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Contribution of singly and doubly ionized argon to the autoionization (Auger) spectrum of argon excited by bombardment of magnesium and scandium surfaces

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Abstract. Electron spectra produced by bombarding targets of Mg and Sc using argon ions accelerated through potentials between 300 V and 5 kV are reported for different electron energies in the ionizer box of a hot filament type ion gun. By suitable choice of ionizer energy, beams of Ar^+ and beams of mixed Ar^+ and Ar^{2+} ions could be produced. It is shown that Ar^+ and Ar^{2+} ions can both give rise to similar argon Auger spectra but the behaviour of the intensities of the Auger peaks differs with the ionic species. In the case of excitation by Ar^+ ions no spectrum is visible below a threshold energy (280 eV for Sc, 2.8 keV for Mg) but beyond threshold the size of the Auger peak increases with ion energy. With Ar^{2+} excitation no threshold was observed down to the lowest accelerating potential used and the Auger signal was found to decrease with increase in ion energy. This behaviour is consistent with two different mechanisms being responsible for the Ar^{**} state which initiates the autoionization process.

1. Introduction

The electron spectrum of Ne produced when Ne ions bombard solid targets of elements such as Mg or Al at the start of the third period shows considerable fine structure which is broadly similar to the spectra obtained in the case of gas phase collisions [1–3]. Exact details of the excitation mechanism remain to be clarified but the spectra can be indexed largely in terms of collisionally excited processes in Ne^{**} with two 2p electrons promoted to autoionizing states. The excited neutral atom then relaxes by an Auger process to give a singly charged ion and a free electron. The electron spectra of Ar and Kr [3, 4] recorded under similar conditions also show structure, although not to the same extent as Ne. The spectrum for Ar and Kr can be indexed on the basis of similar initial states to those of Ne, with an appropriate principal quantum number n: states with open shell structures $np^4(n+1)s^2$, $np^4(n+1)s(n+1)p$ and $np^4nd(n+1)s$ are excited and decay to the ground state of the singly charged ion with the emission of an electron [4].

Guillemot *et al* [5] commenting on the work of Blum *et al* [3] suggested that the electron spectrum of Ar produced by argon ions incident on a magnesium target arises solely because of the presence of Ar^{2+} ions in the ion beam used to excite the spectrum. Guillemot *et al* reported that when they used velocity selected ions containing only Ar^+ to excite an electron spectrum no structure was observed in the Ar region but that spectra similar to those published were obtained when Ar^{2+} ions were used. In this they agree with the work of Eeken *et al* [6] who showed that Ar^{2+} ions were responsible for similar structure in the electron spectrum of Ar scattered from Pb. Eeken *et al* considered the possible interaction mechanisms in some detail and concluded that the incoming ion is neutralized by resonant transfer and de-excites

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before contact with the surface. Guillemot *et al* [7] studied the scattering of velocity selected Ar^{2+} from Mg and Al and concluded that, as in the case of Pb, the excited states of Ar^{**} were produced by electron capture in the incoming trajectory and that the excited atoms decayed by Auger emission before striking the surface, a result confirmed by measurement of the Doppler shift in the emitted electrons.

In our work on the Ar and Kr spectra [3, 4] the ion gun used was of a simple hot filament type, without velocity selection, and with the electron energy in the ionizer box set at a high value to maximize beam current, so that the beam certainly contained multiply ionized Ar. The suggestion of Guillemot *et al* [5] would seem reasonable in these circumstances. However, Brenten *et al* [8], using velocity selected Ar^{+} ions, recorded similar spectra to that reported by Nixon *et al* [4] when scattering Ar^{+} from a thin film of potassium. For singly charged ions to produce Auger electrons, collision with a target atom is required to create a doubly ionized state which is screened at the metal surface. An excited atom then emerges from the surface, e.g. for Ar in a configuration such as $3p^4 4s^2$ or $3p^4 3d4s$. The accessible states are identical to those available to neutralize Ar^{2+} but the emission energies will be different due to a reduction in the velocity of the incident Ar^{+} ion on collision and a consequent difference in the Doppler shift. Moreover, the relative probabilities of the various possible excited states being involved in the emission process will not be the same for Ar^{+} and Ar^{2+} ions.

