Title
ELECTRON BINDING ENERGIES FOR HIGHLY IONIZED FISSION FRAGMENT ATOMS

Permalink
https://escholarship.org/uc/item/0bg1c3v3

Authors
Watson, R.L.
Rasmussen, J.O.

Publication Date
1967-01-10

UCRL-17290

University of California

Ernest O. Lawrence Radiation Laboratory

ELECTRON BINDING ENERGIES FOR HIGHLY IONIZED FISSION FRAGMENT ATOMS

Berkeley, California

To be submitted to Journal of Chemical Physics

UCRL-17290
Preprint

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

ELECTRON BINDING ENERGIES FOR HIGHLY IONIZED FISSION FRAGMENT ATOMS

R. L. Watson and J. O. Rasmussen

January 10, 1967

ELECTRON BINDING ENERGIES FOR HIGHLY IONIZED FISSION FRAGMENT ATOMS

R. L. Watson and J. O. Rasmussen

Lawrence Radiation Laboratory
University of California
Berkeley, California

January 10, 1967

I. INTRODUCTION

Recent experiments involving the measurement of gamma rays and their associated internal conversion electrons emitted from primary ^{252}Cf fission fragments have demonstrated that it is now possible to resolve discrete line spectra for many fragments.[1] Although the masses of the fragments undergoing the observed nuclear transitions are simultaneously measured in these experiments, no direct means exists for determining their atomic numbers. It may be possible, however, to ascertain the atomic number of the specific isotope responsible for many of the nuclear transitions by correlating gamma-ray and internal conversion electron energies, the difference in these two energies being equal to the electron binding energy.

It has long been known that primary fission fragments are formed in high states of ionization.[2] Due to the large velocities attained by fission fragments ($\sim 10^9$ cm/sec) immediately upon fissioning, they are unable to carry along many of their outer orbital electrons and hence become highly ionized. Measurements of ^{235}U fission fragment initial ionic charges have indicated that states of ionization ranging from +20 to +24 are commonly attained.[3,4] Since the electron binding energies are directly affected by the state of ionization in an atom, it therefore becomes important to know how the electron binding energies vary as a function of ionic charge before attempting to determine the nuclear charges of fission fragments on the basis of electron binding energy measurements. For this reason, we have undertaken to calculate the binding energies of several atoms which span the region of ^{252}Cf fission products (namely Sr, Pd, Xe and Sm) as a function of ionic charge.

Qualitatively, the effect on the binding energies of stripping a number of outer electrons from a neutral atom may be understood by picturing the electronic charge as residing on concentric spheres centered about the nucleus. Fig. 1a illustrates the repulsive potential due to the electron shells which would be felt by a test charge as it was brought toward the nucleus of such an atom. Before the first shell of charge is reached, the potential is given by $38\ e^2/r$. As this shell is penetrated, its contribution to the potential becomes a constant C_1 and the further increase is due to the remaining charge 36e. The repulsive potential continues to increase in the same fashion until the K shell is penetrated at which point, it becomes constant. The attractive potential on the other hand, is given by $-38\ e^2/r$ and is due to the nuclear charge. By adding these two potentials, the binding potential is obtained and this potential establishes the binding energies of the various electrons.

In Fig. 1b are shown the same potentials for a strontium atom with its two outer electron shells stripped. It is seen that the net effect is to lower the binding potential by the amount $C_1 + C_2$. It is expected, then, that the binding energies of an ionized atom will be higher than those of a neutral atom and furthermore, that these increases in binding energies should be nearly the same for all occupied orbitals of the ion.

II. DESCRIPTION OF CALCULATIONS

The binding energy calculations were carried out using a computer program designed by Roothaan and Bagus[5] employing a non-relativistic Hartree-Fock self-consistent field (SCF) method. The program utilizes an LCAO expansion procedure developed by Roothaan.[6]

In applying the LCAO method, each orbital φ_i is expanded in terms of a given set of suitable basis functions χ_p. Advantage is taken of the symmetry properties afforded by Roothaan's open-shell formulation which permits the orbitals to be grouped in sets, each set transforming under symmetry operations according to an irreducible representation of the symmetry group. Hence, each occupied orbital of a given species and subspecies is constructed from a linear combination of the basis orbitals of the same species and subspecies such that

$$\varphi_{i\lambda\alpha} = \sum_p \chi_{p\lambda\alpha}\, C_{\lambda pi} = \tilde{\chi}_{\lambda\alpha}\, \tilde{C}_{\lambda i} \quad , \tag{1}$$

where the basis functions are given by

$$\chi_{p\lambda\alpha}(r,\theta,\varphi) = R_{\lambda p}(r)\ Y_{\lambda\alpha}(\theta,\varphi) \quad . \tag{2}$$

The indices $i\lambda\alpha$ and $p\lambda\alpha$ are analogous to the quantum numbers nlm used to specify hydrogen-like wave functions. The radial parts of the basis functions used in the computer program are normalized Slater-type functions given by

$$R_{\lambda p}(r) = (2n_{\lambda p})!^{-\frac{1}{2}} \quad (2\xi_{\lambda p})^{n_{\lambda p}+\frac{1}{2}}\ r^{n_{\lambda p}-1}\ e^{-\xi_{\lambda p}r} \quad . \tag{3}$$

In brief, the computational process starts with a set of trial wave functions of the type given in Eq. (1). This requires input estimates of the Slater orbital exponents $\xi_{\lambda p}$ and the vectors $\tilde{C}_{\lambda i}$. Using the basis functions, the integrals[7] entering the Hartree-Fock Hamiltonian are calculated, and an iterative process entered into in which the eigenvectors are solved for repeatedly until the input and output vectors agree within a certain threshold. The iterative schemes used in the program to obtain convergent solutions from as few successive iterations as possible are described in detail by Roothaan and Bagus.

