Production and Decay of Double L Vacancies in Argon and Phosphorus*

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Measurements have been made at two laboratories which indicate that the structure reported at 450–550eV in the electron spectrum from Ar^+-Ar collisions by Ogurtsov, Flaks, and Avakyan is spurious. It is argued that the double L vacancies which they invoke to explain the structure are more likely to decay by the two-step Auger process $L^2{\rightarrow}LM^2{\rightarrow}M^4$ than by the one-step process $L^2{\rightarrow}M^3$ suggested by these authors. Evidence supporting this is found in our electron spectra from P^+-Ar collisions, where it is known from energy-loss and charge-state measurements that double L vacancies are produced in phosphorus.

I. INTRODUCTION

Fano and Lichten[1] have interpreted energy-loss measurements[2,3] in Ar^+-Ar collisions in terms of the now well-known molecular-orbital promotion model. The three energy-loss peaks observed are presumed to be due to the promotion of zero, one, and two L electrons from the pair of colliding atoms. These and more recent energy-loss measurements[4,5] for Ar^+-Ar collisions do not have sufficient resolution to unambiguously distinguish the promotion of two electrons in one atom from the promotion of one electron in each of the two atoms. However, the spectrum of Auger electrons ejected after such promotions would be different in the two cases and can be used to determine which process actually takes place.

Ogurtsov, Flaks, and Avakyan[6] (hereafter referred to as OFA) have presented spectra of electrons detected at 54.5° in 15-keV Ar^+-Ar collisions in which there appears to be structure in the energy region 450–550 eV. Without identifying lines, they assign this group to transitions of the type $L^2_{2,3}{\rightarrow}M^3 + e^-$. If correct, this would indicate not only that is it probable that double vacancy states are produced in argon atoms in such low-energy collisions, but also that these states decay by a one-step process involving the simultaneous filling of two vacancies with all of the excess energy being given to a single M-shell electron, which is then ejected.

Though this result might be of considerable significance, it has never been confirmed. We have attempted to obtain such spectra under similar conditions by experiments on four different sets of apparatus at two laboratories, but have found that such structure, if it exists at all, must have a cross section three to four orders of magnitude smaller than that given by OFA. We also present evidence from the Auger spectrum of phosphorus, which indicates that when such double L-shell vacancies are created, they decay by a two-step process involving the emission of two Auger electrons, rather than the one-step process suggested by OFA.

II. EXPERIMENTAL APPARATUS

Data are presented here from experiments using four different sets of apparatus. Certain common features of all four will be described first, followed by brief separate descriptions of each.

In all cases the ion beam was momentum analyzed and finely collimated before entering the target region and caught in a shielded and biased Faraday cup after passing through the target gas. Most runs were at a gas pressure of 1–2 mtorr. Electrons leaving from a short length of the beam at the scattering center passed through an electrostatic energy analyzer and were detected by an electron multiplier. Individual electron pulses from the detector were amplified and shaped by logic circuits for counting. Magnetic fields at the scattering center and analyzer were reduced to below 10 mG by three pairs of Helmholtz coils. At this level, the field would have little or no effect on electrons above 100 eV, which is the range of interest of this experiment. The collision chamber, the electrostatic analyzer plates, and the pipes connecting them were coated with colloidal graphite (Aquadag) to minimize reflection and secondary emission of electrons from the surfaces. High-purity argon (maximum 0.005% impurities) from commercial sources was used, and the gas lines to the chamber were evacuated and flushed at least twice before measurements were made.

Care was taken to prevent secondary electrons

from surfaces struck by the ion beam from reach-
ing the detector. This is extremely important
since the production of secondaries from solid
surfaces is much more copious than from the
target gas. The estimated uncertainty in the ab-
solute values of the cross sections presented here
is 50% up to about 300 eV. This comes mainly
from uncertainties in the detection efficiency and
the pressure measurement.

The four sets of apparatus will be labeled A–D,
and are as follows.

