Energy transfers in the quasielastic scattering of 70–1250-eV electrons by surfaces

N. E. Erickson and C. J. Powell
Surface Science Division, National Institute of Standards and Technology, Gaithersburg, Maryland 20899*
(Received 16 May 1989)

We have observed energy transfers of up to about 200 meV in the quasielastic scattering of 70–1250-eV electrons by sputtered surfaces of polycrystalline copper, silver, and gold. The experiment consisted of measuring shifts in positions of elastic peaks with a double-pass cylindrical mirror analyzer for different voltages applied to the cathode of the electron gun. The shifts are believed due to changing cross sections for phonon excitations with electron energy. The results are significant in the use of the elastic peak technique for high-accuracy calibrations of the energy scales of electron spectrometers.

I. INTRODUCTION

We report here observations of energy transfers in the quasielastic scattering of low-energy (70–1250 eV) electrons by polycrystalline copper, silver, and gold. Our incident beam was from a thermionic source and not monochromated. The experiment consisted of measuring differences in the positions of the elastic peaks using an electron spectrometer for different voltages applied to the tungsten cathode.

Elastic electron scattering by crystals (diffraction) involves momentum transfer by the crystal lattice, and any energy loss (from conservation of energy and momentum) would be vanishingly small. Boersch, Wolter, and Schoenebeck,[1] however, have observed recoil energy losses ranging from about 0.1 to 5 eV in the large-angle ($\theta \geq 45°$) elastic scattering of 20–40-keV electrons by polycrystalline C, Al_2O_3, Ni, Ag, and Pt. These recoil losses varied systematically with average atomic mass, scattering angle, and incident energy, and could be quantitatively accounted for by assuming that the elastic scattering was by single atoms and not the lattice as a whole. The values of the energy transfers we observe for electrons of much lower incident energy are much greater than would be expected from simple extrapolation of the Boersch *et al.* formula and appear to be due to other mechanisms (e.g., phonon excitation).

We describe our experiment in the next section and present the results in Sec. III. The results are discussed in Sec. IV where, in particular, we point out the relevance of these observations in the use of elastic peaks for the calibration of the energy scales of electron spectrometers.[2]

II. EXPERIMENT

The scattering experiments were performed with a Perkin Elmer, Physical Electronics model 549 system intended for x-ray photoelectron spectroscopy and Auger-electron spectroscopy. The system consists of a double-pass cylindrical-mirror analyzer (CMA) with a concentric electron gun. Electrons from the gun bombard a target at an angle of incidence of 30° to the surface normal. Electrons scattered through an average angle of 138° were decelerated to a constant energy, here usually 50 eV, and enter the CMA.

Our experiment consisted of applying a voltage V_c to the gun cathode and of measuring the energy distribution of the scattered electrons in the vicinity of the elastic peak. A fixed voltage, here usually 29.412 V, was applied between the CMA inner and outer cylinders; for our CMA, this voltage corresponds to a pass energy eV_p of 50 eV. A computer program stepped the voltage V_a applied to the retarding grid and inner cylinder of the CMA, stored the counts collected for a fixed period of time, and recorded V_a which was measured with a calibrated $6\frac{1}{2}$ digit voltmeter. The same voltmeter was used to measure V_c. We found it necessary to raster the incident beam on the target surface in the field of view of the analyzer in order to avoid analyzer artifacts.[3] Although the measured peaks had full widths at half maximum intensity of about 1 eV, we could locate peak maxima by fitting a quadratic function to the upper 30% of the peak with a precision of typically 5 meV (1 standard deviation).

The results reported here were obtained with polycrystalline Cu, Ag, and Au foils. The surfaces were cleaned by a 4.5-keV argon-ion bombardment but the foils were not annealed.

III. RESULTS

It is convenient to refer all electron energies to the Fermi level of the target material. The incident electron energy E_i at the specimen is

$$E_i = eV_c + \phi_c + E_t , \tag{1}$$

where ϕ_c is the thermionic work function of the tungsten cathode and E_t is the most probable thermal energy of thermionically emitted electrons from the cathode. We estimate E_t to be approximately kT where T is the cathode temperature; the actual value of E_t depends on the gun design and on the gun operating conditions.[4] Our gun was operated under temperature-limited conditions (i.e., minimum cathode temperature and maximum anode voltage) to eliminate space-charge effects.

