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# The neon Auger spectrum produced by ion bombardment of aluminium and silicon surfaces

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Abstract. Measurements are reported of the Auger (autoionization) spectrum of Ne produced by bombarding AI and Si surfaces with Ne<sup>+</sup> ions with energies in the range 400 eV to 5 keV. The shift in the Ne peak energies with incident ion energy is shown to follow a very simple Doppler model. The data are found to contain many small Auger peaks in addition to the two characteristic peaks recorded by previous workers. This new structure is shown to be consistent with gas-phase data and with measurements of the autoionizing states in Ne I.

#### 1. Introduction

Auger electron emission from solids under bombardment by energetic ions is a well known phenomenon. Such spectra are often very different from electron-excited Auger spectra and generally show more structure with narrower peak shapes. Some of the emitted electrons have been identified as arising from decay of autoionizing states in neutral atoms produced by electron promotion in a compound molecule briefly formed under ion bombardment. Thus, Auger decay can occur in neutral atoms and if the bombardment frees these atoms from the surface, the decay will be an atomic process without any involvement of the band structure of the solid. See [1] for reviews of ion excited Auger emission.

In addition to Auger processes which occur in the sputtered target atoms, Auger decay can also occur from excited states of the incident species. Auger emission, or electron emission from autoionizing states, in the bombarding species has been investigated by several researchers in the case of bombardment with Ne<sup>+</sup> ions [2-7]. The incident ion undergoes neutralization as it approaches the surface and. after interaction, it leaves as an excited atom. Zampieri et al [6] showed that the characteristic Ne electron spectrum was essentially identical for Ne<sup>+</sup> ions or Ne neutrals striking an Al target. Pepper and Aron [7] have shown the importance of using angle-resolved measurements for ion-induced Auger spectroscopy, they found significant differences in Auger spectra measured at different angles of collection relative to the direction of incidence of the ion beam. Pepper [8] explained these differences in terms of Doppler shift in the energy of electrons emitted from moving atoms leading to changes in the emission energy and peak shape with incident energy and scattering angle. Zampieri et al [6] measured the Ne Auger spectrum produced by collision of Ne<sup>+</sup> ions with Mg, Al and Si surfaces and found that the spectra were broadly similar with only two characteristic peaks in each case. They compared their

data with gas-phase measurements [9, 10] which show many smaller peaks in addition to one or two large peaks, depending on the method of excitation. Zampieri *et al* concluded that such extra structure was absent in the Ne electron spectra produced by collision with solids and explained this by postulating that tunnelling to the solid removed the higher excited states by resonant ionization and neutralization.

The present paper reports measurements made on the Ne autoionization spectra produced by the interaction of Ne<sup>+</sup> beams with energies in the range 0.4 keV to 5 keV with Si and Al surfaces. The data obtained are of much improved signalto-noise ratio than previous data. This has enabled us to analyse the Doppler shifts which occur with different ion beam energies in detail. We have been able to examine the structure of such spectra more closely than previous workers and we are able to show that the characteristic Ne electron spectrum has more, rather than less, structure than gas-phase spectra recorded with similar incidence energies.

#### 2. Experimental details

Measurements were made in a UHV chamber with a base pressure of  $3 \times 10^{-10}$  mbar, this pressure rose to  $2 \times 10^{-6}$  mbar when Ne gas was admitted to the ion gun. Spectra were obtained with a concentric hemispherical analyser operated in a constant pass energy mode; this gave an instrumental half width of  $\simeq 0.5$  eV which was virtually constant across the range of measurement. In the configuration used, the spectrometer had an acceptance half angle of about 2°. Ions were produced by a Kratos mini beam 1 ion gun operated in the fine-beam mode; the energy of the electron beam used to produce ions in the gun was set to 50 eV to minimize the production of doubly ionized species. Altering the electron beam energy to 90 eV produced no observable change in the spectra.

Measurements were made in the forward scattering direction. The ion beam, the spectrometer optic axis and the surface normal were coplanar in a horizontal plane. The angle between the ion beam and the spectrometer axis was fixed at 146° in these measurements and the specimen could be rotated about a vertical axis. The only noticeable effect of changing the angle of incidence of the ion beam was to change the intensity of the peaks in the spectra so the specimen was set to give an angle of incidence of the ion beam with the surface of about 15° which was the approximate position of maximum signal. This configuration is closest to the position labelled  $-90^{\circ}$  by Pepper and Aron [7] and is quite different from the geometry of Zampieri et al [6].