The basis functions are optimized by the variation of the Slater orbital exponents. The method of variation involves complete SCF calculations of the total energy for a series of values of the orbital exponent in question. An extrapolation is then performed to obtain the value of the orbital exponent which minimizes the total energy.

III. RESULTS OF CALCULATIONS

The K binding energies were obtained by computing the total energies of both the ion in question and of the ion with one 1s electron removed. The difference between these two computed total energies, then, is the K binding energy of the ion. In all cases, the total energies were calculated with minimal basis sets (one basis function for each occupied orbital) using fully optimized orbital exponents.

The K binding energies for the neutral atoms are well known.[8] The K binding energies for the single electron atoms (ionic charge of Z-1) are easily calculable from the Sommerfeld relativistic hydrogen atom equation[9] given by

$$E_{n,\ell} = -\frac{2\pi^2\mu e^4}{h^2}\,\frac{Z^2}{n^2}\left[1 + \frac{\alpha^2 Z^2}{n}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\right]$$

$$E_{1,0} = -\,\mathrm{ChR}_{\infty}\left(\frac{M}{M+m}\right) Z^2\left[1 + \frac{\alpha^2 Z^2}{4}\right] \quad , \qquad (4)$$

where α is the Sommerfeld fine structure constant and R_∞ is the Rydberg constant for an infinitely heavy nucleus. Inserting the appropriate values, this equation reduces to

$$E_{1,0} = -13.606 \times 10^{-3}\, Z^2 \left(1 + 13.314 \times 10^{-6}\, Z^2\right) \text{ keV} \quad . \qquad (5)$$

By comparing the calculated values for the neutral and single electron cases with the values obtained from Ref. 8 and Eq. (5), the error in the calculated values was found to range from 1.8% for strontium to 4.9% for samarium. This error was attributed to calculational error arising from the use of minimal basis sets, and to correlation and relativistic energy effects not taken into consideration by the computation.

The relative error was very nearly the same for both the neutral and the single-electron cases. On this basis, the relative error in the calculated values was assumed to be constant with respect to ionic charge state and a linear adjustment was made on all calculated K binding energy values such that the two extremes of ionic charge states (neutral and single electron) agreed with the values obtained from Ref. 8 and Eq. (5).

These values were then plotted as a function of ionic charge and a smooth curve was fitted through the points. The adjusted K binding energy curves for Sr, Pd, Xe and Sm are shown in Figs. 2, 3, 4 and 5, respectively. These curves are believed to be accurate to ±0.07 keV. Similar curves are given in Figs. 6 and 7 for the adjusted 2s and 2p binding energies as a function of ionic charge. The values of the single orbital eigenvalues (orbital energies) were taken as the unadjusted binding energies of all orbitals other than the 1s orbitals (Koopman's theorem[10]). For completeness, the unadjusted orbital energies for the rest of the electron orbitals in the atoms considered are listed in Table 1.

Using the results of the binding energy calculations on Sr, Pd, Xe and Sm, we determined an empirical formula for computing the K binding energies of atoms from Z = 34 to Z = 66 in any state of ionization:

$$E_{\text{ion}} = E_{\text{neut.}} \left[1 + f\left(\frac{n_e}{Z}\right) e^{-aZ} \right] , \qquad (6)$$

where E_{ion} = K binding energy of the ion

$E_{\text{neut.}}$ = K binding energy of the neutral atom

Z = atomic number

n_e = ionic charge of the ion

a = 1.8484×10^{-2} (empirical constant) .

The function $f(n_e/Z)$ is a seventh-degree polynomial in $(n_e/Z)^{3/2}$:

$$f\left(\frac{n_e}{Z}\right) = \sum_{k=1}^{7} C_k \left[\left(\frac{n_e}{Z}\right)^{3/2} \right]^k , \qquad (7)$$

where

$C_1 = 0.2491$

$C_2 = -0.6131$

$C_3 = 4.001$

$C_4 = -10.28$

$C_5 = 14.88$

$C_6 = -11.55$

$C_7 = 3.861$.

Equation 6 reproduces the binding energy curves of Figs. 2 through 5 with a maximum deviation of ±0.04 keV for all states of ionization except the single electron state which is easily calculable from Eq. (4).

IV. DISCUSSION

The calculated K and L electron binding energies as well as the Kα X-ray energies for the neutral atoms and for the probable ionic charge states formed in the spontaneous fission of ^{252}Cf are listed in Table 2 and the K binding energy increase is plotted as a function of atomic number for these charge states in Fig. 8. Based upon the available measurements of ionic charge states of fission fragments, we have estimated the most probable initial charges for Sr, Pd, Xe and Sm fission fragments arising from the spontaneous fission of ^{252}Cf to be +21, +23, +24 and +26 respectively. It is interesting to note in Fig. 8 that the present calculations yield K binding energy increases of approximately 0.9 keV ($\Delta E_{ave} = 0.93$ keV) for each of these ions and hence tend to indicate that this increase is nearly constant over the whole region of fission products.