The most probable energy of electrons in the elastic peak E_e measured by the analyzer is

$$E_e = eV_a + eV_p + \phi_a , \tag{2}$$

where ϕ_a is the average work function of the analyzer; the CMA cylinders are fabricated from copper which, for our instrument, is well oxidized.

The difference between the incident electron energy and the elastic peak energy is

$$\Delta E = E_i - E_e$$
$$= e(V_c - V_a - V_p) + (\phi_c - \phi_a) + E_t . \quad (3)$$

If there were no energy transfer to the target, ΔE would be zero and the difference between the energies corresponding to the two externally measured voltages V_c and V_a would be

$$e(V_c - V_a) = eV_p - (\phi_c - \phi_a) - E_t . \quad (4)$$

The values of each term on the right-hand side of Eq. (2) are not known with high accuracy but each term is expected to be independent of V_c. That is, the right-hand side of Eq. (4) should be constant for a given set of operating conditions (cathode temperature and voltage between the CMA cylinders).

We have found experimentally, however, that $e(V_c - V_a)$ is a function of V_c in the range of 67–1247 V and, to a lesser extent, of specimen material; that is, ΔE in Eq. (3) is a function of V_c. It is not possible for us to measure absolute values of ΔE since the terms on the right-hand side of Eq. (4) are not well known for our instrument. To present our results in the most meaningful way, we have assumed $eV_p = 50.000$ eV and arbitrarily selected $(\phi_c - \phi_a) + E_t$ to be 0.350 eV to ensure that all values of ΔE from Eq. (3) were positive; the latter choice is believed to be reasonable considering likely values of ϕ_c, ϕ_a, and E_t.[4,5]

Figures 1–3 show plots of ΔE as just defined for copper, silver, and gold as a function of electron energy. The range of ΔE values corresponding to the extreme values of V_c is 155, 199, and 170 meV for Cu, Ag, and Au, respectively.

We also show in Figs. 1–3 the recoil energy loss ΔE_r calculated using the model of Boersch *et al.*[1] From conservation of energy and momentum for single elastic scattering of 20–40-keV electrons by a single atom, they find

$$\Delta E_r = (4m/M)E \sin^2(\theta/2) , \quad (5)$$

where m is the electron mass, M the atomic weight for the target atom, E the incident energy, and θ the scattering angle. For our instrument, the mean value of θ is 138°. The range of ΔE_r values corresponding to the experimental range of V_c is 35, 21, and 11 meV for Cu, Ag, and Au, respectively. These values are smaller than the experimental ranges by factors of 4.4, 9.5, and 15.5, respectively.

The experimental values of ΔE in Figs. 1–3 show an approximately linear dependence on V_c, as expected from Eq. (5), but there is weak structure for all three materials at values of V_c between about 300 and 600 eV. There is also a small material dependence but not as indicated by Eq. (5). We have made preliminary measurements of ΔE for Al which, from Eq. (5), would be expected to be larger

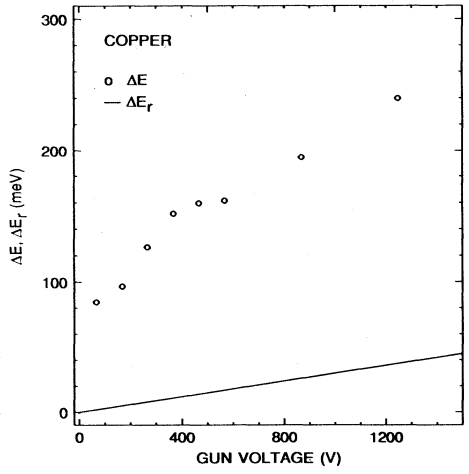

FIG. 1. Plot of the energy transfer ΔE (O) for copper as defined by Eq. (3) and calculated values of the recoil energy ΔE_r (solid line) as defined by Eq. (5) as a function of voltage applied to the gun cathode.