We have recently completed systematic measurements of the collisionally excited electron spectra from elements Ca–V [9] and found measurable electron spectra from the bombarding ions Ne, Ar and Kr. This paper reports the results of a detailed study of the electron spectrum of Ar obtained from Mg and Sc targets in an attempt to understand in more detail the origin of such spectra. The purpose of this paper is not to classify uniquely the spectral features observed but to identify which come from neutralization of Ar^{2+} ions and which come from further ionization of Ar^{+}.

2. Experiment

Details of the spectrometer and ion gun have been reported previously [1]. The spectrometer was operated in a constant pass energy mode with a mean hemisphere energy of 22 eV. This gave an instrumental half width of $\sim$0.4 eV, constant over the energy range reported here. Careful measurement using an electron gun indicated that the energy calibration of the spectrometer was linear in the range used, although absolute calibration of the electron energy is difficult because of work function differences and offset potentials in the spectrometer.

In the measurements described below slight changes were made to the set-up used to record the spectra reported in the earlier papers. The angles of incidence (15°) was similar to that used previously but the negative bias used to post-accelerate electrons in to the spectrometer was not used and the specimens were grounded during measurement. In the Kratos Minbeam ion gun used in these and previous measurements, ions are produced in the ion source by means of a beam of electrons accelerated through a potential which may be varied by the user, the ionizer electron energy (IE). As supplied, the control box did not allow an IE below 50 eV and for the measurements described below the control box for the ion gun was modified to permit electron energies in the ionizer box below the limit set by the manufacturer. By reducing the ionizer electron energy below the second ionization potential of Ar the presence of Ar^{2+} ions can be eliminated. Lowering the ionizer energy reduced the electron beam current, and hence the ion beam current, which is the reason why some of the spectra shown below are noisy.

Specimens were cut from polycrystalline foils of Mg and Sc, both of 99.9% purity. The data recorded below were obtained from a dual specimen consisting of a 7 mm wide Sc specimen mounted above a 7 mm Mg specimen. The specimen was moved 6 mm between

measurements so cross contamination by sputtered material would be unlikely. However, all the results reported below were confirmed by separate measurements on single specimens. The use of the dual specimen enabled comparison between spectra to be made under identical conditions. Specimens were cleaned by bombardment with 3 keV Ar ions and were monitored by electron excited AES during cleaning. Ion excited spectra were not recorded until the characteristic metallic Auger peaks had fully developed and the oxygen and carbon levels had merged into the background in the electron excited spectra.

All the graphs shown below have had a smooth background subtracted and in some case they have been 'normalized' by dividing the spectra by the measured ion current, although, as indicated below, this does not actually give a response per unit beam current in all cases.

3. Results and discussion

Figure 1 shows the electron spectrum of Ar excited by collision of Ar ions produced with an ionizer energy of 100 eV and accelerated through 4 kV to strike a scandium target. The rest frame energy of the principal peak is estimated as 11.4 eV, see below. The shape of the spectrum is broadly similar to that from an Al target [4] where the principal peak has an estimated rest frame energy of 12.0 eV. A Dirac–Fock calculation [4] estimates the energy of Auger emission from the $3p^4 4s^2(^3P)$ excited state to the ground state of Ar^+ as being in the range 11.2 to 11.4 eV, in very good agreement with the energy of the principal peak measured from Sc targets. The smaller broad peak seen at an energy $\sim$1.4 eV above the main peak in figure 1 may contain a contribution from the $3p^4 4s^2(^1D)$ excited state, calculated to lie $\sim$2.1 eV above the $3p^4 4s^2(^3P)$ state, and it may also contain contributions from initial states in the $3p^4 4s3p$ configuration since calculation suggests that the energies of some of these multiplets lie between the $3p^4 4s^2(^3P)$ and $3p^4 4s^2(^1D)$ states [4].

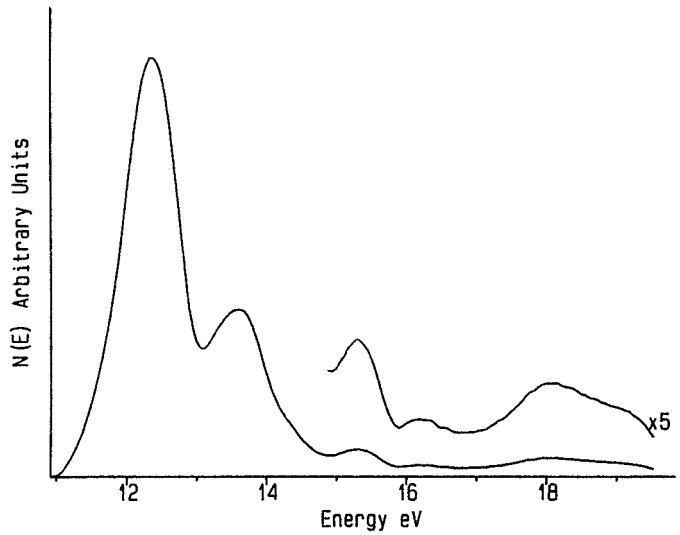

Figure 1. Auger spectrum of Ar from an Sc target using an ionizer electron energy (IE) of 100 eV and a beam accelerating potential of 4 kV.