Recently, determinations of the distribution of nuclear charge formed in fission based upon measurements of K X-ray energies have been reported by Glendenin and Griffin[11] and by Kapoor, Bowman and Thompson.[12] These studies have raised the question of whether or not the effect of ionization on the X-ray energies may be neglected. The present calculations indicate, as may be seen from Table 2, that the Kα X-ray energies of typical fission fragments are shifted by 50 ev or less. Hence, the neglect of corrections for the effect of ionization in the above-mentioned experiments was indeed justified.

In Fig. 9 is shown a plot of the relative increase in K binding energy versus the relative ionization for Sr, Pd, Xe and Sm. On the enlarged section of this figure are shown several experimentally measured energy shifts made in conjunction with a recent study of the fission fragment conversion electrons.[13] The horizontal error bars represent the statistical uncertainty associated with the energy determination and the vertical error bars extend over an arbitrary 1 charge unit on either side of the estimated fragment ionic charge. Although the points for Z=44 and Z=56 tend to indicate somewhat lower ionic charges than expected, the measurements are too rough to use for anything other than an illustration of experimentally observed binding energy shifts. (A number of experimental uncertainties may have contributed a significant amount of systematic error to these measurements.)

It is interesting to note that utilization of the binding energy shifts experienced by atoms as a result of ionization or perturbation of their outer electrons has already been reported by Hagstrom, Nordling and Siegbahn[14] in determinations of chemical valence states. They have detected K binding energy shifts between the 0 and 4+ and the 0 and 6+ valence states in sulfur of 4.3 ev and 5.5 ev respectively with an accuracy of 0.2 ev.

Conceivably, the relatively large shifts in binding energies between adjacent charge states in highly ionized fission fragments (~ 70 ev) could be used to study in detail the distribution of ionic charge resulting from fission. Hypothetically, internal conversion electrons arising from nuclear transitions offer a direct means of measuring these binding energy shifts. The application is obscured, however, by a number of experimental difficulties stemming from the fact that the fragments are traveling at relatively high velocities which for any single isotope may vary by as much as 15%.

ACKNOWLEDGMENTS

We wish to thank Mr. Donald Raimondi for providing us with a copy of the SCF program and Mrs. Claudette Rugge for help with the polynomial fitting program. The suggestions and interest of Dr. Stanley G. Thompson were also greatly appreciated. This work was done under the auspices of the U. S. Atomic Energy Commission.

REFERENCES

1. H. R. Bowman, S. G. Thompson, R. L. Watson, S. S. Kapoor and J. O. Rasmussen, in Physics and Chemistry of Fission, (IAEA, Austria, 1965), p. 125.
2. N. Bohr, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd., 18, 8 (1940).
3. B. L. Cohen, Phys. Rev. 104, 1046 (1956).
4. H. Opower, E. Konecny and G. Siegert, Zeitschrift Für Naturforschung, 20, 131 (1965).
5. C. C. J. Roothaan and P. S. Bagus, Methods in Computational Physics (Academic Press, New York, 1963), Vol. II, p. 85.
6. C. C. J. Roothaan, Rev. of Mod. Phys., 32, 179 (1960).
7. C. C. J. Roothaan, L. M. Sachs, A. W. Weiss, Rev. of Mod. Phys., 32, 186 (1960).
8. S. Hagström, C. Nordling and K. Siegbahn, in Alpha-, Beta-, and Gamma-Ray Spectroscopy, Vol. I, edited by K. Siegbahn (North-Holland Publishing Co., Amsterdam, 1965), p. 845.
9. R. M. Eisberg, Fundamentals of Modern Physics (John Wiley and Sons, New York, 1964), p. 356.
10. T. Koopmans, Physica 1, 104 (1933).
11. L. E. Glendenin and H. C. Griffin, Phys. Letters 15, 153 (1965).
12. S. S. Kapoor, H. R. Bowman and S. G. Thompson, Phys. Rev. 140, B 1310 (1965).
13. R. L. Watson, A Study of the Internal Conversion Electrons Emitted Within Three Nanoseconds after the Spontaneous Fission of ^{252}Cf (Ph.D. Thesis), University of California Lawrence Radiation Laboratory Report UCRL-16798, July 1966.
14. S. Hagström, C. Nordling and K. Siegbahn, Zeitschrift für Physik 178, 439 (1964).

FIGURE CAPTIONS

Fig. 1. Idealized electrostatic potential energy diagram for a) a neutron strontium atom b) a strontium +10 ion.

Fig. 2. Calculated K binding energy of a strontium atom as a function of its ionic charge.

Fig. 3. Calculated K binding energy of a palladium atom as a function of its ionic charge.

Fig. 4. Calculated K binding energy of a xenon atom as a function of its ionic charge.

Fig. 5. Calculated K binding energy of a samarium atom as a function of its ionic charge.

Fig. 6. Calculated L binding energies of a strontium and palladium atom as a function of their ionic charges.

