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MNN Auger spectrum of uranium

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Experimental measurements of the electron-excited *MNN* Auger spectrum of uranium are presented over the energy range 2–3 keV. Unambiguous identification of the nine strong *MNN* lines involving initial M_4 or M_5 holes is made by varying the electron excitation energy and through comparison of observed transitions with predicted energies and intensities. Agreement between experiment and theory is generally very good with the exception of the $M_4N_5N_{6,7}$ transition, which is anomalously weak.

I. INTRODUCTION

The element uranium, with 92 electrons, has numerous possibilities for Auger electron emission. Coghlan and Clausing[1] have calculated the energies of over 1000 Auger transitions involving electrons in just the *M* through *Q* shells of the atom. Several investigators[2–9] have reported measuring the low-energy (below 1 keV) portion of the Auger electron spectrum of uranium and have identified many of the Auger transitions involving *N*, *O*, and valence (*P*,*Q*) level electrons. The higher-energy region of the Auger spectrum has received comparatively little attention. Zender *et al.*[10] measured self-excited Auger emission resulting from beta decay of ^{233}Pa, but the possibility of interference from *L*-shell Coster-Kronig transitions prevented identification of *M*-shell Auger emission. In this paper we report the results of experiments designed to measure *MNN* Auger emission from uranium over the range 2–3 keV using electron-beam excitation. Several new Auger lines have been observed and identified, including the uranium transition with the highest multiplicity, the $M_5N_{6,7}N_{6,7}$ line.

II. EXPERIMENTAL

A sample of depleted ^{238}U was cleaned in vacuum (base pressure <25 nPa) by a combination of Ar^+ bombardment and heating to 600 °C in order to remove the preexisting oxide layer. All measurements were made using a monoenergetic electron beam for excitation (2–5 keV) and a cylindrical mirror electron-energy analyzer. The analyzer was calibrated to an accuracy of better than 5 eV from elastic scattering measurements using 2000-, 2500-, and 3000-eV electron beams. The Auger signals were detected using conventional modulation techniques with synchronous detection and were recorded as derivative energy spectra. Signal averaging of several hundred individual scans was used to further enhance the signal-to-noise ratio. During these long experiments, the sample was continuously bombarded with 1 keV Ar^+ (~ 1 μA/cm^2) to prevent buildup of surface contamination. Over the spectral range of 2–3 keV a second-order polynomial was subtracted from the data to remove the slowly varying background. This facilitated presentation in the figure without significantly affecting the peak positions or amplitudes. The signal intensities in the spectra were normalized to the line at 2768 eV.

III. RESULTS

After numerous cleaning cycles, no evidence of surface contamination was observed in the low-energy (below 1 keV) portion of the Auger spectrum (Fig. 1). In particular, the carbon peak minimum

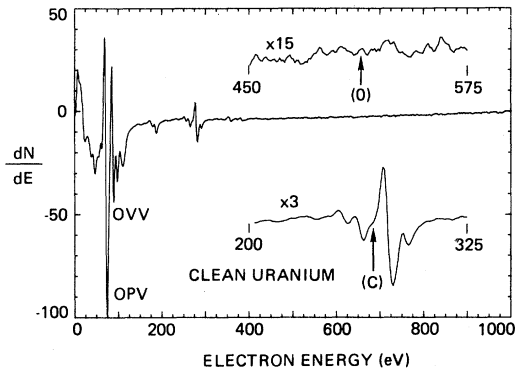

FIG. 1. Low-energy region of electron excited ^{238}U Auger spectrum. Primary electron-beam energy: 2 keV; current: 2 μA; modulation amplitude: 1 eV peak to peak. Average of 200 scans, 30 sec/scan, 30 msec time constant. Signal response relative to $M_5N_{6,7}N_{6,7}$ transition at 2768 eV.