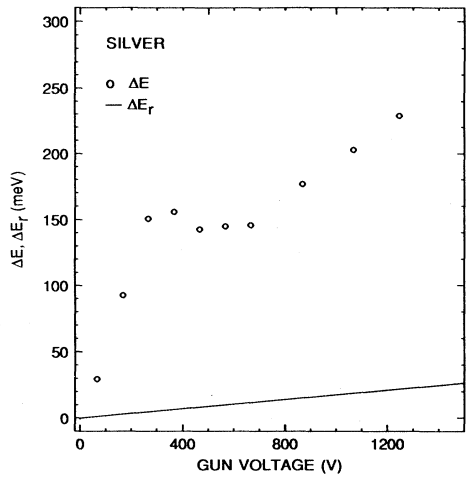

FIG. 2. Plot of the energy transfer ΔE (O) for silver and the recoil energy ΔE_r (solid line) as a function of gun voltage.

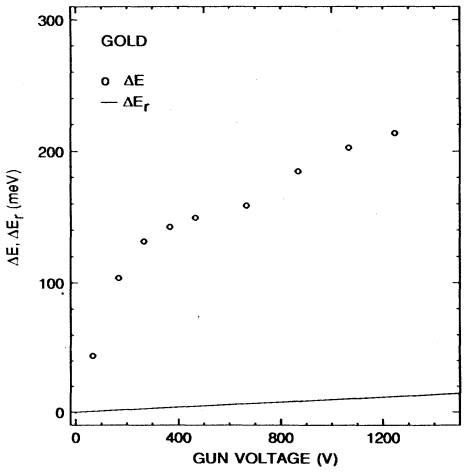

FIG. 3. Plot of the energy transfer ΔE (O) for gold and the recoil energy ΔE_r (solid line) as a function of gun voltage.

than those for the other elements. We find, however, that the ΔE values for Al are close to those for Cu.

We wanted to be sure that the observed ΔE values were not an electron-optical artifact of the analyzer. We have previously found that elastic-peak positions could vary if the incident electron beam was deflected to different points on the target surface within the analyzer field of view. Some dependence of this type is expected on account of the complex relationships between source position, angular acceptance, and energy aberrations for the CMA.[6] Additional effects have been found for our instrument and attributed to mechanical imperfections.[3] We have found, nevertheless, that rastering of the incident beam over the specimen surface in the analyzer field of view is an effective means of averaging analyzer aberrations and allows consistent data to be acquired for different incident energies.

The analyzer field of view is a function both of electron energy and of pass energy.[7] Our CMA behaves semiquantitatively as expected although deviations attributed to instrumental imperfections have been found.[8] We have checked for a possible instrumental effect on measured ΔE values by reducing the pass energy eV_p down to 10 eV; no effect was found.

IV. DISCUSSION

As noted in the previous section, we were not able to measure absolute values of ΔE due to lack of sufficiently accurate knowledge of the value of $(\phi_c - \phi_a) + E_t$. While our selection of the value of 0.350 eV for the net value of this quantity is arbitrary, the value is believed to be reasonable.

The range of the observed ΔE values, up to about 200 meV, for Cu, Ag, and Au in our incident energy range is appreciably greater than expected from the simple atomic model found useful by Boersch *et al.*[1] at much higher incident energies. It therefore appears that other energy-transfer mechanisms need to be considered.

The ΔE values we observe are roughly comparable to phonon-excitation energies.[9] For our incident energies and disordered surfaces prepared by ion sputtering, phonon excitations will be likely. At the incident energies of 20–40 keV used by Boersch *et al.*,[1] phonon-excitation cross sections will be much smaller and the recoil losses can be estimated by considering elastic scattering by single atoms.

Without an electron monochromator and a high-resolution analyzer, we cannot observe directly the spectrum due to single and multiple phonon excitations. Although we measure with our instrument only the envelope due to elastic and inelastic scattering events, we believe it reasonable that the maxima in our measured elastic peaks should shift with incident energy and to a lesser extent with material due to changing cross sections for phonon excitations.[9]

Our results are significant in the use of elastic peaks for the calibration of the energy scales of electron spectrometers with high accuracy.[2] We had intended to use measured elastic peaks from the scattering of electrons of known incident energy to calibrate the energy scale of our analyzer to better than 20 meV in order to make high-accuracy measurements of photoelectron binding energies and Auger-electron kinetic energies which could then be used for the calibration of other instruments. We expected to determine E_i in Eq. (1) from an accurate measurement of V_c and an experimental determination of $(\phi_c + E_t)$ from a comparison of an elastic peak with $V_c \approx 1248$ eV and a measurement of the Fermi edge in a valence-band photoemission spectrum of nickel excited by magnesium x rays.[2] We found, however, as reported here that measured elastic peaks from Cu, Ag, and Au did not track the applied voltages V_c in the energy range of interest with the required accuracy.