The absence of calibration standards in electron spectroscopy makes the exact energy calibration of an electron spectrometer difficult and this difficulty is compounded in the case of the spectra from the ion incident species by the presence of significant Doppler shifts.

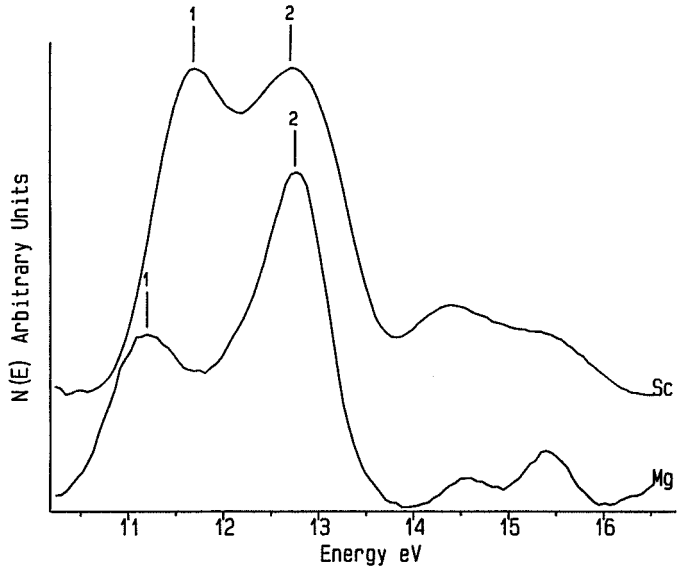

Figure 2. Auger spectra from Sc and Mg using an IE of 100 eV. Beam accelerating potential, 4 kV for Mg and 900 V for Sc.

Under the conditions of our measurements, it has been shown that the Doppler shift obeys a simple relationship [1, 3, 4] with

$$E_M = E_0 + k(E_I - E_L)^N$$

where E_M is the measured value of the electron energy, E_I is the incident ion energy and E_0 is identified as the rest frame energy. The parameters k, E_L and N are treated as adjustable parameters to give a best fit curve and the values obtained compared with theoretical predictions. Within this model the rest frame energy for the Ar $3p^4 4s^2(^3P)$ peak from Al was found to be (12.0 ± 0.2) eV [4]. The same procedure applied to the Ne spectrum excited by collision with an Al target gave (24.3 ± 0.1) eV for the Ne $3s^2(^1D)$ peak. The rest frame energy of this peak has been measured as 23.55 eV in the gas phase by Anderson and Olsen [13] using a traceable calibration method. This gives a correction for our spectrometer of 0.7 eV to account for cpd and offset potentials. Applying this correction to the Ar data from Al we obtain a value for the $3p^4 4s^2(^3P)$ peak of (11.3 ± 0.2) eV which agrees with the predicted energies from a Dirac–Fock calculation of 11.2 eV to 11.4 eV [4]. If a similar process is applied to the Mg data the corresponding value for the Ne calibration peak is (23.8 ± 0.1) eV, a value of 0.5 eV lower than the energy from the Al target, and this is consistent with the difference in cpd predicted from the work functions of Al and Mg [14]. However, if this value is used to correct the measured value of the Ar $3p^4 4s^2(^3P)$ peak from Mg a value of (12.3 ± 0.2) eV is obtained, which is significantly higher than the value from the Al target. This seems to suggest that the presence of the target affects the energy of the emitted electron as indicated by Eeken *et al* [6] in their model calculations.