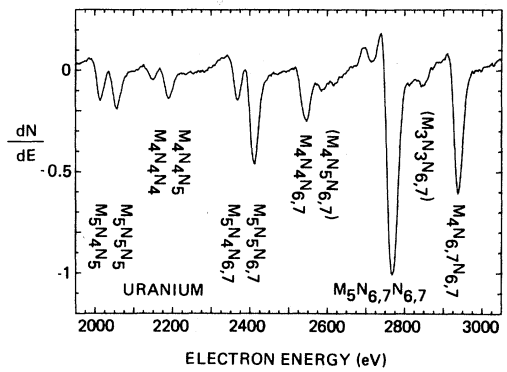

FIG. 2. *MNN* region of electron excited ^{238}U Auger spectrum. Primary electron-beam energy: 5 keV; current: 15 μA; modulation amplitude: 10 eV. Average of 900 scans, other conditions same as Fig. 1. Signal response normalized to transition at 2768 eV.

(at 271 eV), which occurs between two strong uranium transitions (position indicated in Fig. 1 inset) disappeared. The procedure also removed all oxygen detectable at 511 eV. All remaining features have been attributed to uranium Auger transitions.[11]

The spectral region from 2000–3000 eV was found to contain several prominent uranium Auger transitions (Fig. 2). The most intense features occur at 2938 and 2768 eV while other features are seen at lower energies including doublets near 2030, 2160, and 2390 eV as well as single transitions at 2545 and 2710 eV. Through comparison with calculated Auger transition energies (below), it appears that all of these lines result from *MNN* transitions.

The electron beam (5 keV) used to excite the sample was not sufficiently energetic to create *L*-shell vacancies, which require greater than 17 keV for their formation. Consequently, *L*-shell Coster-Kronig transitions, which may emit electrons with energies in this range, cannot be responsible for the observed lines. When the electron-beam energy was reduced from 5.0 to 3.5 keV, the high-energy Auger structure disappeared. This is consistent with our *MNN* assignments since *M*-shell ionization requires excitation greater than 3.55 keV.

The escape depth of the *MNN* Auger electrons from uranium is relatively large compared with the

TABLE I. Uranium $M_{4,5}NN$ Auger transitions.

Transition			Energy			Intensity[a]	
M	*N*	*N*	Obs.	Calc.[b]	Multi.[c]	Obs.	Calc.[d]
4	4	4	2146	2146	0.04	0.06	0.07
4	4	5	2190	2189	0.09	0.11	0.15
4	4	6,7	2545	2542	0.21	0.23	0.23
4	5	5		2231	0.11		0.02
4	5	6,7	2585	2584	0.31	*wk*	0.15
4	6,7	6,7	2938	2941	0.67	0.58	0.67
5	4	4		1970	0.07		0.01
5	4	5	2014	2013	0.13	0.16	0.16
5	4	6,7	2367	2366	0.31	0.18	0.15
5	5	5	2056	2055	0.16	0.14	0.18
5	5	6,7	2411	2408	0.46	0.38	0.42
5	6,7	6,7	2768	2765	1.00	1.00	1.00

[a]Normalized to $M_5N_{6,7}N_{6,7}$ transition.
[b]From Eq. (1) with $\Delta=0.60$.
[c]Transition multiplicities.
[d]Reference 22.

OPV and *OVV* Auger lines seen at lower energies. For the transition at 2768 eV, the escape depth (mean free path) is about 40 Å while the 70-eV $O_{4,5}P_{2,3}V$ Auger electron escape depth is about 4 Å.[12] The relative surface insensitivity of the *MNN* Auger lines was observed in measurements of a carbon-covered uranium surface, which exhibited strong *MNN* emission and the absence of *OPV* lines.

The energies of the Auger transitions observed in the range 2000–3000 eV are given in Table I. The peak minima in the derivative energy spectrum are listed, and no attempt has been made to estimate the zero crossing energy since positive maxima were not evident. Calculated Auger energies for *MNN* transitions are also listed and were calculated according to the semiempirical formula[13]

$$E_{WXY}(Z)=E_W(Z)-E_X(Z)-E_Y(Z+\Delta)\,, \quad (1)$$

where $E_{WXY}(Z)$ is the energy of the emitted *WXY* Auger electron from element Z, E_W, E_X, and E_Y are the binding energies of the appropriate levels involved in the transition, and $E(Z+\Delta) \equiv(1-\Delta)E(Z)+(\Delta)E(Z+1)$. The parameter Δ accounts for the positive charge that results from the formation of a W-level vacancy. This extra charge increases the binding energy of the ion's Y level to approach that of the next heavier element, $E_Y(Z+1)$. Using the Siegbahn *et al.*[14] tabulation of binding energies (Table II), very good agreement was obtained between the calculated and observed Auger transition energies when Δ was set equal to 0.6.