Apparatus A. This apparatus at the Institute
of Physics at Aarhus was built by Dahl. The de-
sign is shown in Fig. 1. The 60° cylindrical ana-
lyzer and detector can be rotated continuously to
give angles relative to the ion beam from 20° to
160°. The ion beam is completely enclosed by a
pipe both before and after passing through the gas
cell to confine any secondaries which may be pro-
duced by the beam. Pumping ports in these pipes
are covered by screens at a negative bias. The
analyzer and detector are likewise completely
enclosed and pumping holes have biased screens
on them. The circular aperture S_3 is imaged by
the analyzer at the slit S_5. The sizes of S_3, S_4,
and S_5 are such that no electrons passed by them
can strike the plates of the analyzer. The energy
resolution is 0.9%. The cone of the Mullard Chan-
nel Electron Multiplier B 419 B1 could be biased
either positively or negatively, and negative volt-
ages of as much as –100 V were used in this work.
This tended to reduce the background due to spu-
rious low-energy electrons, although due to the
semiconducting nature of the cone surface, the
entire cone was not at the same potential.

Apparatus B. This apparatus at the Institute
of Physics at Aarhus is designed for electron-ion
coincidence studies.[7] A 90°, 35-mm-radius,
spherical electrostatic analyzer provides a large
solid angle of acceptance for the electrons. This
feature makes the electron-ion coincidence appa-
ratus well suited also for electron studies in which
the production cross section is exceedingly small,
as is the case for Auger electrons originating
from an $L^2 \rightarrow M^3$ process. The analyzer accepts
electrons which are emitted $96° \pm 3°$ from the beam
direction. The observed target length is 1 mm.
The energy resolution is 1.5%. The electron de-
tection system is a Mullard Channel Electron
Multiplier B 419 B1. To suppress contributions
from low-energy background electrons, a small
negative potential is applied to the detector-en-
trance cone. The incident ion beam is defined by
two circular 0.8- and 0.5-mm-diameter dia-
phragms, 300 mm apart. The beam current pass-
ing through the gas is monitored by a shielded
Faraday cup.

Apparatus C. This is a chamber originally
built by Rudd and Jorgensen[8] and slightly modified
by Cacak and Jorgensen,[9] who took the Ar^+-Ar
data quoted here at a resolution of 4.2%. Their
published data went only to 350 eV, as the statis-
tics were relatively poor beyond that energy for
some parameters. However, if one is willing to
accept a relatively large statistical error, these
data are of use out to 700 eV. The chamber has
fixed ports at eight angles from 10° to 160° and
uses a 127° electrostatic analyzer and a Dumont
Cu-Be box-and-dynode-type electron multiplier
detector.

Apparatus D. Originally used by Rudd, Sautter,
and Bailey,[10] this apparatus has nine fixed ports
from 10° to 160° and is similar to C, except that a
parallel-plate analyzer is used in place of the
cylindrical one. The energy resolution is 4.6%.

In this apparatus a small count rate was present
which was proportional to the beam current and
gas pressure, but which was independent of any
biases or magnetic fields and was approximately
constant from an analyzer setting of 300–1000 V.
These counts were attributed to high-energy pho-
tons from the collision center which reflected from
the back plate directly into the detector. It is
also possible that neutral argon atoms or high-
energy ions could contribute to this residual count
rate. This problem was noted before and partially
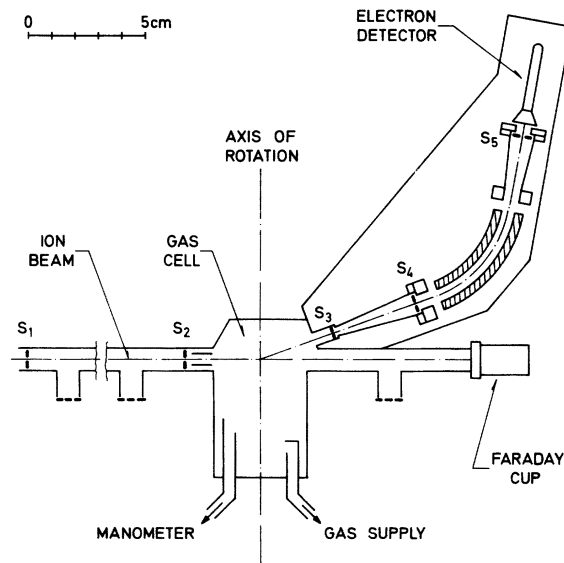corrected by coating the back plate with a colloidal