We therefore conclude that the elastic-peak method should not be used for energy-scale calibration in the range 70–1250 eV if accuracies better than about 0.2 eV are required. The elastic-peak technique is now routinely used for the calibration of the energy scale of Auger-electron spectrometers with incident energies often of 2 keV. Such calibrations, by extrapolation of Figs. 1–3, should not be relied on to better than about 0.4 eV. The desired accuracies of core-electron binding energies measured by x-ray photoelectron spectroscopy are now about 0.1 eV, and those of Auger-electron kinetic energies are about 1 eV, although it is likely that higher accuracies in the latter measurements could be useful in identification of the chemical state from the chemical shifts of Auger lines.

Ibach[10] has looked for and found no shift of true elastic peaks recorded at high-energy resolution in the specular scattering of 7- and 251-eV electrons by a Ni(110) surface at an angle of incidence of 59°. In our experiment, however, we observe the convolution of all inelastic (presumably phonon) and elastic scatterings possible for our conditions (large scattering angle, large analyzer acceptance angle, and disordered target surface). The continuous shift of our quasielastic peaks with increasing incident energy is presumably associated with an increasing probability of exciting modes of higher energy or with the possibility of multiphonon excitations.

V. SUMMARY

We have observed energy transfers in the quasielastic scattering of 70–1250-eV electrons sputtered Cu, Ag, and Au. It was not readily possible for us to measure absolute values for the energy transfers, but the range of values for our incident energies was up to about 200 meV with a small dependence on material. These energy transfers appear to be associated with different probabilities for phonon excitations as a function of incident energy.

In our experiment, we measured shifts in the measured positions of elastic peaks with a double-pass cylindrical-mirror analyzer for different voltages applied to the cathode of the electron gun. The energy scales of these and other analyzers are often calibrated using the elastic-peak method and a single known voltage, generally 2000 V, applied to the cathode of the electron gun. Our results indicate that the calibration accuracy will not be better than 0.2 eV in the 70–1250-eV energy range and, by extrapolation, is not expected to be better than about 0.4 eV if the calibration is performed at 2 keV.

ACKNOWLEDGMENTS

We thank Dr. H. Ibach for useful discussions and for communicating results from his laboratory.

---

*Formerly National Bureau of Standards.

[1]H. Boersch, R. Wolter, and H. Schoenebeck, Z. Phys. **199**, 124 (1967).

[2]See, for example, C. J. Powell and A. Mandl, Phys. Rev. B **6**, 4418 (1972); C. J. Powell, N. E. Erickson, and T. Jach, J. Vac. Sci. Technol. **20**, 625 (1982).

[3]N. E. Erickson and C. J. Powell, J. Vac. Sci. Technol. A **4**, 1551 (1986).

[4]R. D. Young, Phys. Rev. **113**, 110 (1959).

[5]J. Holzl and F. K. Schulte, in *Solid Surface Physics,* Springer Tracts in Modern Physics, Vol. 85 (Springer, New York, 1979), p. 1.

[6]C. F. Eagen and E. N. Sickafus, Rev. Sci. Instrum. **48**, 1269 (1977).

[7]M. P. Seah and H. J. Mathieu, Rev. Sci. Instrum. **56**, 703 (1985).

[8]N. E. Erickson and C. J. Powell, Surf. Interface Anal. **9**, 111 (1986).

[9]H. Ibach and D. L. Mills, *Electron Energy Loss Spectroscopy and Surface Vibrations* (Academic, New York, 1982); M. Rocca, H. Ibach, S. Lehwald, and T. S. Rahman, in *Structure and Dynamics of Surfaces I,* edited by W. Schommers and P. von Blanckenhagen, Topics in Current Physics, Vol. 41 (Springer, New York, 1986), p. 245; D. L. Mills, J. Electron Spectrosc. Relat. Phenom. **44**, 239 (1987).

[10]H. Ibach (private communication).