IV. DISCUSSION

The *MNN* uranium Auger transitions, while much less prominent than the valence-level transitions seen at lower energies, are sufficiently intense so as to permit observation. Transitions of the type *WXX* are often the strongest Auger lines observed experimentally, a consequence of electron-electron interactions being most probable between similar orbitals.

The two most intense *MNN* transitions form a doublet at 2768 ($M_5N_{6,7}N_{6,7}$) and 2938 ($M_4N_{6,7}N_{6,7}$) eV. This doublet arises from spin-orbit splitting of the $3d$ electrons, into the M_4 ($3d_{3/2}$) and M_5 ($3d_{5/2}$) levels, which are separated by $\sim$170 eV.

The doublets seen near 2030, 2160, and 2390 eV can be attributed to spin-orbit splitting of the $4d$ electrons, which are split into the N_4 ($4d_{3/2}$) level at 780 eV and the N_5 ($4d_{5/2}$) level at 738 eV. The energy spacing between the transitions in each of these doublets is 42±3 eV, the same as the energy difference between the N_4 and N_5 levels.

Spin-orbit splitting of the $4f$ electrons, which has frequently been observed in photoelectron spectra of uranium,[15,16] was not visible. Instrumental resolution was not sufficient to distinguish between possible Auger transitions involving the N_6 ($4f_{5/2}$) and N_7 ($4f_{7/2}$) levels, which have about a 10 eV energy difference.

The observed Auger transition energies are consistently 28–30 eV higher than those predicted us-

TABLE II. Electron binding energies (eV) for uranium and neptunium.

Shell	Orbital	Pop.	$Z=92$[a]	$Z=92$[b]	$Z=92$[c]	$Z=92$[d]	$Z=93$[e]
M_3	$3p_{3/2}$	4	4304				4435
M_4	$3d_{3/2}$	4	3728				3850
M_5	$3d_{5/2}$	6	3552				3664
N_1	$4s_{1/2}$	2	1442				1501
N_2	$4p_{1/2}$	2	1273				1328
N_3	$4p_{3/2}$	4	1045		1043.0	1043.4	1087
N_4	$4d_{3/2}$	4	780	776.6	778.3	778.3	817
N_5	$4d_{5/2}$	6	738	734.8	736.2	736.2	773
N_6	$4f_{5/2}$	6	392	387.5	388.2	388.1	415
N_7	$4f_{7/2}$	8	381	377.5	377.4	377.2	404

[a]Siegbahn *et al.*, Ref. 14.
[b]Park and Houston, Ref. 19.
[c]Fuggle *et al.*, Ref. 15.
[d]Allen *et al.*, Ref. 16.
[e]Hagström and Fadley, Ref. 20.

ing the relativistic theory of Chen *et al.*[17] This is a reasonable agreement considering the difficulty of accurately constructing relativistic wave functions for uranium. Better agreement is obtained when a semiempirical method, such as the $Z+\Delta$ approach given in Eq. (1), is used to account for relaxation effects in the Auger process.

Subsequent to the binding-energy compilations of Bearden and Burr[18] and Siegbahn *et al.*,[14] Fuggle and co-workers[15] have measured *N*-, *O*-, and *P*-level binding energies using photoelectron spectroscopy for oxidized and metallic uranium. They found a shift of about 3 eV in going from the oxide to the metal and noted that their values for oxidized uranium agreed with the values for metallic uranium reported in the earlier compilations. Similar results have been reported by Park and Houston[19] and by Allen, Trickle, and Tucker[16] (Table II).

When Δ is treated as a free parameter in Eq. (1), the best agreement with our experimental data occurs at $\Delta=0.60$ if the Bearden and Burr or Siegbahn *et al.* binding-energy data is used. Use of either the Fuggle *et al.* or Park and Houston clean metal data requires slightly higher Δ values for best agreement (0.71 and 0.77, respectively). This increase in Δ compensates for the absence in the clean metal of an oxide induced binding-energy shift.

