Reassessment of energy transfers in the quasielastic scattering of 250–3000 eV electrons at surfaces

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Measurements are reported of the quasielastic scattering energy losses of electrons of 250–3000 eV from clean Cu, Ag, and Au in order to verify the large loss values recently observed by Erickson and Powell. Large loss values, if they were valid, would lead to a range of interesting analytical possibilities. However, here it is shown that the losses are small and are in agreement with the single-particle scattering model of Boersch *et al.* A null method is used which allows the energy of the unscattered beam to be referenced at each energy so that the energy losses may be determined directly with an accuracy of 15 meV. It is concluded that the measurements in the study of Erickson and Powell may have included a contribution from the cathode supply circuit that increased as the energy increased. The very low values of the losses observed here are predicted to be significant in surface analysis only for scattering from elements with atomic numbers less than 20.

I. INTRODUCTION

In general, in electron scattering at solid surfaces the factor of 10^5 in mass between a target atom and the energetic electron means that, in the absence of electronic excitation, any energy loss of the latter is very small and is generally ignored. The scattering is considered as quasielastic. Of course, there are well-defined energy losses in the solid which do arise from thermal or optical phonons,[1] bond excitations,[2] lattice excitations, and collective electron oscillations,[3] which appear in the emission spectrum of energies below the peak due to the quasielastically scattered electrons, but these are not a present concern.

Recently, Erickson and Powell[4] showed that, while the energy losses were indeed small, they were not negligible. They show that the energy losses increase from zero at low energies to values in the range 150–250 meV for electron energies in the range 300–1500 eV for Cu, Ag, and Au. The variations in the loss energy as a function of the beam energy appear to have weak structures which were thought to be associated with structure in the elastic-scattering cross sections. Erickson and Powell show that the simple model of Boersch, Wolter, and Schoenebeck[5] for the single-electron, single-target-atom collision is about an order of magnitude in error with the simple model giving losses of up to only 30 meV or so against measurements of up to 250 meV. These higher losses were proposed as possibly due to unresolved phonon excitations. The simple model gives, for energy losses ΔE small compared with the electron energy E, the relation

$$\Delta E = \frac{4mE \sin^2\theta/2}{M} , \tag{1}$$

where m, M, and θ are the electron mass, the target atom mass, and the scattering angle, respectively.

With the increasing use of synchrotrons for photoelectron spectroscopy at very high resolution, such energy losses of 250 meV per collision may now be observed and would be a very useful tool. For instance, McConville *et al.*[6] resolve chemical states very clearly in the oxidation of aluminum with a system giving an energy resolution of 150 meV and peak full widths at half maximum (FWHM) below 300 meV. Again, the highly monochromated x-ray photoemission spectroscopy (XPS) system of Gelius *et al.*,[7] and recent commercial instruments, work in this regime. In these systems it would be possible, therefore, to distinguish between unscattered electrons and those that have undergone a single wide-angle scattering event. This distinction would allow one to discriminate between photoelectrons from adsorbates emitted directly and those backreflected from the substrate. Additionally, in angle-resolved XPS the major disturbing effects of elastic scattering[8] could be removed by selecting only those photoelectrons of the higher energy.

Since the intensity of the quasielastic peak is usually very high in spectrometers, the incident electron beam current may be reduced to very low values, much lower than the currents required for Auger electron spectroscopy (AES) by a factor of 10^3 or 10^4. Thus, if the energy losses of 150–250 meV could be uniquely ascribed to a particular element, one would have a surface analytical technique of great sensitivity. It could be used with lithographed field emitters[9] with energy spreads of less than 0.2 eV (Ref. 10) to form an extremely compact very-high-resolution analytical scanning electron microscope. The spatial resolution would be limited solely by the probe size and not by multiple scattering within the sample. In addition, the low beam current would minimize damage effects. For these reasons it was deemed important to verify the measurements of Erickson and Powell.[4]