Fig. 7. Calculated L binding energies of a xenon and samarium atom as a function of their ionic charges.

Fig. 8. The calculated increase in K binding energy for several probable fission fragment ionic charge states as a function of nuclear charge. The dashed line indicates the approximate constancy of the K binding energy increase for the probable charge states of +21, +23, +24 and +26 spanning the whole region of ^{252}Cf fission product isotopes.

Fig. 9. Comparison of the relative increase in K binding energy as a function of total ionization for strontium, palladium, xenon and samarium. Enlarged section contains several experimentally measured points taken from Ref. 13.

Table 1. Calculated orbital energies (keV).

Strontium	3s	3p	3d	4s	4p	5s
Sr Neutral	0.347	0.280	0.132	0.048	0.028	0.004
Sr^{+8}	0.474	0.407	0.260	0.150		
Sr^{+20}	0.996	0.933				

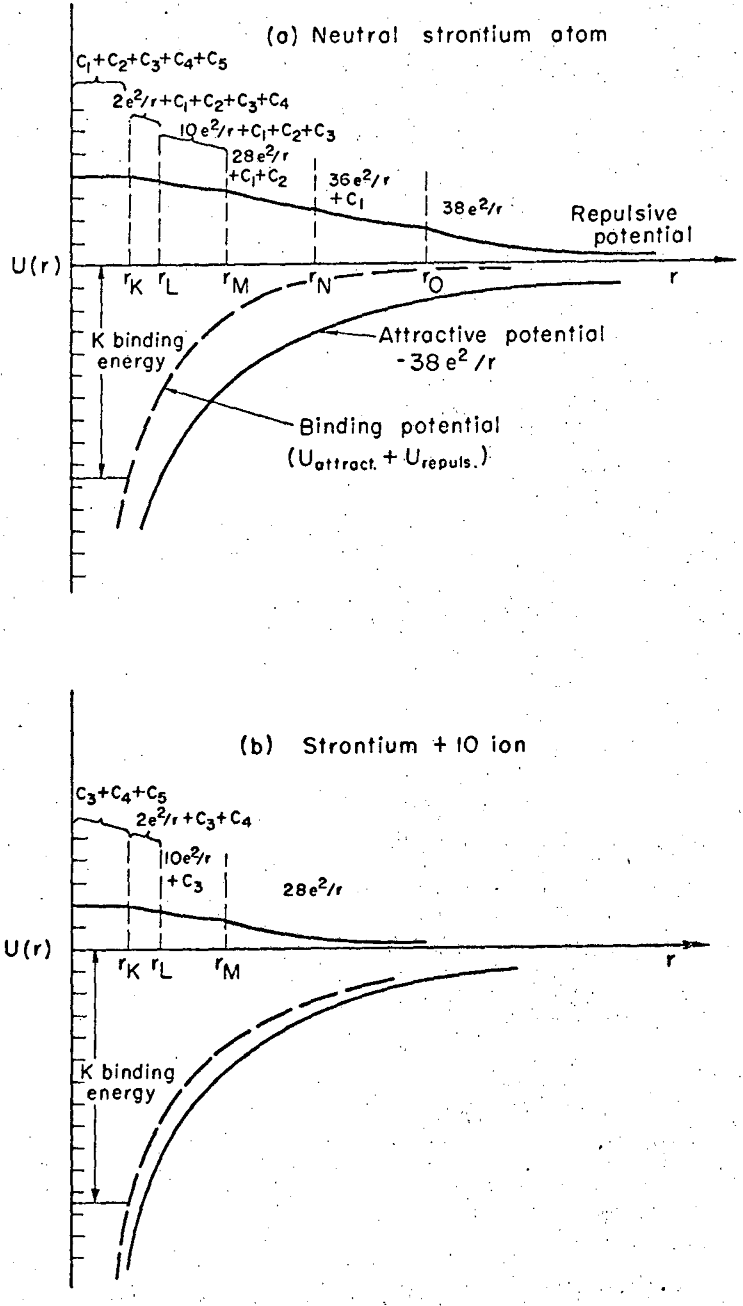
Palladium	3s	3p	3d	4s	4p	4d
Pd Neutral	0.628	0.537	0.335	0.081	0.050	0.005
Pd^{+10}	0.836	0.747	0.544	0.272	0.237	
Pd^{+18}	1.085	0.998	0.800			
Pd^{+28}	1.717	1.642				

Xenon	3s	3p	3d	4s	4p	4d	5s	5p
Xe Neutral	1.058	0.948	0.690	0.200	0.157	0.067	0.022	0.010
Xe^{+8}	1.169	1.059	0.802	0.309	0.265	0.175		
Xe^{+18}	1.512	1.402	1.145	0.596	0.548			
Xe^{+26}	1.845	1.739	1.489					
Xe^{+36}	2.628	2.543						

Samarium	3s	3p	3d	4s	4p	4d	5s	5p
Sm^{+8}	1.739	1.608	1.293	0.483	0.427	0.302	0.163	0.140
Sm^{+16}	1.920	1.791	1.479	0.655	0.599	0.476		
Sm^{+26}	2.381	2.255	1.944	1.029	0.970			
Sm^{+34}	2.794	2.673	2.374					
Sm^{+44}	3.729	3.638						