Two specimens each measuring 7 mm  $\times$  12 mm were mounted one above the other on the specimen holder. One specimen was cut from a 99.999% Si crystal (doped with 0.005 ppm P). The other specimen was a polycrystalline Al sheet also of purity 99.999%. Before recording ion-induced electron spectra the specimens were cleaned by argon ion bombardment until the carbon and oxygen peaks measured with electron induced AES had merged into the background.

## 3. Results and discussion

#### 3.1. Main features

The Ne Auger spectrum produced by bombarding Al with 5 keV Ne<sup>+</sup> ions is shown in figure 1 and the spectrum produced by similar ions striking a Si substrate is shown in

figure 2. As may be seen from the ratio of peak to background, the Auger signal from the Al substrate is stronger, in agreement with previous measurements. In contrast to the results of Zampieri *et al* [6] a spectrum can readily be obtained with 5 keV ions from Si. These spectra are similar to published data in that they are dominated by two peaks; these are labelled 1 and 3 in figures 1 and 2. Other small peaks may just be distinguished in these spectra. If the kinetic energy is reduced to 500 eV the spectrum shown in figure 3 is obtained from the Al specimen. Some changes can be clearly seen; the ratio of peaks 1 to 3 has increased in agreement with the observations of Zampieri *et al* [6], the small peak labelled 2 has receded into the background and the energies of peaks 1 and 3 have shifted to lower values.



Figure 1. Neon Auger spectrum, 5 keV Ne<sup>+</sup> ions Figure 2. As figure 1, but for silicon. incident on aluminium.

This shift in energy has been observed before and is attributed to a Doppler shift. Pepper [8] has explained the shift on the basis of a model involving detailed consideration of the excitation and scattering processes. We will try a much simpler approach. An ion with incident energy  $E_{\rm I}$  is neutralized as it approaches the target. It interacts with the target losing energy  $E_{\rm L}$  and emerges in an autoionizing state. The atom relaxes by emitting an electron along the spectrometer axis at an angle  $\theta$  to the direction of motion, this electron has energy  $E_{\rm A}$  in the rest frame of the atom and is measured with an energy  $E_{\rm M}$  in the laboratory. The cosine rule gives

$$E_{\rm M} = E_{\rm A} + (m/M)E_{\rm I} + \sqrt{4E_{\rm A}(E_{\rm I} - E_{\rm L})m/M}\cos\theta$$
 (1)

where m is the mass of the electron and M the mass of the Ne atom. If we assume a flat target surface then, with an incidence glancing angle of 15°, excited atoms will be reflected from the surface with emission glancing angles between 15° and 0°. The angle between the ion beam and spectrometer axis is 146° so this will give values for  $\theta$  between 4° (specular) and 19° (grazing exit) and we can put  $\cos \theta \simeq 1$  in equation (1).

The second term on the right will be small except at very high ion energies so equation (1) reduces to

$$E_{\rm M} = E_{\rm A} + (4m/M)^{1/2} \sqrt{E_{\rm A}} \sqrt{E_{\rm I} - E_{\rm L}}.$$
 (2)

Data were recorded for a number of primary beam energies in the range 0.4 keV to 5 keV and the values of the energies of peaks 1 and 3 are plotted in figure 4. A function of the form

$$E_{\rm M} = E_{\rm A} + K(E_{\rm I} - E_{\rm L})^{N} \tag{3}$$

was fitted to the two sets of eighteen points shown in the figure by means of a leastsquares curve-fitting routine. It is clear that the fit is very good and a correlation coefficient > 0.99 is found. The values of the constants obtained were

for peak 1	$E_{\rm A} = 21.1 \pm 0.2   {\rm eV}$	$E_{\rm L} = 340 \pm 30 \text{ eV}$
	$K=0.07\pm0.02$	$N=0.45\pm0.03$
for peak 2	$E_{\rm A} = 24.3 \pm 0.1 {\rm eV}$	$E_{\rm L} = 360 \pm 20 \text{ eV}$
	$K = 0.06 \pm 0.01 \text{ eV}$	$N = 0.46 \pm 0.02.$

Equation (2) gives the values N = 0.5 and K = 0.052, values close to those obtained by fitting equation (3) to the data. An independent check on the value of  $E_{\rm L}$  may be made by looking for the energy threshold for excitation of the Ne peaks. The lowest ion energy for which the peaks could be observed was 380 eV. Plotting the peak heights as a function of incident energy in the range 0.4 keV to 0.8 keV gave an extrapolated value for zero intensity of 340 eV, a value in good agreement with the measurements of Ferrante and Pepper [2]. It proved impossible to fit a model which assumed that the incident ion lost a constant fraction of its initial energy in the interaction.