Possible further suggestions for observing different losses would arise through the sum of several scattering events instead of one. If, for instance, n events were required to reach the angle θ, then

$$\Delta E = \frac{4mEn}{M} \sin^2\left[\frac{\theta}{2n}\right] \tag{2}$$

on the assumption that the n scatterings were all in the same azimuths, or approximately

$$\Delta E = \frac{4mEn}{M} \sin^2 \left[\frac{\theta}{2n^{0.5}} \right] \quad (3)$$

if the n scatterings were in random azimuths. However, Monte Carlo calculations[11] show that the scattering should be dominated by the single-scattering relation of Eq. (1) for Cu, Ag, and Au in the energy range 250–3000 eV. Thus Eqs. (2) and (3) represent extreme cases which are unlikely. Equation (2) leads to energy losses lower than the single-scattering model, but Eq. (3), which is more realistic, predicts an increase of 30% for $n=2$, 60% for $n=10$, and 66% as n approaches infinity, compared to Eq. (1). This figure is insufficient to explain the results of Erickson and Powell and so the unresolved phonon excitations or some unidentified mechanism must be involved if their data are correct. In the next section we describe the method for the present measurements and the development of a null method which allows the absolute value of the true losses to be deduced.

II. EXPERIMENT

The apparatus used for this study is a modified VG Scientific ESCALAB II known as the *metrology spectrometer*. Details of this instrument are given elsewhere.[12] Briefly, electrons of 0–2500-eV energy may be analyzed after scattering from the sample by a spherical sector analyzer with a lens set at 142.3° to the electron gun. In this work, to obtain the highest resolution, the analyzer is operated at a retardation ratio of 100 with entrance and exit slits set to give a resolution of 0.25% of the analyzer pass energy (i.e., 0.0025% of the total energy).

As the system is very efficient in the pulse-counting mode, the electron-gun filament temperature was reduced as far as possible to reduce both the thermal spread of the electrons and the potential gradient across the emitting region of the filament. In the experiment of Erickson and Powell,[4] the energy of the incident electrons could be changed by changing the cathode potential which could be measured with a calibrated 6.5-digit voltmeter. The change in energy of the reflected electrons was then measured with a double-pass cylindrical-mirror analyzer operated at a pass energy of 50 eV by the change in the retardation voltage measured on the same voltmeter. This would appear to be an approach which would greatly reduce any measurement errors due to voltmeter drift. This approach was tried in our equipment but it was clear that measuring the electron-beam energy by measuring the cathode supply potential was not adequate. In the electronic circuits, the cathode potential is correctly set at the filament center by appropriate controls but problems may occur due to the potential drop down the filament. This drop could be 0.5 V over the emitting region of the hot zone of the filament. In any electron-gun system, the electron optics are not fixed if the beam energy is changed. In some systems, a fixed extraction voltage is used in order to maintain a constant beam current at all energies and then the subsequent lenses must be refocused to retain a defined spot at each energy. In other systems, the lens ratios are all kept fixed so that focus is maintained but then the beam current rapidly falls as the energy is reduced. In both cases, the region of the emission from the filament that reaches the sample will depend on the beam energy. The potential of this region defines the voltage difference between the peak of the emission and the point for the local Fermi level addressed by the beam energy measuring voltmeter. This latter point is usually a center tap across the filament leads. The above postulate was rapidly confirmed by measuring the elastic peak shifts caused at a fixed energy by altering the strength of the first condenser lens. Variations of this lens caused shifts of up to 150 meV in the quasielastic peak. Variations of the strength of the final focus lens, however, only caused energy shifts less than the measurement repeatability of 7 meV. Thus, a new experimental procedure was sought which avoided the above changes in the beam energy. A further factor for consideration was the problem of defining the energy of the unscattered beam. Erickson and Powell appear to have chosen an arbitrary value which is consistent with the measured energy-loss behavior as the energy is reduced to around 100 eV; however, it was deemed safer to measure the unscattered value directly here.

As a result of the above considerations the following procedure was adopted. The electron beam was set at 1500 eV and the spectrometer was adjusted to record over a 2.5-eV range centered at 1500 eV. The energy of the beam at the sample was then changed simply by changing the sample potential. In this way none of the errors of energy measurements are propagated through to the final result and, more importantly, no changes are made to the electron emission and beam-forming system. This system worked very well with retardations of up to 1250 eV or acceleration of 1500 eV to give data in the energy range 250–3000 eV. By using a composite sample of Ag and Au regions on a Cu substrate, data for all three elements could be recorded with the minimum of time and sample changes. The surfaces of all three materials were in the same plane so that all could be cleaned by sputtering with 4.5-keV argon ions simultaneously, without cross contamination.

