $E_1 = 300$ and 312 eV, produces a 4% resolution under ideal, i.e. equal peak intensity, conditions. From Eq. 1 this result implies that at best with this configuration and unfiltered He^+ source the instrument will not resolve Au at $m_c = 197$ from elements with $m_c > 101$. In the unmasked ISS mode the resolution is 7% which limits the separation for Au to elements with $m_c \leq 74$. This limit is extremely poor by comparison with, for example, the separation of Ni ($m_c = 58.7$) from Cu ($m_c = 63.5$) with Ne^+ and a state-of-the-art ISS instrument.² Despite these shortcomings in resolution, the unmodified CMA unit, as described below, can be very useful in the ISS mode as an adjunct to UPS with Auger electron analysis capabilities.

Figure 4 shows tracings of data as taken for scattering of He^+ from 'a'-Au, and 'b', 'c', and 'd'- $\text{UO}_2(111)$. With an unmasked aperture as seen in 'a', the Au peak is relatively sharp on this scale, but from $\text{UO}_2(111)$ as in 'b' the peaks are broad with no signal above background in the expected U region. Data similar to UO_2 are collected from U metal with a small oxygen surface impurity although the peak intensities are much weaker and decrease toward the noise level at sample temperatures above 600°C, i.e., where oxygen returns to the bulk.⁴ With $\text{UO}_2(111)$ at room temperature, the

major peak diminishes with continued exposure to the ion beam presumably as the oxide is reduced,⁷ as indicated by a smaller but definite decrease in oxygen Auger signal. Heating the UO_2 sample to 600°C and above restores the peak until eventually after prolonged, i.e., 10 h at $3 \mu\text{A}$ on 10 mm^2 , the intensity begins to decrease irreversibly. Apparently excess oxygen in the near-surface region of slightly non-stoichiometric UO_2 diffuses to the surface until it is depleted, and, in an effect we observed for the first time during our many studies of this material, causes the surface to become insulating. With the sample at ambient temperature an intense peak indicated by the arrow in Fig. 4c is observed, but it diminishes with heating as in 'b'; possibly this peak represents another scattering, or perhaps secondaries.

The peak then in Fig. 4b would appear to represent He^+ scattered from oxygen on $\text{UO}_2(111)$, and if so then in the forward direction, i.e., at $\theta < 90^\circ$ as in Fig. 2. (The locations 1, 2, and 3 on Fig. 4b are the same as in Figs. 1 and 2.) A plot of the measured peak position in V_a versus E_i is shown in Fig. 5. For comparison also shown are data for 1) He^+ scattered from a Au reference, (He^+/Au), and 2) elastically scattered electrons. For the latter the least-squares slope is $(1.705 \pm .005)^{-1}$ which is in excellent agreement with the PHI value of $(1.706)^{-1}$. Although not shown here, for He^+ with an ungrounded sample, which reflects ions elastically at a hundred-fold increase in intensity, the slope is $(1.730 \pm 0.020)^{-1}$. This number confirms within 2% that the instrument indeed is an energy filter for positive ions as well as electrons. We are uncertain as to what effect a charged, floating specimen has upon focus, beam position, etc., that might affect measured energies. So in the following we simply convert analyzer voltage,

V_a , to detected energy, E_d , by the electron conversion factor, i.e.,
 $E_d(\text{eV}) = 1.706 eV_{e_1}$ with the understanding that E_d as determined could be in error systematically 2% or so.

The data points for He^+ scattering in Fig. 5 fall on straight lines, and for He^+/Au are within the predicted range: $dE_d(\text{obs})/dE_{e_1} = 0.942$, with a standard deviation of several determinations of 0.007, whereas the range calculated by Eq. 1 for an open aperture is 0.934-0.987. This agreement with Au may be somewhat fortuitous, however. At $\theta = 90 \pm 7^\circ$, the slope is 0.931(obs) compared to 0.960(calc), and if the collector is masked to restrict detection to ions only at $\theta > 90^\circ$, the slope is 0.900(obs) compared to a range of 0.934-0.960(calc). Calculated values and experimental least-squares slopes are given here to three decimal places, but little should be concluded from differences of a few percent since the absolute E_d values may be in error by as much as 2%. More questionable perhaps is the positive intercept of 10 ± 5 eV in E_{e_1} ; for e^- the intercept is -5 eV. This comparatively small value with Au may be an instrumental artifact, but an intercept was observed in every case with He^+ on all samples. With Ne^+ or Ar^+ such intercepts outside the range of experimental error of ca. 5 eV were not detected.