Spectra of the type shown in figure 1 are only obtained for a particular range of incident ion energies. If different energies are used spectra of quite different appearances may be obtained. Figure 2 shows the spectrum recorded from Mg at an accelerating potential of 4 kV and from Sc using a potential of 900 V; the Mg spectrum has been shifted by -1.1 eV and scaled to the same amplitude as the Sc spectrum for comparison purposes; the higher energy of the peak

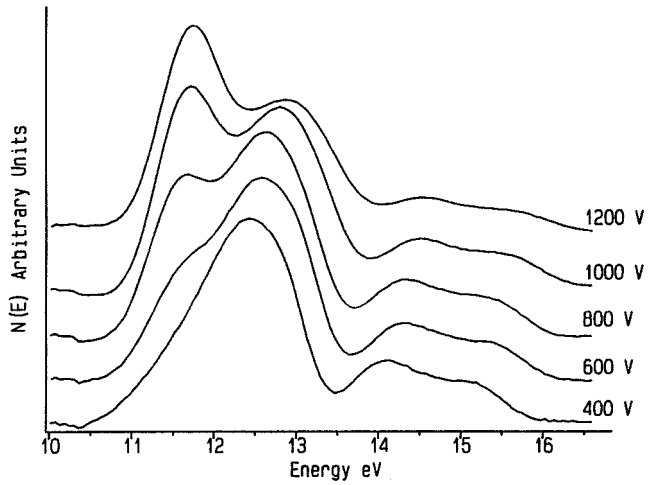

Figure 3. Auger spectra from Sc using an IE of 100 eV with accelerating potentials shown on the curves.

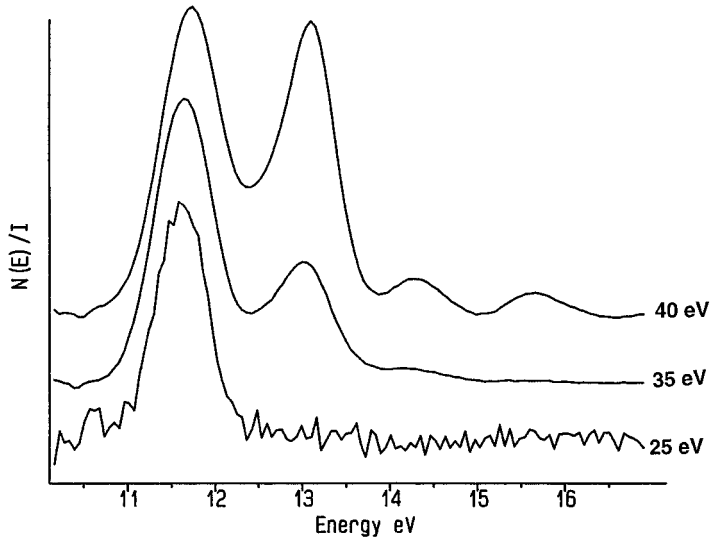

Figure 4. Normalized Auger spectra from Sc using an ion accelerating potential of 900 V with ionizer energies shown on the curves.

from the Mg target is consistent with a larger Doppler shift occasioned by the higher energy ions. In both cases an extra strong peak can be observed in addition to the single large peak seen in the spectra of the shape shown in figure 1. In the case of Sc the large peak shown in figure 1 is the peak 1 in figure 2 while for Mg the large peak found with lower ion energies corresponds to peak 2 in figure 2. The sequence of the development of these 'extra' peaks may be seen in figure 3 which shows the spectra from the Sc target at accelerating potentials between 400 V and 1200 V. At low energies peak 1 is absent and as the energy increases peak 2 broadens and peak 1 emerges. As the ion beam energy is further increased peak 1 grows in amplitude and peak 2 reduces until, at high energies, the spectrum shown in figure 1 is

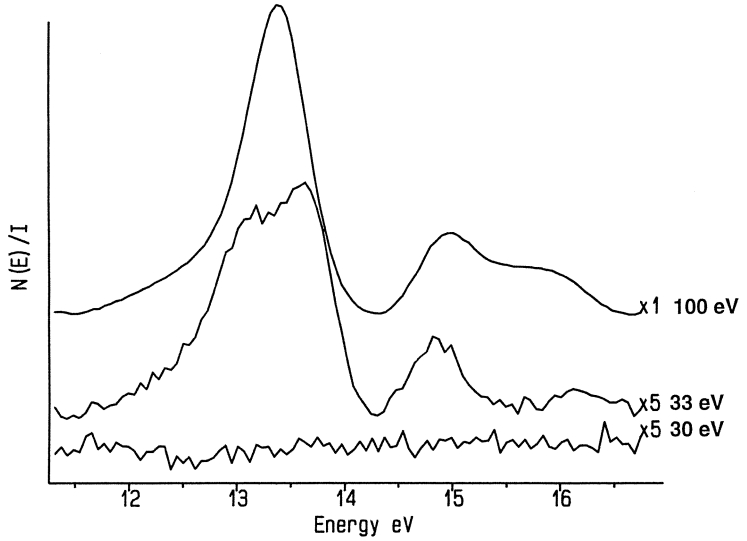

Figure 5. Normalized Auger spectra from Mg using an ion accelerating potential of 800 V with ionizer energies shown on the curves.