To eliminate drift effects and to give a reference, the shift for Cu at an electron-beam energy of 1000 eV was recorded after each of the measurements at each energy on each material. In the text that follows, this shift will be referred to as the copper intermediate reference point. To obtain the unscattered reference, a potential of -1500 V was applied to the target and, by retracting the sample a short distance, the electron beam could be steered directly into the spectrometer without striking the sample. To reduce the signal to a comparable level to that for the Cu intermediate reference point and to fill the entrance slit of the analyzer, the beam was defocused for this analysis. With the sample in this new position, the absolute shift for the Cu intermediate reference point at 1000 eV could be established. A schematic of the equipotentials and the steering of the beam into the analyzer is shown in the inset to Fig. 1.

In all of this work, the quasielastic peak shape was as shown in Fig. 1, with a FWHM of 0.61 eV. For each da-

tum, between three and five individual spectra were recorded and each peak position from this repeated measurement had a standard uncertainty of, on average, 7 meV.

III. RESULTS AND DISCUSSION

As small shifts in the position of the peak shown in Fig. 1 may arise through changes in the peak shape, two measures of the peak position were recorded. The first position is at the 50% intensity value on the high-energy side of the peak and the second is at the peak itself. In the figures that follow, these are represented by filled and unfilled symbols, respectively.

The results for Au, Ag, and Cu are shown in Fig. 2. The solid lines are the predicted results for the single-scattering model giving rise to Eq. (1). Here, because the retarding field in front of the sample increases the electron angle of incidence as well as the angle of emission of the collected electrons, Eq. (1) is slightly modified. These refraction effects are actually quite small but lead to

$$\Delta E = \frac{4m}{M}(E - 200) , \tag{4}$$

where E is now in eV. This function, shown by the solid lines in Fig. 2, describes the data within a standard deviation of 15 meV. These results are very different from those of Erickson and Powell[4] and show none of the structure exhibited in their work.

To test if the data of Erickson and Powell were consistent with a model based on fixed shifts of the peak position at each energy which arise from their particular electron-gun emission characteristics plus the effects of the single-scattering model, we plot in Figs. 3(a) and 3(b) the difference between their Cu and Ag data and their Au and Ag data, respectively, by the filled symbols. Also in these plots, shown by the solid lines, are the predictions according to Eq. (1) for their scattering angle of 138°. Added to these plots are the present data from Fig. 2, shown by the unfilled symbols and the relevant predic-

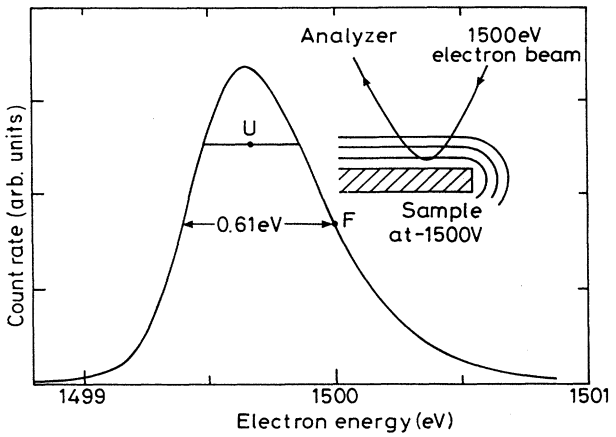

FIG. 1. The quasielastic peak shape with a schematic of the equipotentials around the biased sample (inset). Points U and F are used to characterize the energy shifts of the peak as described in the caption to Fig. 2.