The data for $\text{He}^+/\text{UO}_2(111)$ with the sample at 700°C are within the forward scattering region for He^+/O but the intercept in E_{e_1} ranges from 25-50 eV, and the slope $dE_d(\text{obs})/dE_{e_1} = 0.371 \pm 0.013$ which, although greater than the $48^\circ < \theta < 132^\circ$ analyzer range⁹ of 0.425-0.846(calc), is approximately the extreme cutoff value of 0.879(calc) for forward scattering at $\theta = 42^\circ$. Again, it cannot be assumed that values of $E_d(\text{obs})$ are better than 2%.

Similar data were taken from U metal with fractional monolayer coverage of oxygen, and from UO_2 at room temperature with the main difference being in intensity as stated above.

Clearly, Fig. 5 by itself demonstrates very little of a conclusive nature with $\text{He}^+/\text{UO}_2(111)$ except that indeed He^+ ions do scatter detectably. By comparison Ne^+ and Ar^+ peaks are readily interpretable as being due to scattering from actinide atoms. The data in Fig. 5, and many similar plots not shown, indicate scattering by oxygen in the forward direction. But in the absence of further evidence one could just as well postulate multiple scattering with losses or some other complicated mechanism perhaps involving U. Such complex interactions may in fact occur, but their investigation was not our principal objective, and certainly not with this experimental arrangement. The simple identification of the surface specie, or species, giving rise to the reproducible $\text{He}^+/\text{UO}_2(111)$ data in Fig. 5 remained our central concern. Auger data eliminated surface impurities as a possible explanation. In an effort to resolve this difficulty we turned to masking the entrance aperture and collecting data at different scattering angles, θ .

With a $90 \pm 7^\circ$ aperture as in Fig. 4d, signals from oxygen and uranium are below the noise level and the only definite peak results from slow secondaries, possibly U^+ , UO^+ or UO_2^+ .⁸ But by masking the entire upper or lower half of the aperture as in Fig. 6, the dilemma with $\text{He}^+/\text{UO}_2(111)$ appears to be resolved. If only those ions in the forward scattering direction are detected by placing a mask over the upper half of the aperture as in line 'b' of Fig. 6, a plot similar to the $\text{He}^+/\text{UO}_2(111)$ line in Fig. 5 results. The intensities are approximately the same, as are the

slope $dE_d(\text{obs})/dE_i = 0.836$ and intercept at 54 eV. As before, the peak intensities decreased with continued exposure to the ion beam. If the mask is placed over the bottom half as in 'a' of Fig. 6, and collection is restricted to backscattered ions, several new features emerge. First, the oxygen region between lines 2 and 3 of Figs. 1, 2 and 5 is eliminated and the peak in Fig. 4b disappears. Second, the intensities are quite low by comparison with 'b' in Fig. 6, the background noise decreases even more, and a peak at higher energy than in 4b but of equal quality emerges. This peak apparently is buried in the noise of Fig. 4b, and is unaffected to a first approximation by beam exposure. A plot of its V_a at maximum versus E_i yields line 'a' of Fig. 6. The slope at $dE_d(\text{obs})/dE_i = 0.925$ is below the expected He^+/U range of 0.945-0.983(calc), but slightly larger than Au at 0.900(obs), as seen, which would indicate a heavier target atom. The conclusion is that 'a' of Fig. 6 represents backscattering from the uranium atoms whereas 'b' and presumably the $\text{He}^+/\text{UO}_2(111)$ data in Fig. 5 are from oxygen in the forward direction. The distinction between U and O apparently has been made, but several difficulties of interpretation, which we do not intend to pursue further ourselves at least with this instrument, remain.

The positive E_i intercept observed in every case with He^+ beams as in Fig. 5 remains an enigma. The effect may simply be an inherent characteristic of our detection scheme or ion beams, but it is puzzling why the intercept with U, Th, and UO_2 should be so much greater than from Au at identical settings, sample position, etc., if the effect is purely instrumental. With oxygen the anomaly may be due at least in part to an artifact of varying forward/back scattering ratio with dominant backscattering at $E_i < 100$ eV or so, i.e., in the inaccessible range here,

and increased forward scattering at higher energies. With wide slits such a process could even cause the slope, dE_d/dE_i , but not the value of E_d itself to exceed the maximum theoretical limit as indicated by the dashed line in Fig. 2. This possibility also suggests with a narrow slit detector at fixed angle that a given reflection conceivably would be detected optimally only in a narrow range of E_i , which could account for the absence of peaks in Fig. 4d. Admittedly this possibility is a bit speculative, but it does imply that angular measurements with these materials on a high-quality, high-resolution ISS instrument would be in order.