Figure 3. Neon Auger spectrum, 0.5 keV Ne<sup>+</sup> ions incident on aluminium.



Figure 4. Variation of the energies of peaks 1 and 3 from Ne<sup>+</sup> on aluminium with incident ion energy. The circles show experimental points and the lines are least-squares fits of the function described in the text.

## 3.2. Fine structure

In addition to peaks 1 and 3 smaller peaks labelled 2 and 4 can be seen in figure 1. Other peaks are present at higher energies. Figure 5 shows the region of the spectrum with energy greater than peak 3 on an amplified scale. The smaller peaks are now emerging. If a smooth background is subtracted from the curve in figure 5 and the resultant amplified, seven additional peaks can be easily resolved, figure 6. As noted above the signals from the Si target were smaller than the signals from the Al substrate but a similar background fitting procedure applied to the Si data reveals the presence of a similar set of peaks, figure 7. Peaks in the Si data have different relative intensities but a shift of 0.3 eV to lower energies causes the peaks from Si to overlay those from Al, except for peak 2 which seems to be at the same energy in both sets of data. This small shift in energies is consistent with a small change in the contact potential difference between specimens and suggests that the peaks occur at the same energies relative to the vacuum level in both specimens, apart from peak 2. This peak would have a lower energy in the Si data if the shift is due to CPD and peak 2 may arise from Ne atoms which decay inside the solid surface with a consequent reduction in the final state energy due to screening by the electrons in the solid. This screening would be expected to be smaller in Si.



Figure 5. Higher-energy neon Auger spectrum, 5 keV Ne<sup>+</sup> ions incident on aluminium.



Figure 6. As figure 5, but with a smooth background subtracted.



Figure 7. As figure 6, but with 5 keV Ne<sup>+</sup> ions incident on silicon.

Some of the peaks may be indexed using the gas-phase data of Andersen and Olsen [10]. The procedure outlined in 3.1. above places the rest-frame energies

of peaks 1 and 3 at 21.1 eV and 24.3 eV. Examination of the results of Andersen and Olsen give transitions from the  $2p^43s^2$  <sup>3</sup>P and the  $2p^43s^2$  <sup>1</sup>D initial states as the only possibilities. Andersen and Olsen measured the energy of electrons ejected from these states as 20.35 eV and 23.55 eV respectively. This suggests an error in our measurements due to contact potential difference and calibration uncertainty of -0.75 eV, a not unreasonable figure. Interestingly, in the Olsen and Anderson data [9] peak 3 (their peak c) is always dominant and peak 1 (their peak a) is small or absent except in the one case where they used accelerated Ne<sup>+</sup> ions to produce a spectrum, then peak 1 dominated and peak 3 was small.

**Table 1.** Column 1 shows measured values. Column 2 shows measured values with constant energy subtracted to bring peak 3 into registry with gas-phase data [10]. Column 3 shows measured values corrected for Doppler shift as described in the text. Column 4 shows gas-phase data of Andersen and Olsen [10]. The initial states are given as footnotes.

Peak	1	2	3	4
1	23.5	20.2	20.4	20.35 <sup>a</sup>
2	25.6	22.3	22.4	22.90 <sup>b</sup>
3	26.8	23.55	23.55	23.55°
4	29.2	25.9	25.7	25.50°, 25.65 <sup>f</sup>
5	30.3	27.0	26.7	26.70 <sup>i</sup>
6	31.3	28.0	27.7	27.30 <sup>j</sup>
7	34.1	30.8	30.4	
8	35.8	32.5	32.0	
9	37.5	34.2	33.5	
10	39.0	35.7	35.0	
11	39.4	36.1	35.4	

a (<sup>3</sup>P)3s<sup>2 3</sup>P.

<sup>b</sup> (<sup>3</sup>P)[3s3p(<sup>3</sup>P)]<sup>3</sup>D, <sup>3</sup>P.

 $^{\circ}$  (<sup>1</sup>D)3s<sup>2</sup> <sup>1</sup>D.

• (<sup>3</sup>P)[3s4s(<sup>3</sup>S)]<sup>1</sup>P.