FIG. 1. Diagram of apparatus A. Analyzer and de-
tector rotate through 360°, thus allowing electron to
be detected from 20° to 160°. Ion beam is collimated
by S_1 and S_2 followed by an electron suppressor and
shield. Circular apertures S_3 and S_4 (both grounded)
collimate electron beam before analyzer.

solution of graphite. This reduced the effect, but
did not eliminate it. For the earlier work at low
energies this residual background represented a
small correction, but in the present work where
very small cross sections were being measured,
steps had to be taken to reduce it still further.
A slot was cut in the back plate large enough to
allow all photons coming through the electron
collimation system to pass through. A wire mesh
grid was put over the slot to eliminate field dis-
tortion, but it was later removed without an ap-
preciable change in the behavior of the analyzer.

The efficiency of the detector decreases sharp-
ly for electrons below about 100 eV. Therefore,
in earlier work we kept the first dynode at a con-
stant positive potential of 200–300 V. We have
found, however, that when detecting electrons
at high energies where the cross sections are
extremely small, the background due to slow
secondary electrons is markedly decreased by
operating the first dynode at a negative bias. Too
large a negative bias, however, causes defocusing
and loss of electrons. The following procedure
was used. For detecting electrons up to 400 eV
the detector bias was varied along with the ana-
lyzer potential so that electrons were accelerated
or decelerated to 200 eV at the first dynode.
Above 400 eV the negative bias was chosen to be
numerically equal to half the electron energy.
The multiplier voltage was adjusted in all cases
to keep the total voltage across the dynode string
constant at 3400 V.

With these precautions the count rate in the

300–900-eV region was reduced to approximately
one count in 10 sec, compared to about 400/sec
at 200 eV. This was not much above the back-
ground count rate, which was about 3/(100 sec)
without the target gas.

To evaluate the contribution to the count rate
due to the photons mentioned above, a bar magnet
was placed in such a way as to provide a magnetic
field of 25–50 G at a point along the electron path
just before the analyzer. This prevented all elec-
trons originating in the collision chamber from
reaching the detector. The remaining count rate
was subtracted from the total count rate to get
the electron count. Absolute cross sections were
calculated from the measured pressure and geom-
etry.[11]

III. EXPERIMENTAL RESULTS

Figure 2 shows several measurements of the
Ar^+-Ar cross sections in this work compared to
the results of OFA. The agreement in absolute
value is good at the 200-eV peak, but poor else-
where. In particular, the upper limit of our cross
sections in the 450–550-eV region is three to four
orders of magnitude smaller than OFA. These
authors have recently indicated[12] that the struc-
ture they reported was probably due to instrumen-
tal effects.

Because the count rates were very small above
300 eV, most of the cross sections measured in
that region had a statistical uncertainty of about
100%. Therefore, the results of this experiment
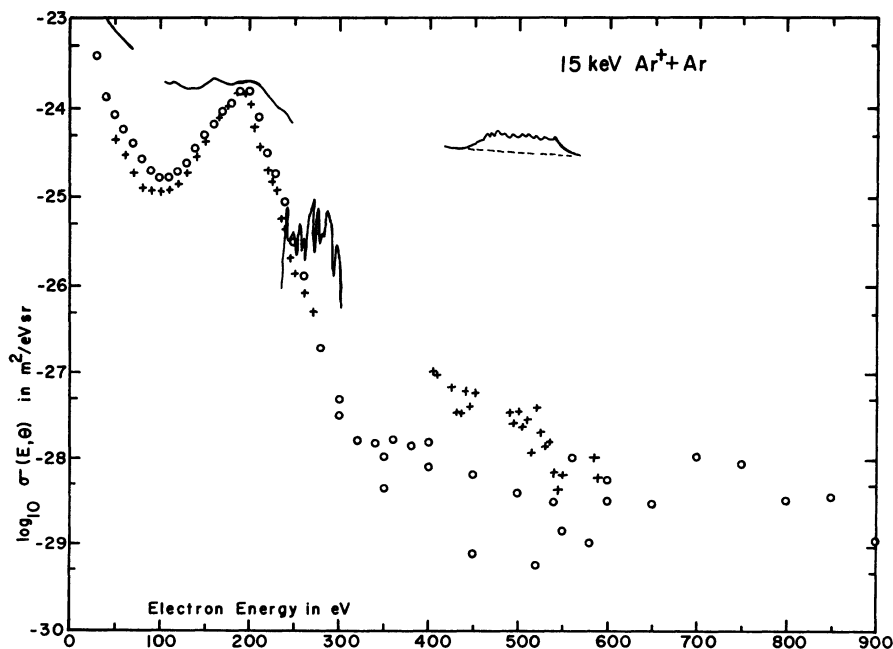are consistent with the hypothesis that the cross