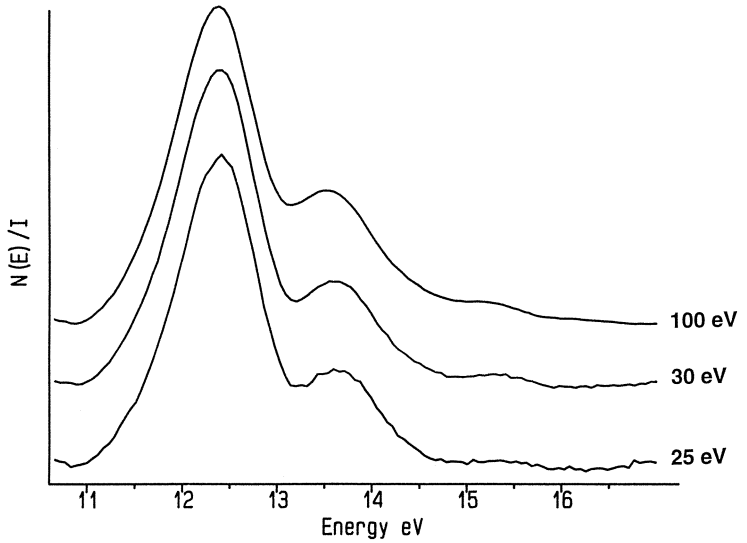

Figure 6. Normalized Auger spectra from Sc using an ion accelerating potential of 4 kV with ionizer energies shown on the curves.

observed. The spectrum from Mg behaves in a similar manner, except that the peak 1 is not detectable at ion accelerating potentials much below 3 kV.

The origins of these different peaks becomes clear if the spectra containing both peaks 1 and 2 are observed as a function of ionizer electron energy as illustrated in figure 4 for Sc; these spectra have been normalized by dividing by the incident ion current. At an IE of 100 eV peak 2 is larger than peak 1 for ions accelerated through 900 V onto Sc, while at an IE of 40 eV peak 1 is now the greater. A further reduction in IE to 35 eV causes a further diminution in

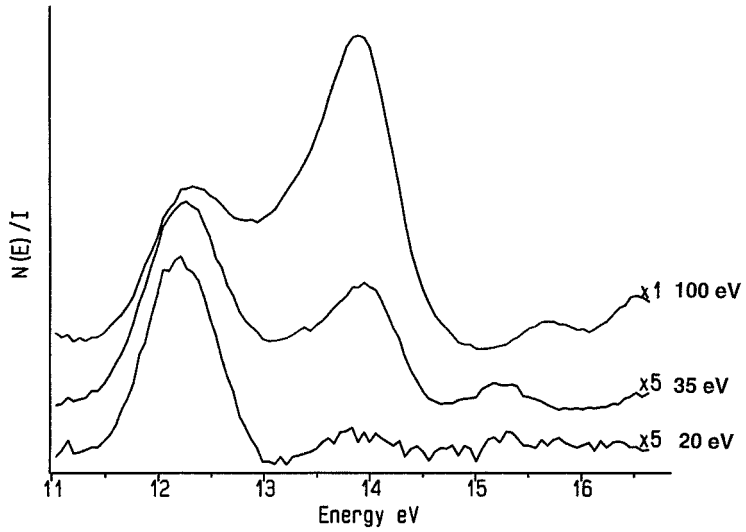

Figure 7. Normalized Auger spectra from Mg using an ion accelerating potential of 4 kV with ionizer energies shown on the curves.

peak 2 while at 25 eV the peak 2 has vanished while the normalized peak 1 has changed little in height. The increase in noise is a consequence of the beam current having reduced from 1.8 μA to 0.1 μA as IE was decreased; the noisy spectra make background fitting difficult and the absence of structure other than the single peak at an IE of 25 eV may not be significant. When this variation in IE is repeated for the spectra obtained at low ion energy from Mg targets, only peak 2 is observed and this vanishes for an IE below 30 eV, figure 5. The high energy spectra also show variation with ionizer electron energy. In the case of ions accelerated through 4 kV onto Sc no significant changes in shape are seen as the IE is reduced and within experimental error the normalized peak height remains constant as the IE is reduced from 100 eV to 25 eV as shown in figure 6. This is definitely not the case for the 4 kV spectra from Mg illustrated in figure 7. Here, as the IE is lowered peak 2 disappears while the normalized peak 1 is essentially unchanged in height.