As a concluding observation, Fig. 7 shows data for Ne^+/Th and Ar^+/Th as well as He^+/Th for comparison. With Ne^+ and Ar^+ , since $m_i > m_c$ (oxygen), detected scattering is from the heavy actinide atom. In each case the data are represented by a straight line. With Ne^+ , the slope $dE_d(obs)/dE_i = 0.893$ as compared to predicted values for 1-0.753, 3-0.844 and 2-0.945, (trajectories 1, 2, 3 of Figs. 1 and 2, according to Eq. 1). A slight preference for forward scattering may be indicated, as is the more definite case with Ar^+ where $dE_d(obs)/dE_i = 0.828$ and 1-0.559, 3-0.706 and 2-0.892. The E_i intercept with Ne^+/Th is 2 eV, with Ar^+/Th it is 5 eV, and no complicating factors are indicated. But the lightest ion, He^+ , if scattered from Th atoms should yield scattering energies greater than Ne^+ or Ar^+ . That it does not added to the Auger evidence of fractional monolayer coverage by oxygen suggests that the He^+/Th data with an unmasked aperture, in agreement with U and UO_2 results, represent forward scattering by surface oxygen impurity. If this is true, and the evidence to date indicates that it is, then one of our original objectives has been achieved: the detection of oxygen in the outermost atomic layer of actinide materials with an unmasked, double-pass CMA as a

complementary adjunct to UPS. These results, however, should suffice to discourage anyone from attempting to distinguish a light element, e.g. Al, from oxygen with an ISS setup such as Fig. 1.