FIG. 2. Cross sections
for electron ejection differ-
ential in energy and angle
for 15-keV Ar^+-Ar colli-
sions. Solid lines: data of
Ogurtsov, Flaks, and
Avakyan (Ref. 6) taken at
54.5°. Crosses: present
data taken at 54.5° on ap-
paratus A. Circles: pre-
sent data taken at 50° on
apparatus D.

section actually falls off exponentially above
300 eV at the same rate as it does between 200
and 300 eV.

In the 230–300-eV range our resolution was not
great enough to detect the fine structure which
OFA reported, but it appears that the general
trend of their cross sections should be decreasing
more than they indicate. A slight bulge in our
curves at 240 eV is the only indication of the
L_1-M^2 Auger transitions suggested to explain the
structure in that range.

It might be expected that a higher primary en-
ergy than 15 keV would be more likely to produce
the double vacancy states and thus the structure
around 500 eV. Figure 3 shows three runs at
50 keV and at a larger emission angle. Again, no
structure is found at that energy and the cross
sections are very small. Runs were also made
at 100 keV with similar results. A portion of
Cacak and Jorgensen's data[9] at 300 keV is also
shown, which indicates no structure at 500 eV.

There are several lines of evidence which in-
dicate that in P$^+$-Ar collisions, double L vacancies

are produced in the phosphorus atom with high
probability, whereas in Ar$^+$-Ar collisions, double
L vacancies in a single atom are less probable.
In the inelastic energy-loss measurements of
Fastrup, Hermann, and Smith,[5] the mean energy
loss in such collisions shows the usual triple peak.
The first one, labeled Q_I, is for an energy loss
involving only outer-shell electrons, while the
next two, Q_{II} and Q_{III}, are due to the removal of
one and two L-shell electrons, respectively, in
addition to the Q_I excitation. From Table I of
Fastrup *et al*., one sees that for P$^+$-Ar collisions,
$Q_{II} - Q_I = B_L(P) \neq B_L(Ar)$ and $Q_{III} - Q_I = B_{L^2}(P)$ but
$Q_{III} - Q_I \neq B_{L^2}(Ar)$ and $Q_{III} - Q_I' \neq B_L(P) + B_L(Ar)$.
For Ar$^+$-Ar collisions, $Q_{III} - Q_{II} = Q_{II} - Q_I = B_L(Ar)$.
Here B_L and B_{L^2} are the binding energies of one
and two $2p$ electrons, respectively. This indicates
that the energy loss involving two L-shell elec-
trons corresponds closely to the energy needed
for the removal of both electrons from the phos-
phorus atom in P$^+$-Ar collisions; but in the case
of Ar$^+$-Ar collisions, the energy loss is more
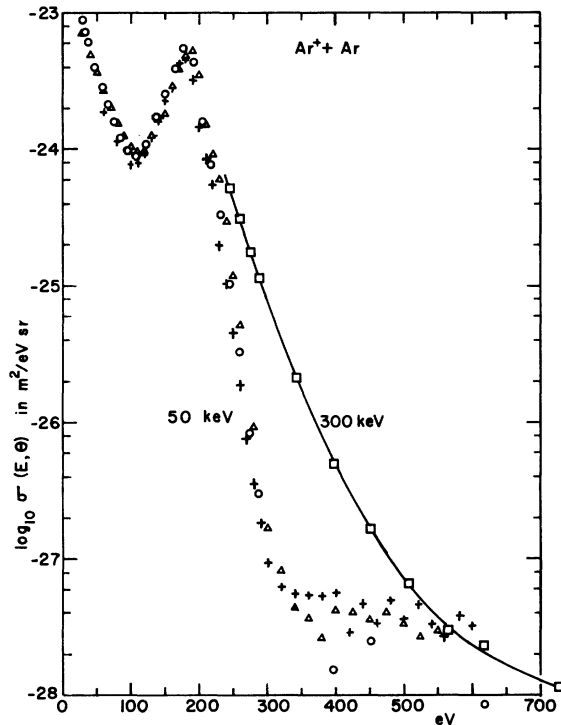nearly equal to that required for the removal of