These observations can be explained if it is assumed that both Ar^+ and Ar^{2+} can give rise to broadly similar shaped electron spectra involving the same basic configurations but with different excitation cross-sections as a function of ion energy and with different Doppler shifts. In the case of Mg at low ion energies, figure 5, the contribution from Ar^+ is absent so when the IE is lowered below the second ionization potential for Ar, thus removing Ar^{2+} from the ion beam, the entire electron spectrum vanishes. The value of IE at which the Ar spectrum disappears is measured as 30 V on the ion gun meter which is slightly above the value of 27.62 V, the second IP of Ar [10], but the meter is uncalibrated and there may well be some screening effects in the ionizer box of the gun. For Mg at high ion energies, figure 7, where the second peak has appeared, reduction in IE below 30 eV causes peak 2, due to Ar^{2+}, to vanish while peak 1, due to Ar^+, remains. The same behaviour is observed with Sc although the energies where peaks 1 and 2 appear and disappear are quite different. At an incident ion potential of 900 V and an IE of 40 eV contributions from both Ar^+ and Ar^{2+} are present, figure 4. Lowering the IE causes a reduction and eventual elimination of the Ar^{2+} contribution. At an incident ion potential of 4 kV, figure 6, only contributions from Ar^+ are present and reduction of the IE has no effect on the spectrum, beyond the introduction of noise due to the sharply

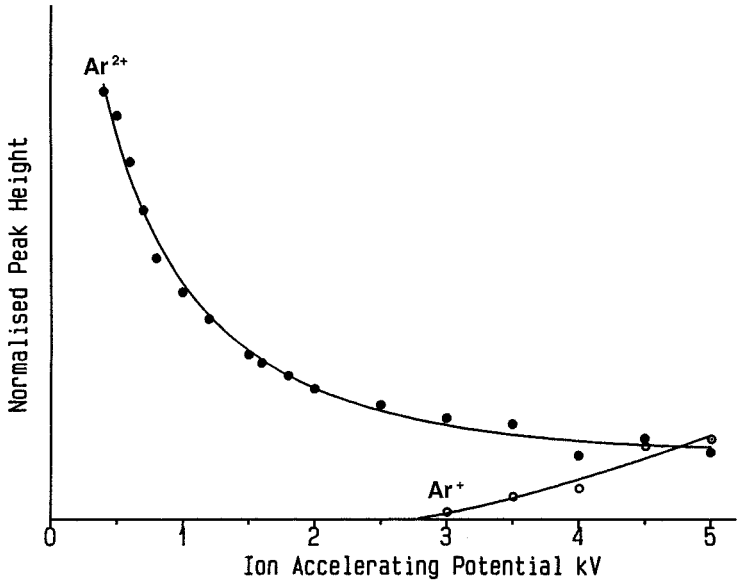

Figure 8. Normalized peak height of the Ar^+ peak (peak 1) and the Ar^{2+} peak (peak 2) from Mg targets as a function of beam energy.

decreased ion beam current. Thus, we conclude that the lower energy peaks labelled 1 in figure 2 are produced by Ar^+ ions and higher energy peaks labelled 2 are produced by Ar^{2+} ions.

One consequence of this is that the calculated parameters in the Doppler model referred to above will be in error since, under the conditions of the measurements reported in [3], the peaks will have been produced by Ar^{2+} ions as suggested by Guillemot *et al* [5]. This means that the doubly charged incident ion will have energy $2E_I$ and the theoretical value of k will increase by a factor of $\sqrt{2}$ to 0.037. The measured value of 0.03 ± 0.04 with this value within error.