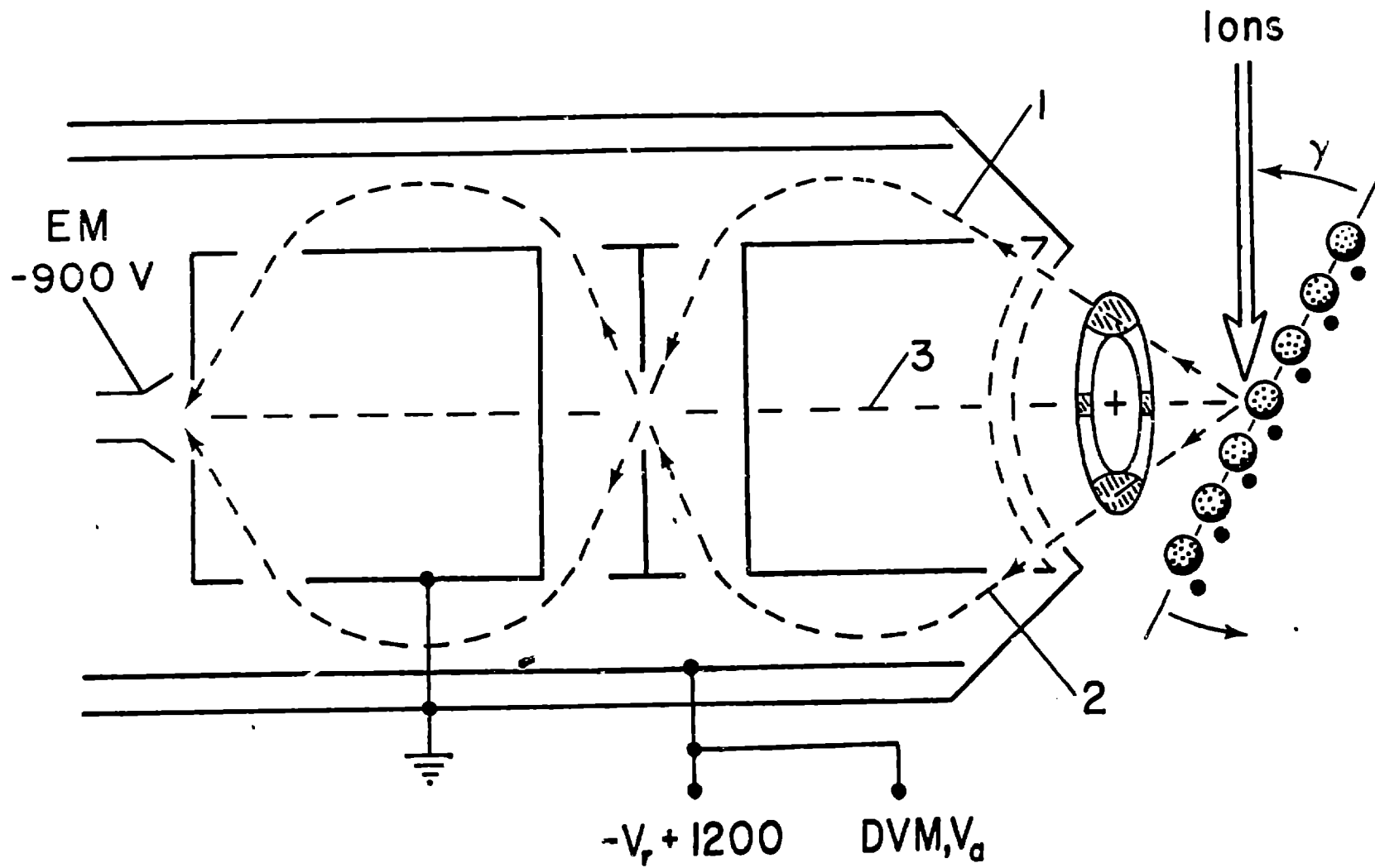
REFERENCES AND NOTES

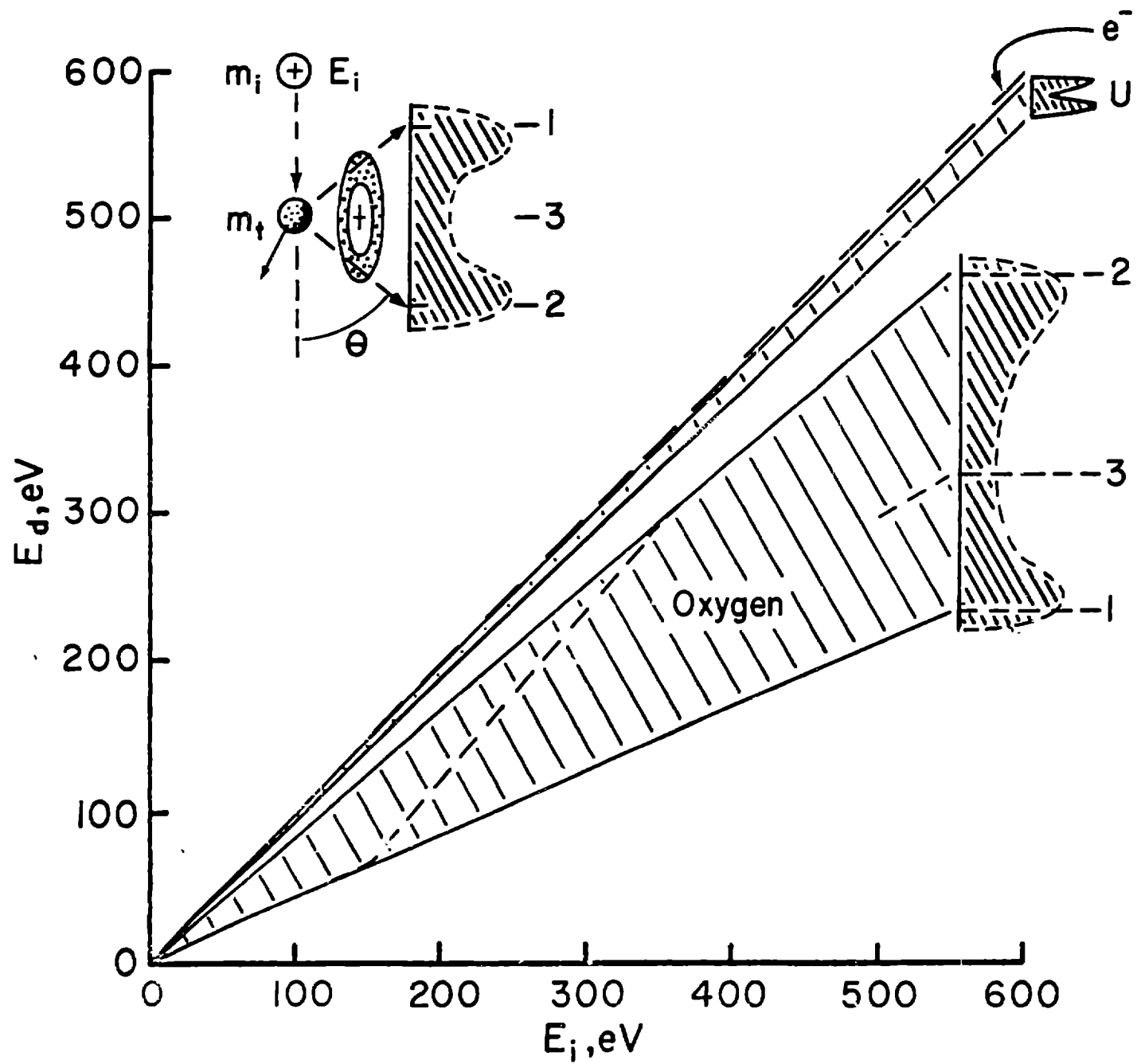
1. H. H. Brongersma and P. M. Mul, Surface Sci. 35, 393 (1973).
2. H. H. Brongersma and T. M. Buck, Surface Sci. 53, 649 (1975).
3. H. Niehus and E. Bauer, Rev. Sci. Instrum. 46, 1275 (1975).
4. W. P. Ellis, Surface Sci. 61, 37 (1976).
5. W. P. Ellis, Surface Sci. 45, 569 (1974).
6. D. P. Smith, J. Appl. Phys. 38, 340 (1967).
7. R. Holm and S. Storp, Appl. Phys. 12, 101 (1977).
8. W. Baun, private communication, (1977).
9. Note: The term, 'analyzer range', as used here denotes the expected energy spread from a binary collision with a 42° detector cone, ($132^\circ \geq \theta \geq 48^\circ$ for scattering angles between lines 1 and 2 of Fig. 1).
With an actual detector acceptance zone of $42 \pm 6^\circ$, the extreme forward angle is 48° relative to the analyzer axis, or $\theta = 42^\circ$ which from Eq. 1 for He^+/O gives $dE_d(\text{calc})/dE_i = 0.879$.