FIG. 3. Cross sections for electron ejection differ-
ential in energy and angle for Ar$^+$-Ar collisions.
Crosses: present data at 50 keV and 96° on apparatus
B. Triangles: present data at 50 keV and 90° on ap-
paratus D. Circles: data taken at 50 keV and 90° on
apparatus C by Cacak and Jorgensen (Ref. 9). Line and
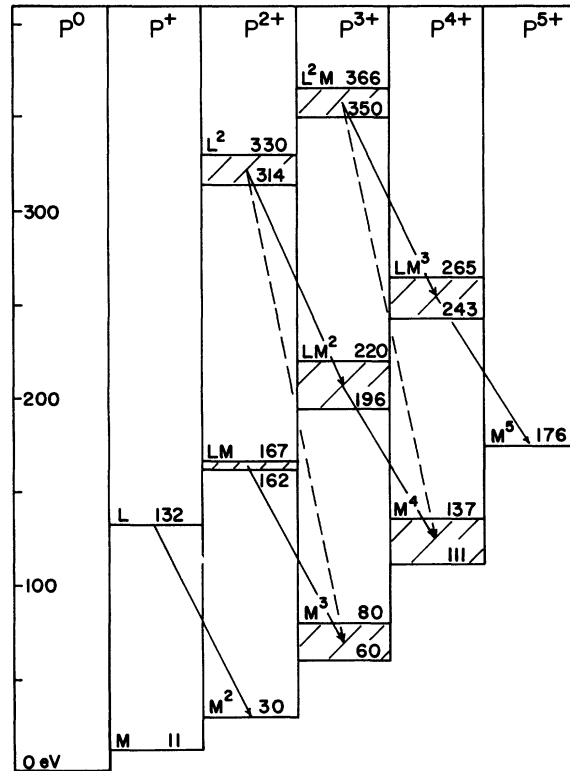squares: data at 300 keV and 90° by Cacak and Jorgen-
sen (Ref. 9).

FIG. 4. Simplified energy-level diagram for phos-
phorus. Only $L_{2,3}$ states are considered. Dotted arrows
show hypothetical one-step transitions from double L
vacancy states. Solid arrows show other Auger transi-
tions.

one L-shell electron from each of the atoms of
the colliding pair. The data, however, are not
able to rule out the possibility that in Ar^+-Ar
collisions, a small fraction of the Q_{III} energy
loss results in the production of double L vacan-
cies in one of the argon atoms.

The evidence that double L vacancies are pro-
duced in phosphorus is supported by charge-state
analysis of the collision products. It has been
shown by Fastrup and co-workers[5] that in P^+-Ar
collisions neither a Q_{II} nor a Q_{III} energy loss
changes the mean-charge state of the argon recoil
from that for a Q_I energy loss.

Evidence that the probability of producing double
L vacancies in one argon atom in Ar^+-Ar colli-
sions is small is also found in the inelastic ener-
gy-loss measurements. It has been shown[5] that
for all asymmetric collisions with argon targets,
$Q_{III} - Q_{II} > Q_{II} - Q_I$, where Q_{III} corresponds to the
production of a double L vacancy in the lower-Z
collision partner. This is consistent with the fact
that the binding energy $B_L{}^2$ of two $2p$ electrons is
more than twice the binding energy of a single $2p$
electron. For Ar^+-Ar collisions, however, it was
found that $Q_{III} - Q_{II} = Q_{II} - Q_I$, which is evidence that
in a Q_{III} energy loss, two L vacancies are pro-
duced, one in each of the target atoms.

The ion-ion coincidence studies of Ar^+-Ar colli-
sions by Kessel and co-workers[13] showed that for
a Q_{III} energy loss, there were no appreciable
correlations between the charge states of the col-
lision products. This was in contrast to a Q_{II} en-
ergy loss, where a definite correlation was ob-
served, corresponding to an L vacancy being pro-
duced in one or the other argon atom. If in a Q_{III}

energy loss, double L vacancies were produced in
one of the argon atoms, then a definite charge-
state correlation should exist.