The transition multiplicities, taken as the product of the electron orbital populations, are listed in Table I. The multiplicity values for transitions of the type *WXX*, where both *X* electrons originate from the same orbital, are slightly less than those listed by Coghlan and Clausing[1] because we have taken into account the vacancy in the orbital emitting the Auger electron. Multiplicities are not, in general, a good measure of Auger line intensities, since electron-transition probabilities also depend upon orbital overlap, spin-orbit coupling, and the chemical environment of the atom. Additionally, observed line intensities are affected by various interatom effects such as electron mean-free-path length, backscattering factors, and inelastic scattering. However, since multiplicities are easily calculated and since they definitely are a factor in determining line intensities, they can provide guidance in making assignments. We note that our assignments give the relative intensities $M_5N_{6,7}N_{6,7} > M_4N_{6,7}N_{6,7} > M_5N_5N_{6,7} > M_5N_4N_{6,7}$, $M_4N_4N_{6,7}$. The multiplicities of these levels have the same ordering. This agreement may be due to the fact that the deep (nonvalence) levels involved in these transitions are shielded from chemical effects. Also, the line energies differ by less than 24%, so interatom effects will be similar for each of these transitions.

The $M_5N_{6,7}N_{6,7}$ transition is the most intense feature in the 2—3-keV spectral region. This transition has the distinction of being the uranium Auger transition with the highest multiplicity. The initial vacancy is in the $3d_{5/2}$ orbital, which initially contains six electrons, while the two electrons involved in the Auger decay both come from the $4f$ levels, which initially contain 14 electrons. No other uranium Auger transition involves such highly populated orbitals. This attribute evidently contributes to the strong intensity of the line.

The Auger transition rates for uranium have been calculated by McGuire[21,22] and provide a more quantitative measure of expected signal intensities. In order to compare these calculations with our intensity measurements, the rates have been normalized to the $M_5N_{6,7}N_{6,7}$ transition. For transitions involving the M_4 core-level vacancy, the rates have been reduced by a factor of $\frac{2}{3}$ to compensate for the difference in the populations of the M_4 $(3d_{3/2})$ and M_5 $(3d_{5/2})$ levels. These levels initially contain four and six electrons, respectively. The agreement between our observed intensities and these calculations, as shown in Table I, is very good.

Generally, the calculated rates are similar to those predicted by the simple multiplicity argument. However, the $M_5N_4N_4$ and $M_4N_5N_5$ transition rates are calculated to be very much smaller, and this explains their absence in our spectrum. Similarly, all transitions within the 2000—3000-eV range involving an initial M_3 $(3p_{3/2})$ ionization have calculated rates too small to be observed, except for one, the $M_3N_3N_{6,7}$. This transition, which has a normalized multiplicity of 0.21 and a calculated rate of 0.18, is probably responsible for the weak feature seen near 2850 eV.

An additional peak is seen at an energy (2710 eV) somewhat lower than the prominent $M_5N_{6,7}N_{6,7}$ transition. This may either be a satellite of the $M_5N_{6,7}N_{6,7}$ since no other strong *MNN* transition is expected at that energy, or the $M_5N_5O_5$ line, which has a large multiplicity (0.20).

Thus we have observed and identified all predicted strong *MNN* transitions in the energy range 2000—3000 eV. There is, however, one significant discrepancy between experiment and theory. Both multiplicity and rate calculations for the $M_4N_5N_{6,7}$ transition (see Table I) indicate that it should be rather intense. Surprisingly, our observations showed only a weak transition at the expected energy, 2585 eV. We have no explanation for this apparent anomaly, but McGuire has suggested[23] that there may be significant cancellation of matrix ele-

ments not brought out in one-electron calculations which could reduce the transition rate to a low value. Further calculations are needed to clarify this point.

V. CONCLUSIONS

The *MNN* Auger lines of uranium have been observed and identified using electron-excited Auger spectroscopy. Good agreement between observed and calculated transition energies was obtained. The intensities of the lines were observed to vary according to the electron populations of the levels participating in the Auger process and are in agreement with calculated transition rates except for the $M_4N_5N_{6,7}$ line, which is anomalously weak. The lines are unaffected by surface contamination and provide a means for observing near surface uranium.

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