An attempt has been made to measure the variation in peak height of peak 1 (Ar^+) and peak 2 (Ar^{2+}) as a function of ion accelerating potential by fitting Gaussian peaks to the measured spectra to give a best fit and dividing the height of the best fit peak by the beam current. The results are shown in figures 8 and 9. Several caveats must be applied to these figures since the measurements of normalized peak height is difficult. One problem noted before [11] is that the ion beam defocuses at low energies and may become larger than the entrance pupil of the electron spectrometer and this will lead to too large a measure of beam current being used in normalization. Where signals become small, and hence noisy, due to the reduction in the beam current at low energies, it becomes difficult to align the ion beam to produce optimum signals. In addition, dividing by totally beam current to normalize signals does not really make sense where the beam current comprises two different fractions giving rise to each of the peaks measured. Provided that the ion fractions do not change with beam energy then the 'normalized' peak heights will be self-consistent, although direct comparisons cannot be made. The amount of Ar^{2+} in the beam may be roughly estimated using data from figure 4. The ratio of the heights of the Ar^+ peaks at IEs of 40 eV and 35 eV is 1.03, while the beam current at 35 eV is 1.66 μA. If we use the height of the Ar^+ peak as a measure of the Ar^+ current this gives an Ar^+ current of 1.71 μA for the 40 eV IE. The measured

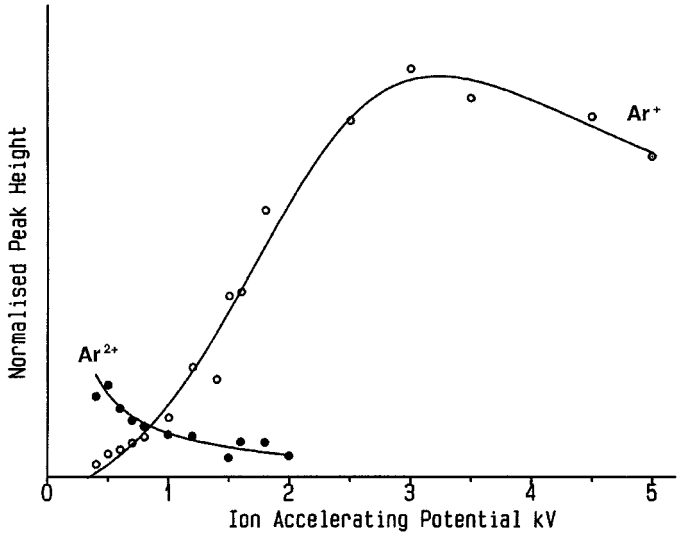

Figure 9. Normalized peak height of the Ar^+ peak (peak 1) and the Ar^{2+} peak (peak 2) from Sc targets as a function of beam energy.

current was 1.82 μA suggesting a contribution of 0.11 μA or 6% from Ar^{2+}, which is of the order estimated by Guillemot *et al* [5] as ∼10% with an IE of 150 eV. This means that the normalized peak heights of the Ar^{2+} peaks will be a very severe underestimate of the relative contribution of Ar^{2+} ions. As the IE is reduced the relative fraction of Ar^{2+} will reduce. The effect of this can be seen in figure 5 where the relative height of the Ar^{2+} peaks from Mg reduce with IE while in the case of Sc, figure 6, where the beam current is close to a true measure of the Ar^+ content, the relative peak height is unchanged for different IE within error.

While figures 8 and 9 do not represent an exact measurement of the variation in cross-section with energy they do present a general picture of the behaviour of the Ar^+ and Ar^{2+} generated peaks. At low energies the Ar^+ spectrum is absent and does not appear until an accelerating potential threshold is reached. Once the principal Ar^+ peak has appeared the peak height increases with ion energy, reaching a broad maximum in the case of Sc to give a variation similar to that of the Ne peak from Al measured by Ferrante and Pepper [12]. In the case of Mg the Ar^+ peak was still increasing at the highest energy achievable with out ion gun, 5 keV. The Ar^{2+} generated peaks behave differently, decreasing in intensity with ion accelerating potential for both Mg and Sc targets. This would seem to agree with the different excitation mechanisms proposed for Ar^+ and Ar^{2+} ions; electron promotion after binary collision with a surface atom for Ar^+ and resonant neutralization on the inward path for Ar^{2+}. In the case of the Ar^+ spectrum from both targets there was a cut-off energy below which the electron spectrum could not be observed. This cut-off energy was estimated by extrapolation of the best fit smooth curves through the data to zero peak height and values of 280 eV for Sc and 2.8 keV for Mg were obtained. Since Guillemot *et al* [5] used selected Ar^+ ions above this energy in their measurements on Mg, the question to be asked is why did they not observe an argon spectrum? The answer probably lies in the signal to noise ratio in their measurements. The Ar spectra taken at high energies from Mg targets (shown in figures 2 and 7) are very much smaller in intensity than the Mg spectrum. At 4 keV incident ion energy the ratio of Ar:Mg principal peaks is ∼1:20. Data published by Guillemot *et al* show very small Mg peaks with

a signal to noise ratio of no better than 15:1 and with this ratio any Ar spectrum would be lost in noise.