FIGURE CAPTIONS

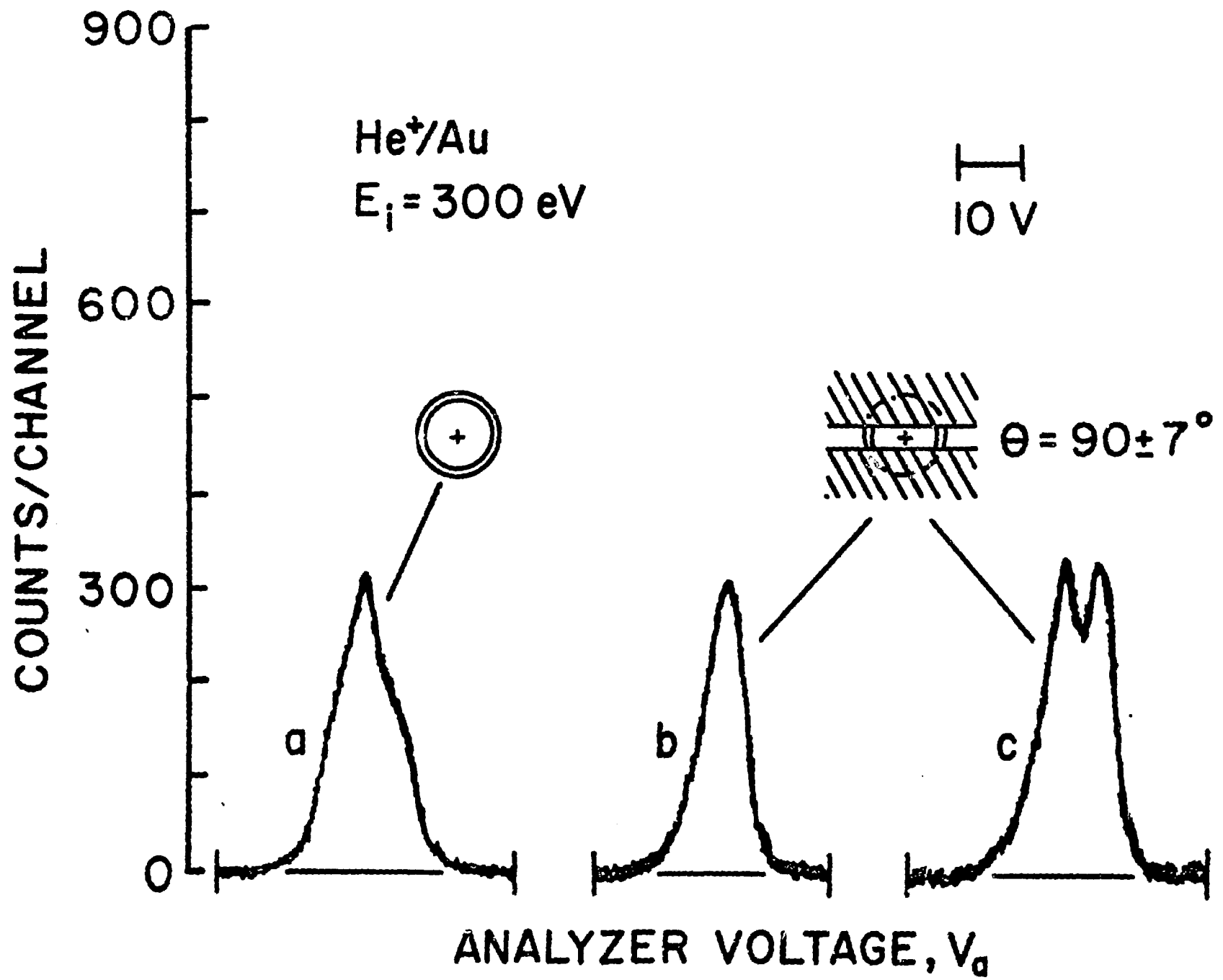
1. Schematic of a double-pass CMA in the ion scattering mode. Ions incident upon the crystal at angle γ are scattered into the $42 \pm 6^\circ$ acceptance cone of the analyzer. 1st stage of electron multiplier, EM, biased at -900 V. Output of ramp is $-V_r$ which is converted to a positive ramp with +1200 V placed in series.
2. Plot of spread in detected energy, E_d , versus incident beam energy, E_i , calculated for He^+ scattered isotropically from U and O according to binary collision model. Assumes detected energy equals true final value. e^- plot is for elastic scattering with slope of unity. Inset: scattering parameters showing instrumental slit function, shaded area. Anisotropic scattering modifies the spread in E_d , as does masking the CMA aperture.
3. Tracings of peak shapes for He^+ scattered from Au at $E_i = 300$ eV for 'a', open CMA aperture and 'b', aperture masked to $\theta = 90 \pm 7^\circ$. Resolution of 4% in E_d illustrated in 'c' at $E_i = 300$ and 312 eV.
4. Tracings of He^+ scattering data for 'a', Au at $E_i = 550$ eV, open aperture; 'b', $\text{UO}_2(111)$ at $E_i = 550$ eV, specimen at 700°C , open aperture, regions for expected U and O peaks shown; 'c', $\text{UO}_2(111)$ at $E_i = 450$ eV, ambient temperature, open aperture; and 'd', $\text{UO}_2(111)$ at $E_i = 400$ eV, 600°C , aperture masked for $\theta = 90 \pm 7^\circ$.
5. Plots of analyzer voltage, V_a , at peak maximum versus incident beam energy, E_i . Open aperture. Experimental data for elastically scattered electrons, He^+ scattered from Au, and He^+ scattered from $\text{UO}_2(111)$ at 700°C . Oxygen region from Figs. 1 and 2 indicates anisotropic scattering from surface oxygen in forward direction.