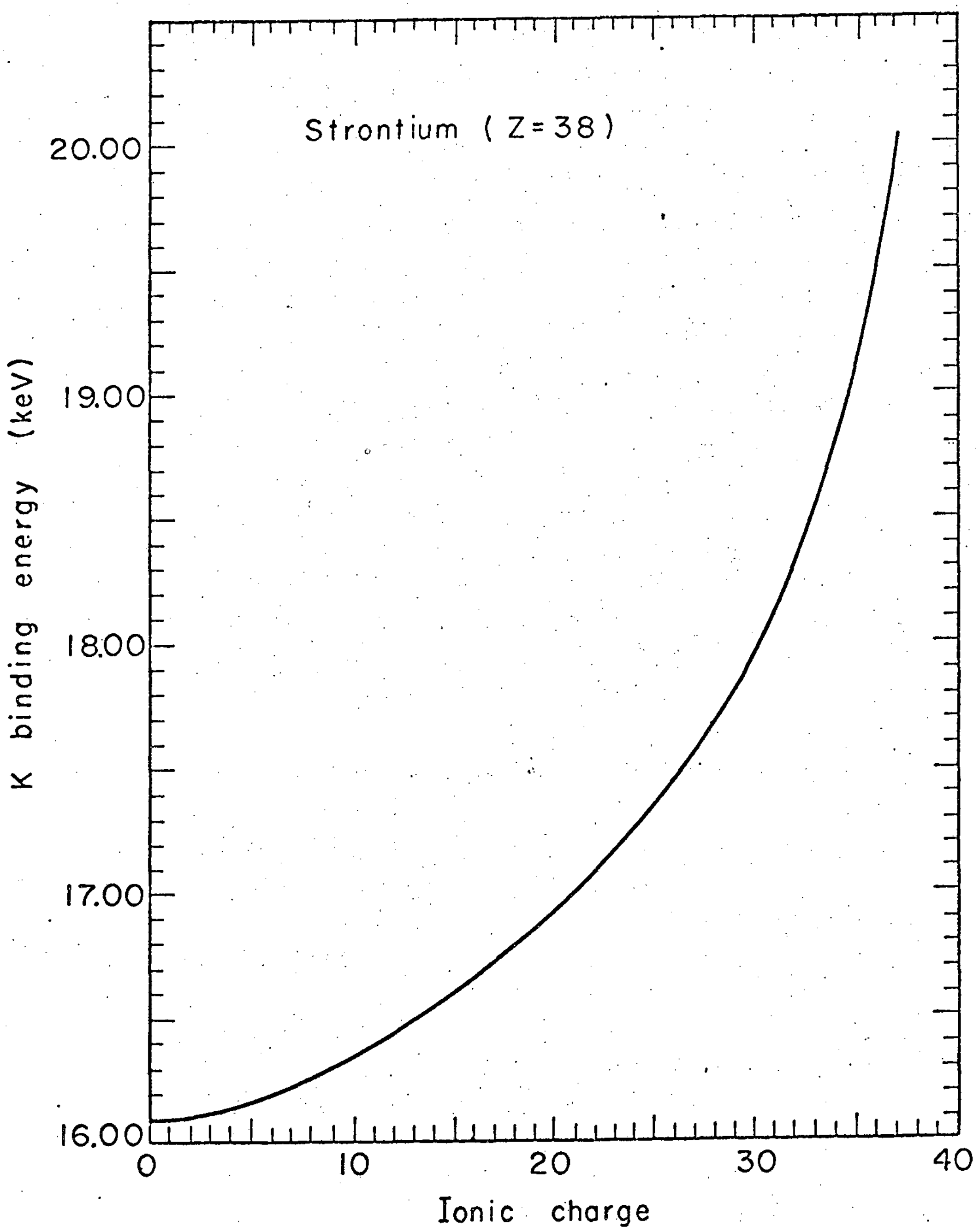
Table 2. K, L and Kα energies for Sr, Pd, Xe and Sm fission fragment ions.

	Electron Binding Energy (keV)			K-α X-Ray
	1S	2S	2P	Energy (keV)
Sr Neutral	16.11	2.21	1.97	14.14
Sr^{+20}	16.94	3.02	2.76	14.18
Sr^{+21}	17.02	3.10	2.84	14.18
Sr^{+22}	17.10	3.18	2.92	14.18
Pd Neutral	24.35	3.61	3.26	21.09
Pd^{+22}	25.22	4.49	4.14	21.08
Pd^{+23}	25.30	4.57	4.22	21.08
Pd^{+24}	25.39	4.65	4.30	21.09
Xe Neutral	34.58	5.45	4.94	29.64
Xe^{+23}	35.42	6.25	5.74	29.68
Xe^{+24}	35.49	6.32	5.81	29.68
Xe^{+25}	35.56	6.38	5.88	29.68
Sm Neutral	46.86	7.74	7.02	39.84
Sm^{+24}	47.67	8.51	7.80	39.87
Sm^{+25}	47.74	8.57	7.85	39.89
Sm^{+26}	47.81	8.63	7.92	39.89