The rest frame energies of the principal peaks in the Ar spectrum from the Sc can be calculated by extrapolation of the experimental data. Values of (11.4 ± 0.1) eV and (12.3 ± 0.2) eV are obtained for the Ar^+ and Ar^{2+} peaks respectively. The difference in energies is significant and may be due to interaction with the substrate, as mentioned previously, although whether both Ar^+ and Ar^{2+} peaks shift with substrate is impossible to say. It would be instructive to perform calibrated measurements on the series of fourth period metals to see whether the Ar^+ $3p^4 4s^2(^3P)$ peaks remain at constant energy. It is clear from the above that the Ar^{2+} peaks does vary with target element.

The above measurements were repeated using a beam of Ne ions accelerated through 1 kV incident on the Mg target. Ne spectra identical to those previously published [3] were obtained. No change was observed in the shape of the spectra as the IE was reduced through the second IP of Ne. A graph of the principal Ne peak height versus IE extrapolated to give a value of 24.7 ± 0.9 V as the onset potential of the Ne^+ beam. This figure is again higher than the first IP of Ne, 21.559 V [10], and if this correction of $\sim$3 V is applied to the measured value of 30 V for the onset potential of the Ar^{2+} peaks the corrected figure agrees with the second IP of Ar within error.

4. Conclusion

Electron spectra consistent with the decay of Ar^{**} atoms can be obtained with both Ar^+ and Ar^{2+} incident ions on Mg and Sc targets. The spectra from Ar^+ ions cannot be excited below a cut-off energy, measured as 280 eV for Sc and 2.8 keV for Mg under the conditions of these measurements. There does not appear to be cut-off potential for spectra from Ar^{2+} ions: the intensity of the normalized spectra was found to increase with decrease in accelerating potential down to the lowest value used in these measurements, 300 V, This behaviour is consistent with the Ar^{**} initial state being generated by different mechanisms, resonant neutralization for Ar^{2+} and binary collision for Ar^+.

The electron spectra from Ar^+ and Ar^{2+} are similar but not identical and further work needs to be done to define the differences precisely. The Ar^{2+} $3p^4 4s^2(^3P)$ peak varies in energy with substrate by small but significant amounts. Further work is needed using different targets to establish the systematics of these processes.

Acknowledgment

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References

[1] Gallon T E and Nixon A P 1992 *J. Phys.: Condens. Matter* **4** 9761
[2] Xu F, Mandarino N, Olivia A, Zoccali P, Camarca M and Bonnano A 1994 *Phys. Rev.* A **50** 4040
[3] Blum V, Brugger A, Nixon A P and Gallon T E 1994 *J. Phys.: Condens. Matter* **6** 9677
[4] Nixon A P, Gallon T E, Yousif F and Matthew J A D 1994 *J. Phys.: Condens. Matter* **6** 2681
[5] Guillemot L, Maazouz M and Esaulov V A J 1996 *J. Phys.: Condens. Matter* **8** 1075
[6] Eeken P, Fluit J M and Niehaus A 1992 *Surf. Sci.* **273** 160
[7] Guillemot L, Lacombe S, Esaulov V A and Urazgildin I F 1995 *Surf. Sci.* **334** 224
[8] Brenten H, Muller H, Niehaus A and Kempter V 1992 *Surf. Sci.* **278** 183
[9] Kim K F, Gallon T E, Matthew J A D and Kersten C 1999 *J. Phys.: Condens. Matter* **11** 5273
[10] Moore C E 1949 *National Bureau of Standards Circular* 476

[11] Gallon T E 1996 *J. Phys.: Condens. Matter* **8** 1081
[12] Ferrante J and Pepper S V 1976 *Surf. Sci.* **57** 420
[13] Andersen N and Olsen J O 1977 *J. Phys. B: At. Mol. Phys.* **10** L719
[14] *Goodfellow CD ROM Catalogue* 1998 (Cambridge: Goodfellow)