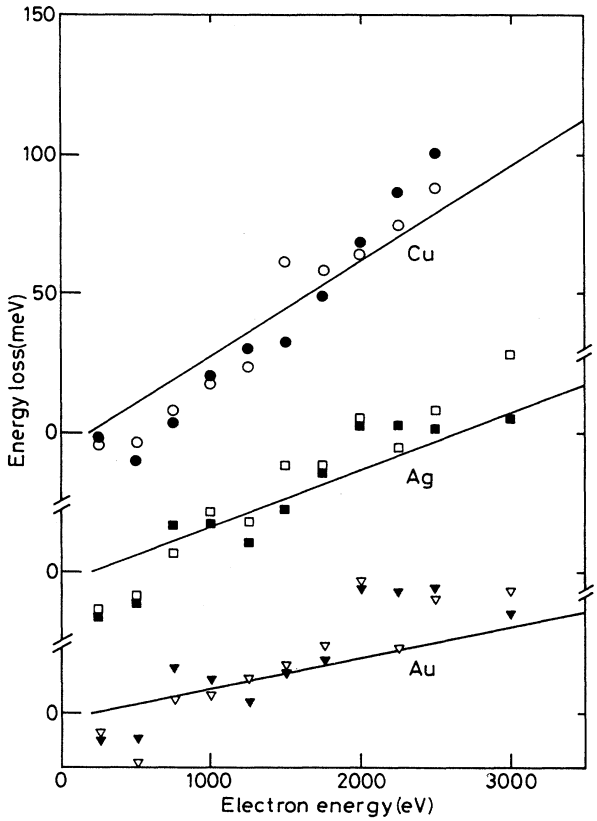

FIG. 2. The energy losses for the quasielastically scattered electrons from Cu, Ag, and Au. The filled symbols represent the shifts at the high-energy half-height point F in Fig. 1 and the unfilled symbols represent the center position at the 75% intensity point U in Fig. 1. The solid line is the predicted loss according to Eq. (4). The copper and silver data are displaced on the ordinate axis with new origins for presentational purposes.

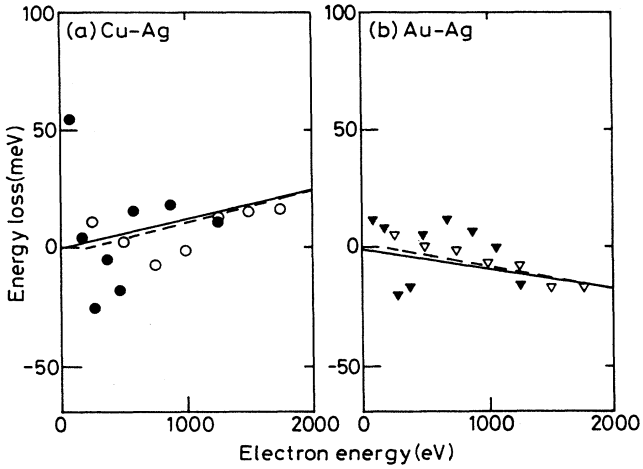

FIG. 3. The energy-loss ordinate gives the difference between the losses measured with respect to the silver loss at each energy for (a) copper and (b) gold as a function of the electron impact energy. The filled symbols represent the measurements of Erickson and Powell (Ref. 4) and the solid line represents the appropriate prediction according to Eq. (1). The unfilled symbols are from the present data and the dotted line is the prediction according to Eq. (4).

tions using Eq. (4), shown by the dotted lines. Within the experimental scatter, the filled and unfilled points in Figs. 3(a) and 3(b) are essentially the same. We conclude from this result that the sole essential difference between the data of Erickson and Powell and the present results is a single beam-energy-dependent term added into the beam energy in their work, probably arising somewhere in the emission stage of their electron gun.

Thus, the data may all be taken to be consistent with the single-scattering model of Boersch, Wolter, and Schoenebeck[5] and there are no anomalous effects due to phonon excitations.

IV. CONCLUSIONS

A study of the quasielastic scattering of electrons in the range 250–3000 eV from Cu, Ag, and Au shows that the single-scattering model of Boersch, Wolter, and Schoenebeck[5] for the electron energy losses is upheld and that the higher value losses seen in the study of Erickson and Powell[4] may arise from an instrumental artifact. As Erickson and Powell pointed out, care should be exercised if reflected electron beams are used to calibrate electron spectrometers. Significant errors in such a calibration can occur if the calibration is performed with a contaminated sample where, at 2000 eV, Eq. (1) indicates that the loss could reach 0.4 eV for a low atomic number material. If clean Au is used and the equation of Boersch, Wolter, and Schoenebeck is applied, the loss errors may be reduced to 10 meV.

For adsorbates on a light substrate, such as an oxide, the energy loss of typical 1200-eV photoelectrons backreflected from the substrate would be around 135 meV. In the better XPS instruments, this loss may appear as a slight broadening on the high-binding-energy side of the peak.

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