MUB-10567

Fig. 1



MUB13956

Fig. 2

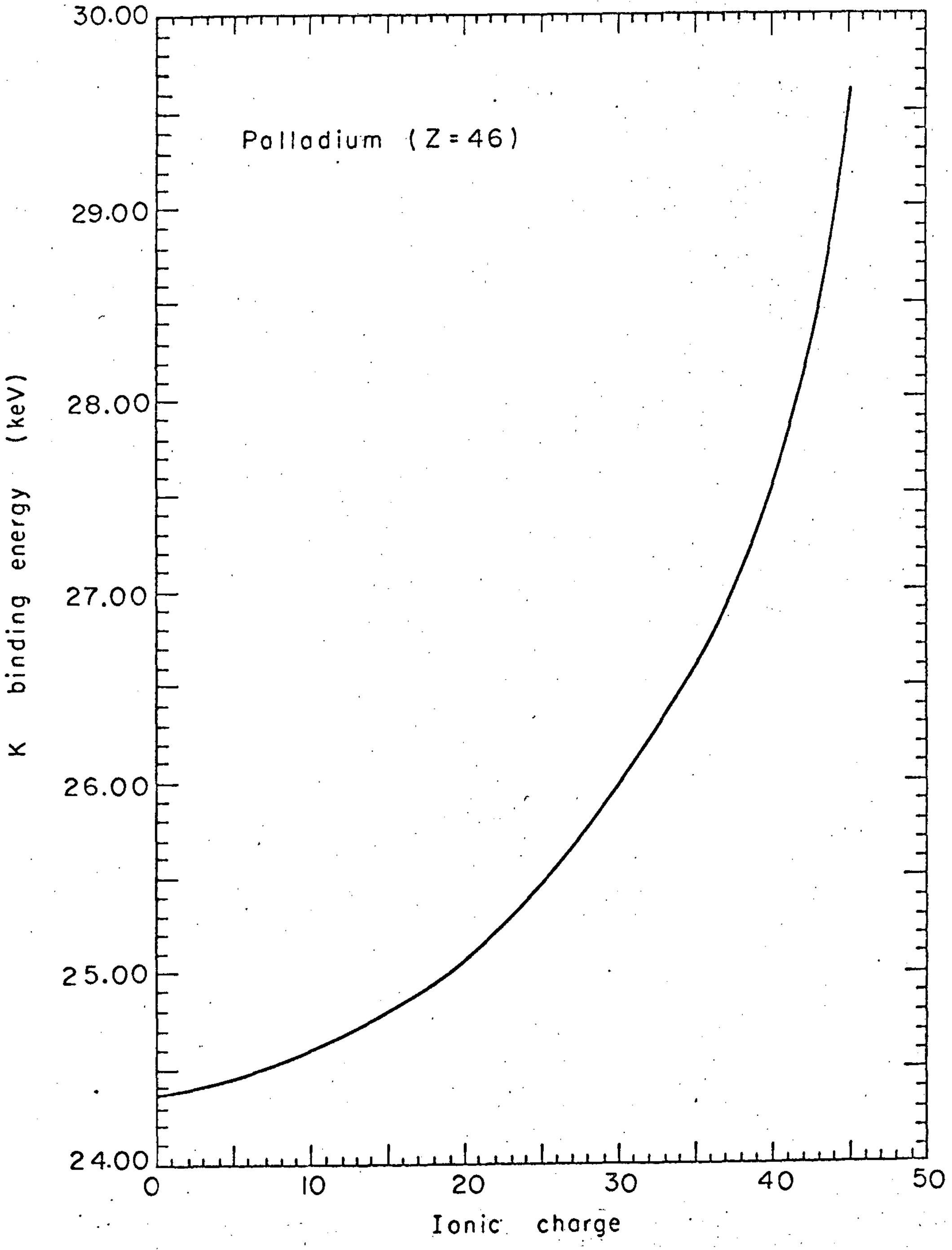

Palladium (Z = 46)
K binding energy (keV)
30.00
29.00
28.00
27.00
26.00
25.00
24.00
0
10
20
30
40
50
Ionic charge