6. Plots of analyzer voltage, V_a , at peak maximum versus incident ion energy, E_i . Experimental data for He^+ scattered from Au, and $\text{UO}_2(111)$ at 600°C . 'a', aperture masked to collect backscattered ions only, U indicated. 'b', forward scattering only, oxygen indicated.
7. Data for scattering of rare-gas ions from metallic Th. Ne^+ and Ar^+ scatter within the range expected from binary-collision model, but He^+ plot indicates only oxygen peaks. Presence of O confirmed by Auger analysis. Open aperture.

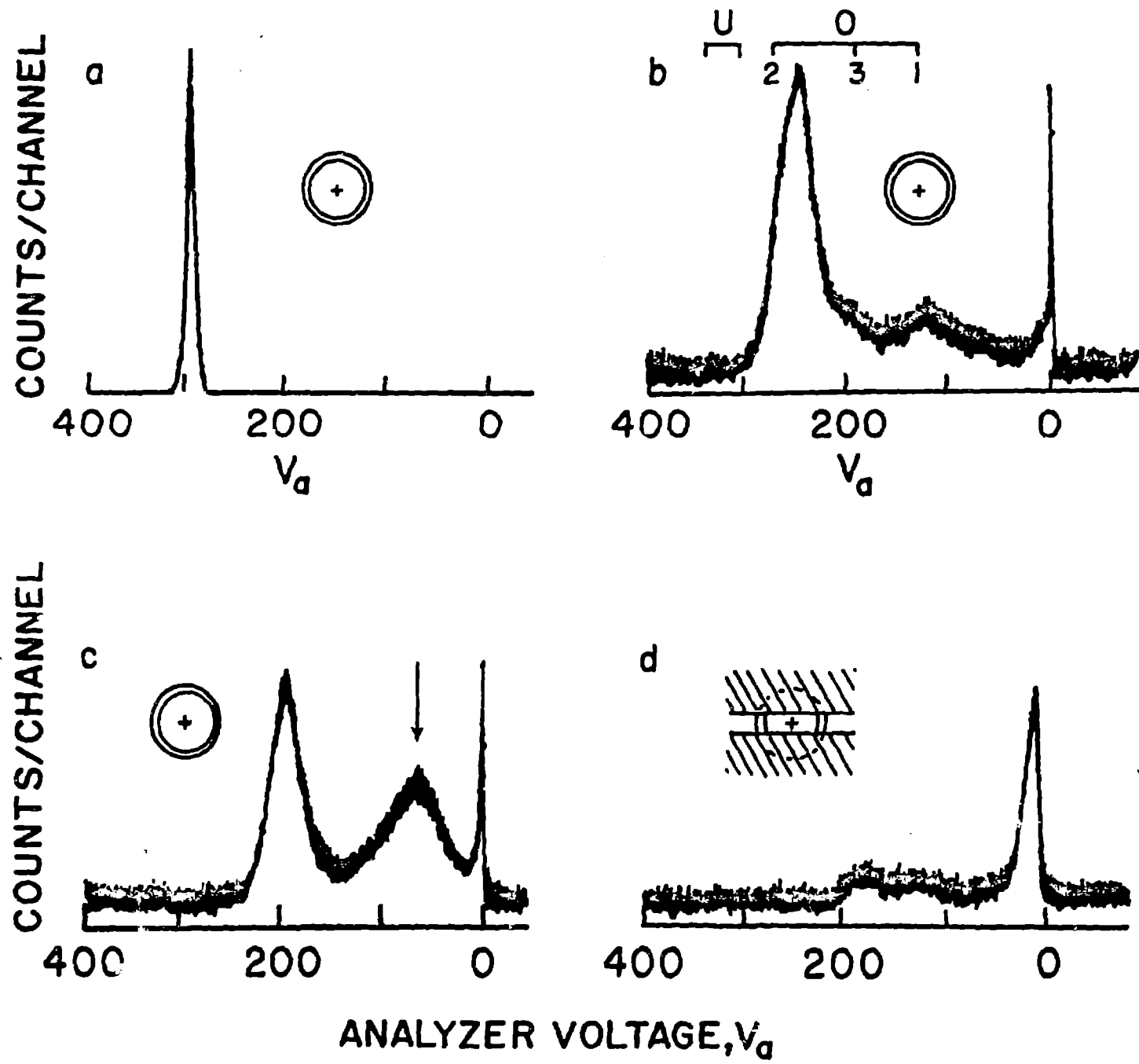


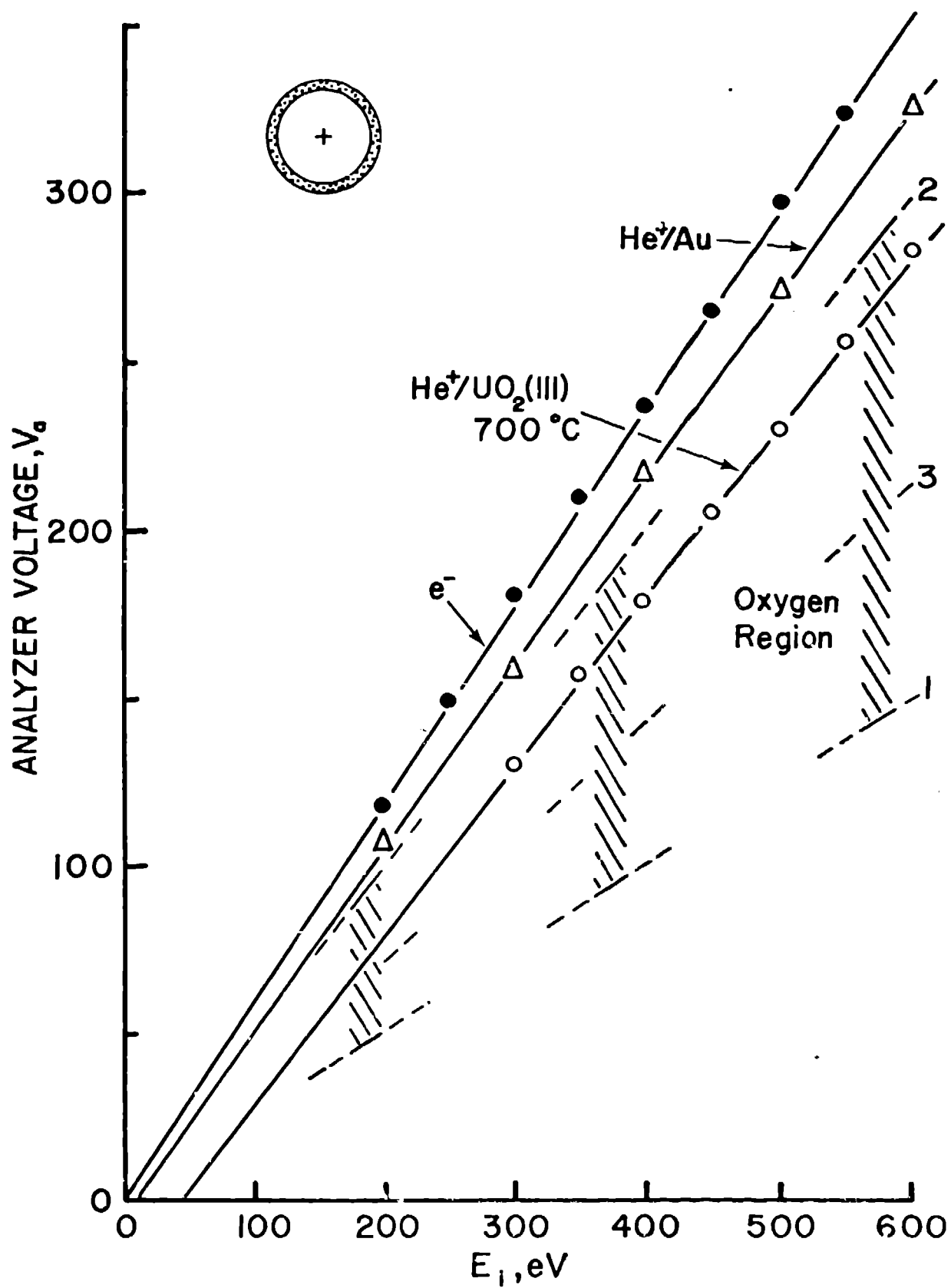


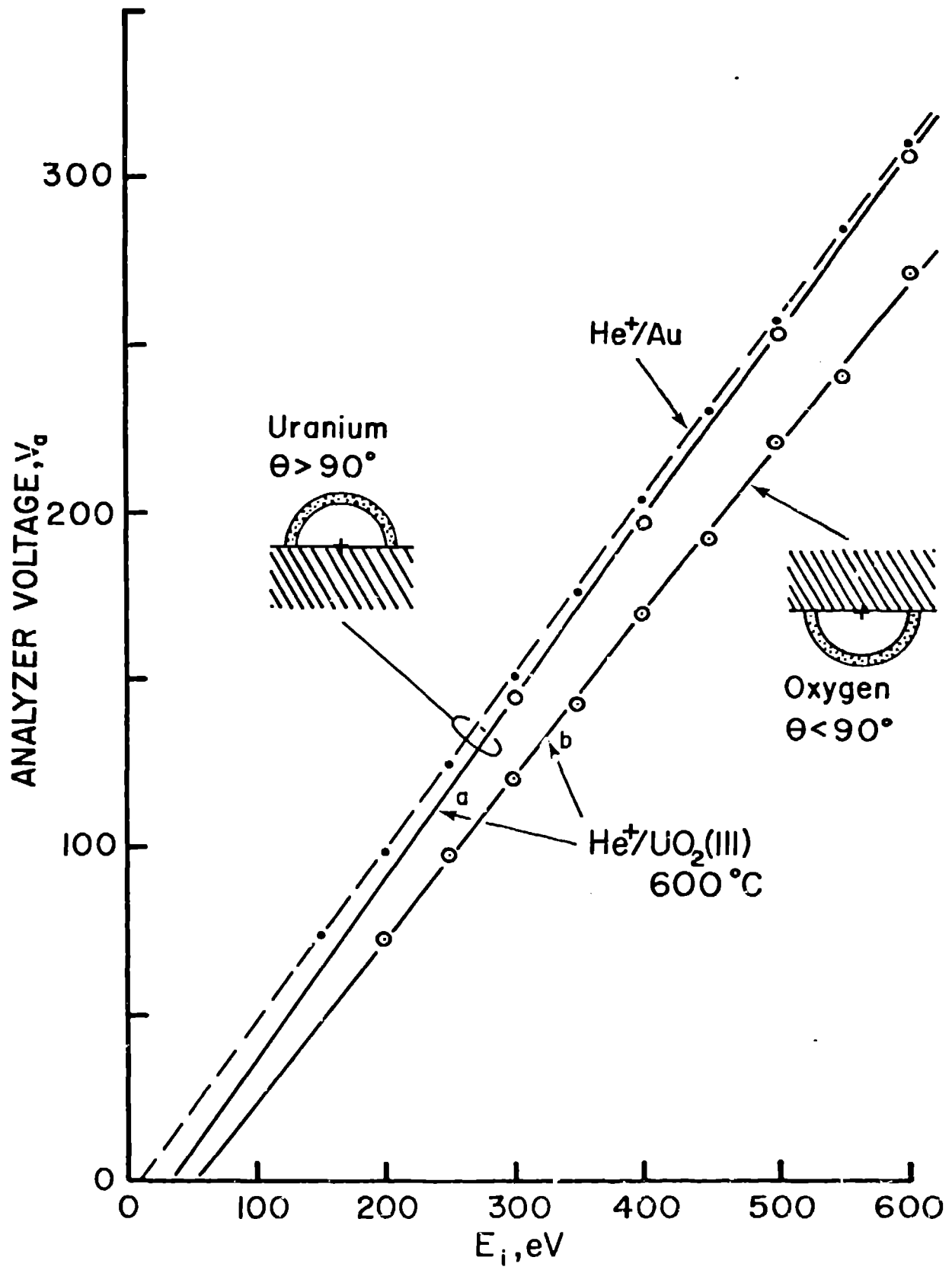
Ellis & Taylor
Fig. 2



Ellis & Taylor
Fig. 3







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Fig. 6