 $(^{1}D)[3s3p(^{3}P)]^{3}F$ 

<sup>1</sup> (<sup>3</sup>P)[3p<sup>2</sup>(<sup>3</sup>P)]<sup>1</sup>D, <sup>1</sup>P.

 $^{j}$  (<sup>1</sup>D)[3s3p(<sup>1</sup>P)]<sup>1</sup>F, <sup>1</sup>P, <sup>1</sup>D.

Column 1 in table 1 shows the energies of the eleven peaks which could be readily resolved with a value of 0.75 eV subtracted from our spectrometer readings. Agreement between the values in table 1 and the data of Andersen and Olsen is bad. However, the data in table 1 are taken with a 5 keV ion beam and are Doppler shifted. If we subtract a further 3.29 eV peak 3 is brought into agreement with peak c; the effect of this on the remaining peaks is shown in column 2. Agreement with the data of Andersen and Olsen is now better but not good. Examination of equation (2) suggests why the two sets of data refuse to come into register. The Doppler shift depends on both the ion energy and the Auger energy. If we fit peak 3 to peak c by means of the relationship

$$E_{\rm M} = E_{\rm A} + C\sqrt{E_{\rm A}}$$

and use this relationship to correct the data in column 1 for Doppler shift then the values shown in column 3 are obtained. The value found for C by this procedure is 0.68 which compares with a value of 0.71 calculated from equation (2) using

 $E_{\rm L} = 360$  eV. Column 4 shows the measurements of Andersen and Olsen using the labelling of their second paper [10]. Candidates can be found for all of our observed structure up to peak 6. This leaves peaks 7-11; there are no peaks present in the Andersen and Olsen data above 30.10 eV so no explanation can be offered for these based on the low-energy gas-phase data. They may arise from excitation of Ne<sup>+</sup> or Ne<sup>++</sup> ions or they may be due to excitation in Al-Ne complexes. Edwards and Rudd [11] recorded peaks with energies up to 38.27 eV when bombarding Ne with He<sup>+</sup>. H<sup>+</sup> and Ne<sup>+</sup> ions in the 150 keV to 250 keV range and were able to index some of these peaks in terms of excitations of Ne<sup>++</sup>. They indexed most of their observations in terms of the promotion of single electrons while Olsen and Andersen suggested that two-electron excitations were much more likely. This makes it difficult to compare and combine the two sets of data since each set of authors uses different labels for peaks in the same energy range. The high-energy data contain many more peaks in the same energy range than the low energy data and it is impossible to determine common peaks with any confidence. Codling, Madden and Ederer [12] have measured the autoionizing states of Ne and their data can be combined with the ionization potential for Ne I [13] to predict the energies of electrons emitted from the autoionizing states. The predicted energy of an electron emitted by decay of the highest autoionizing state measured by Codling et al is 63.4 eV, so peaks 7-11 could certainly arise from the decay of Ne I states. The data of Codling et al contain over 60 resonances in the energy range 45 eV to 85 eV and cannot be used to index the peaks shown in table 1 with any confidence. However, if Auger peak energies are calculated from this data no peaks are predicted in the ranges 27.7-29.0 eV, 31.3-32.1 eV and 33.9-35.0 eV. These gaps are broadly consistent with the data of column 3 in table 1.

#### 4. Conclusions

We have presented the results of careful measurements of the energies of the principal neon Auger peaks excited by ion bombardment of aluminium. Our measurements were made in the forward scattering direction. We have shown that the variation of the peak energies with incident ion energy can be accounted for by means of a simple model in which the incident ion loses only a relatively small amount of energy in interacting with the solid. This excitation energy is independent of the incident ion energy and is in good agreement with the threshold energy for Auger electron production by the incident Ne<sup>+</sup> ions. The Auger spectrum produced by a silicon target is similar to that of aluminium and, in contrast to measurements made in a backscattering direction [6], no cut-off was observed at high incident ion energies.

We have shown that the data from both aluminium and silicon targets contain similar fine structure and we conclude that the suggestion that the presence of the solid suppresses the higher excited states of Ne<sup>+</sup> by resonant tunnelling [5,6] is incorrect. By subtracting a smooth background this structure is easily measured. The values obtained for the Auger energies, when corrected for Doppler shifts, are in good agreement with gas-phase data [10] and are consistent with measurements of the autoionizing states in Ne I [12].

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