Fig. 3

MUB-13954

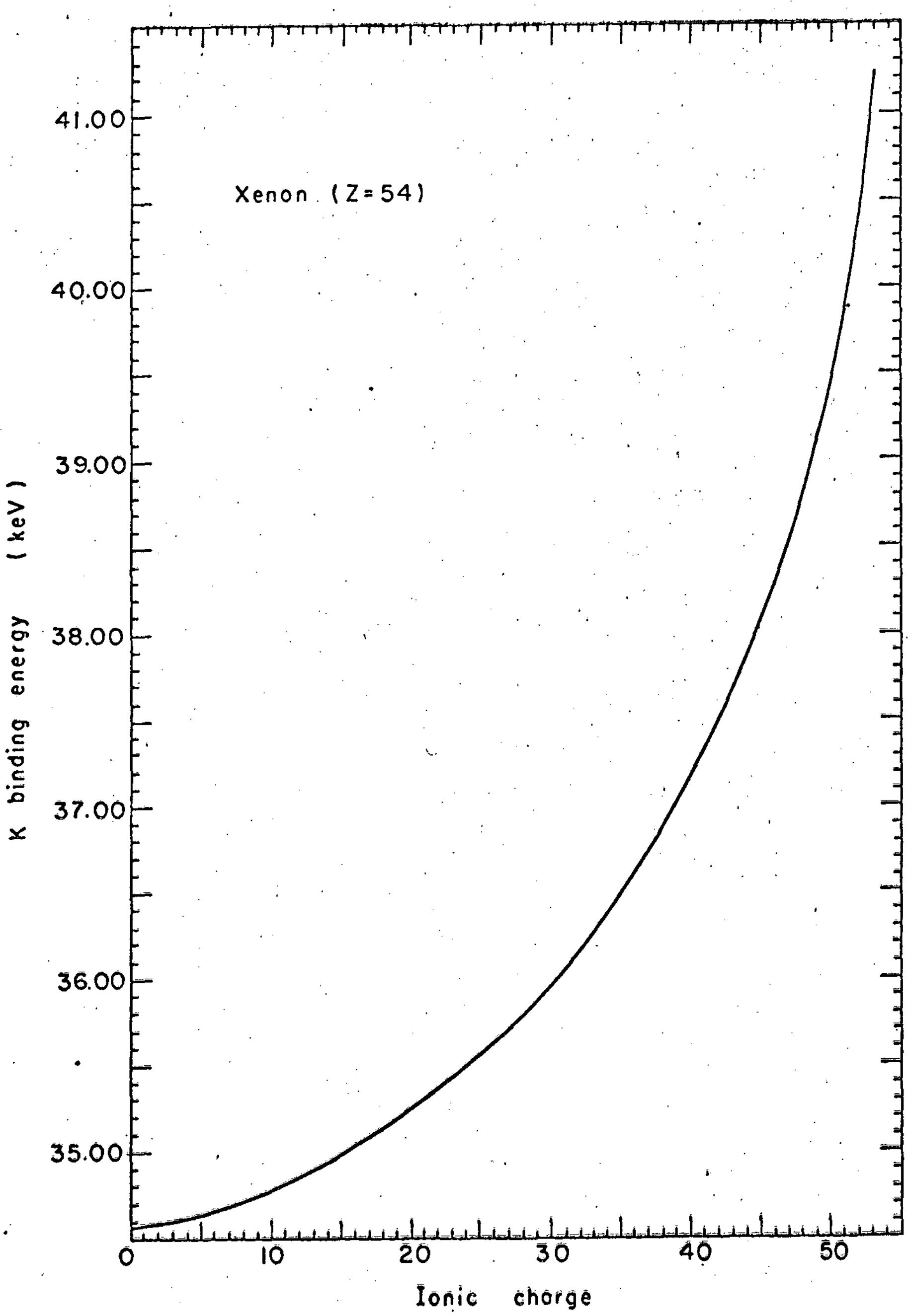

Xenon (Z=54)
K binding energy (keV)
41.00
40.00
39.00
38.00
37.00
36.00
35.00
0
10
20
30
40
50
Ionic charge