Additional evidence that double L vacancies are
formed in phosphorus atoms in P^+-Ar collisions
comes from electron-ion coincidence data. From
the energy-level diagram of Fig. 4 it is seen that
no electrons ejected from a single L vacancy state
can have an energy greater than 89 eV if this re-
sults in a final charge state of P^{5+}. However,
Dahl and Lorents[7] presented electron spectra
taken in coincidence with P^{5+} projectiles which
show structure up to energies well over 100 eV.
Such energies are possible from the transition
$L_{2,3}^2 M_{2,3} - L_{2,3} M^3$, the latter decaying to the
ground state of P^{5+} by a second Auger process
as shown in Fig. 4.

In summing up, it is much more likely that
double L vacancies are produced in phosphorus
in P^+-Ar collisions than in either argon atom
in Ar^+-Ar collisions. This suggests that when
looking for Auger electrons from the $L^2 - M^3$
process suggested by OFA, one would have a
better chance of observing them in P^+-Ar than in
Ar^+-Ar collisions. Such a process in phosphorus
would yield electrons with energies between 213
and 270 eV. In the spectrum of electrons at 20°
from 50-keV P^+-Ar collisions this would cause
structure in the energy region of about 240–300
eV, owing to the Doppler shift.[14] We have studied
this spectrum carefully in this region with appa-
ratus A (see Fig. 5) and find no evidence of struc-
ture. We can put an upper limit on the cross
section for such structure at about 4×10^{-25} m^2/sr
at 20°. This is only 0.2% of the size of the cross
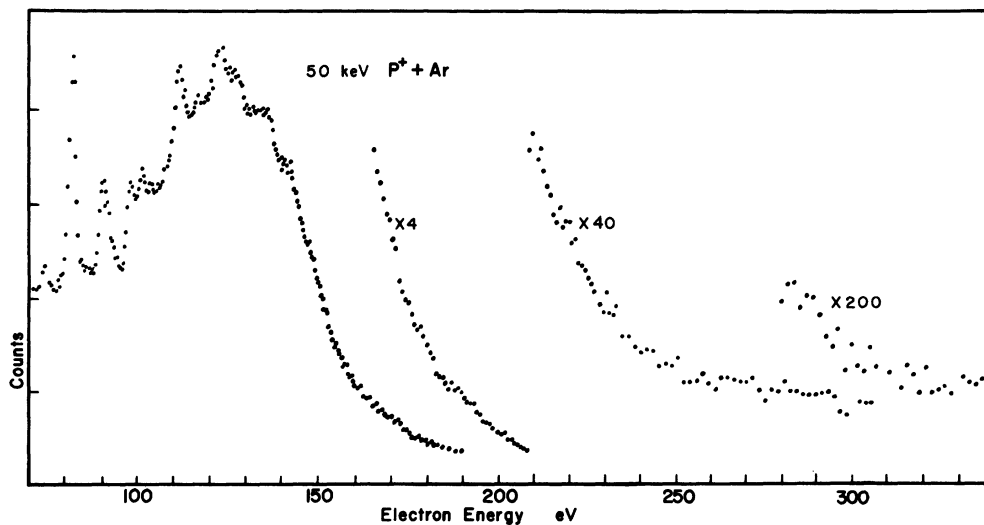

FIG. 5. Electron energy spectrum at 20° from P^+-Ar collisions at 50 keV. Data, taken on apparatus A, represent
counts on a linear scale uncorrected for background and analyzer dispersion.

section for the Auger contribution in the 60–150-eV region.

IV. SUMMARY

Argon electron spectra from which the structure at 450–550 eV reported by OFA is absent have been presented. This indicates either that no double L vacancy states are produced or that if they are, they do not decay by a single Auger transition. Also examined were Auger spectra from phosphorus where it is much more likely that double L vacancy states are produced. However, even here no structure in the Auger spectrum was found in the region expected if such double L vacancies decayed by a one-step Auger process. It is concluded that double L vacancies are much more likely to decay by a two-step than a one-step process.

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