Fig. 4

MUB13953

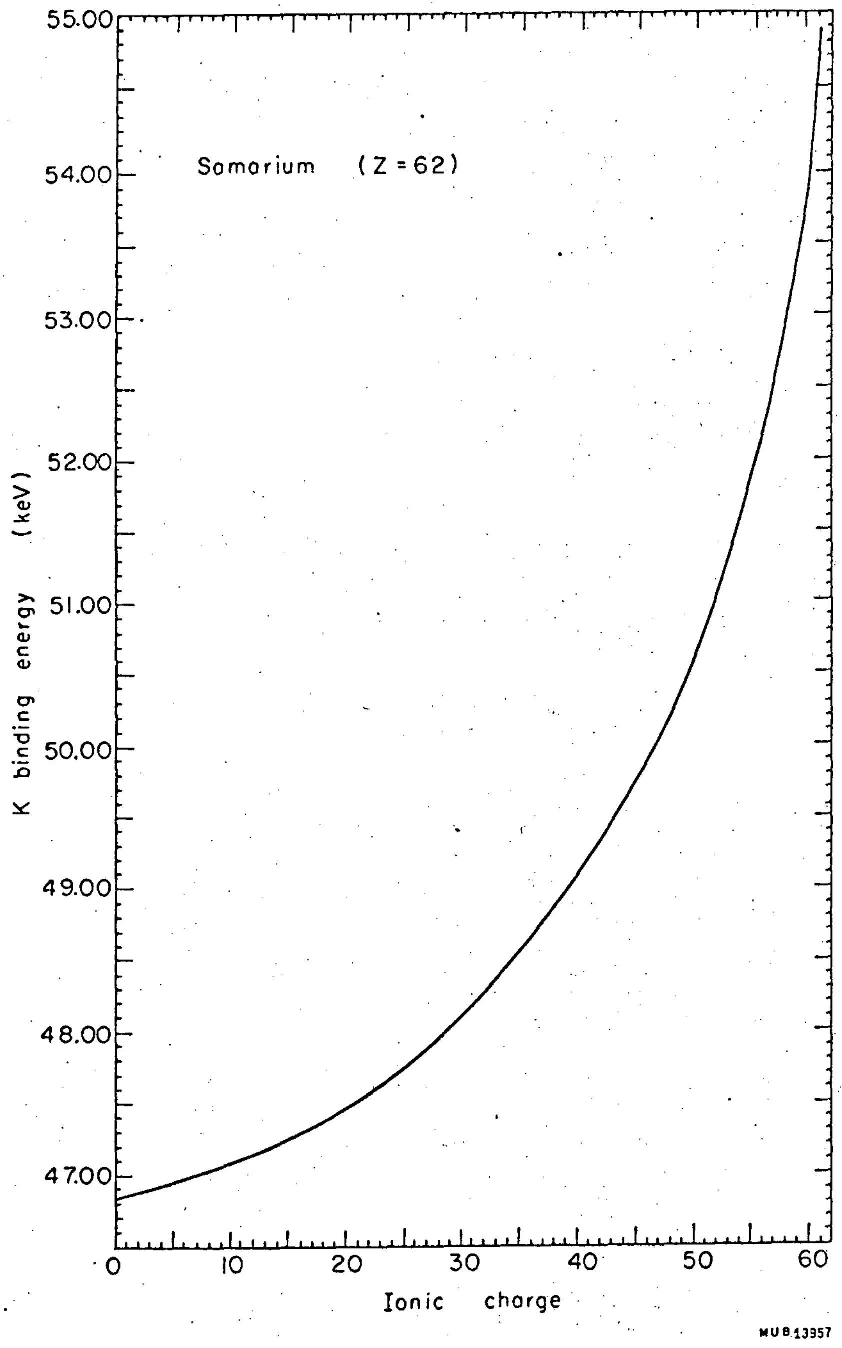
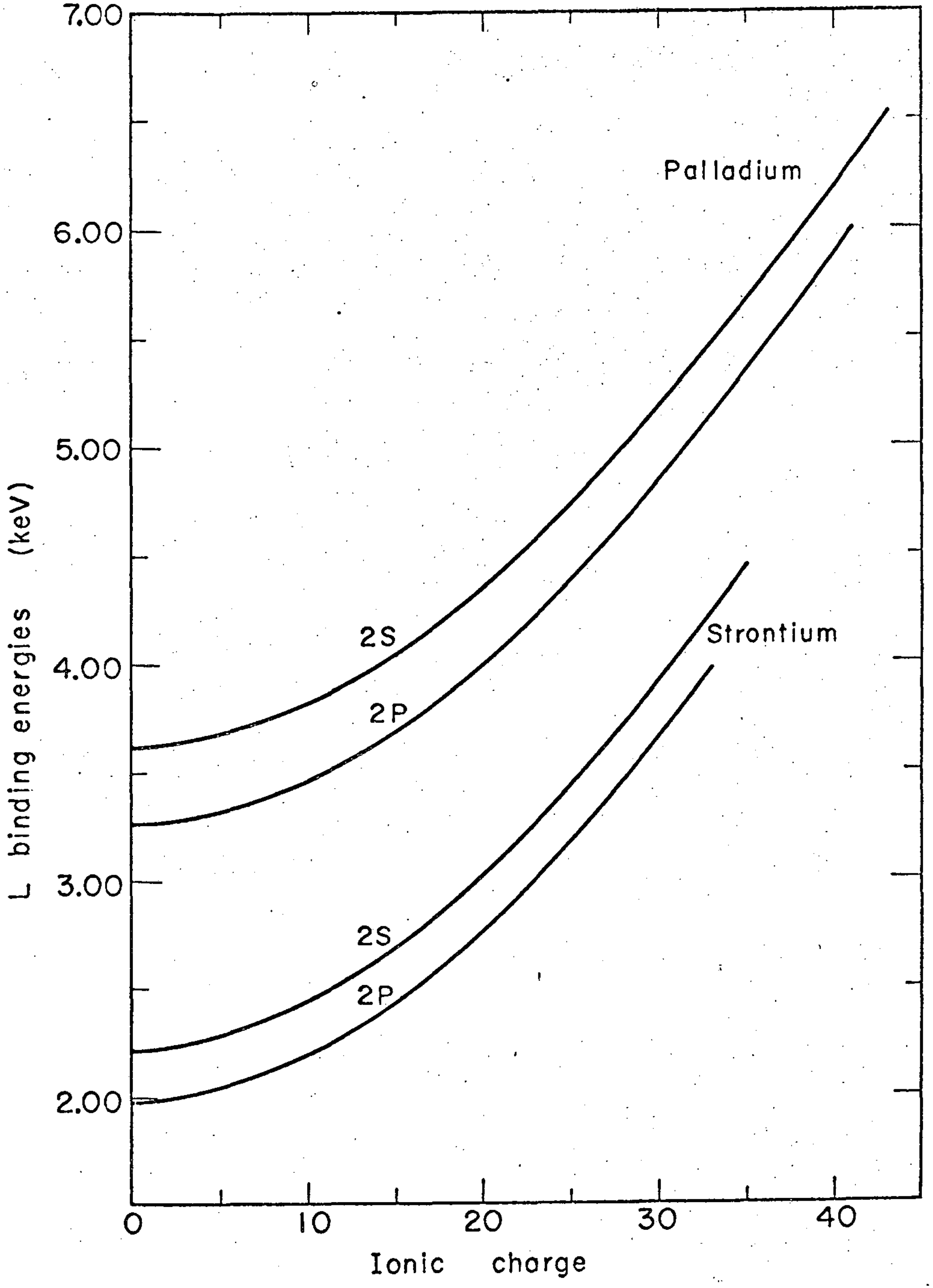
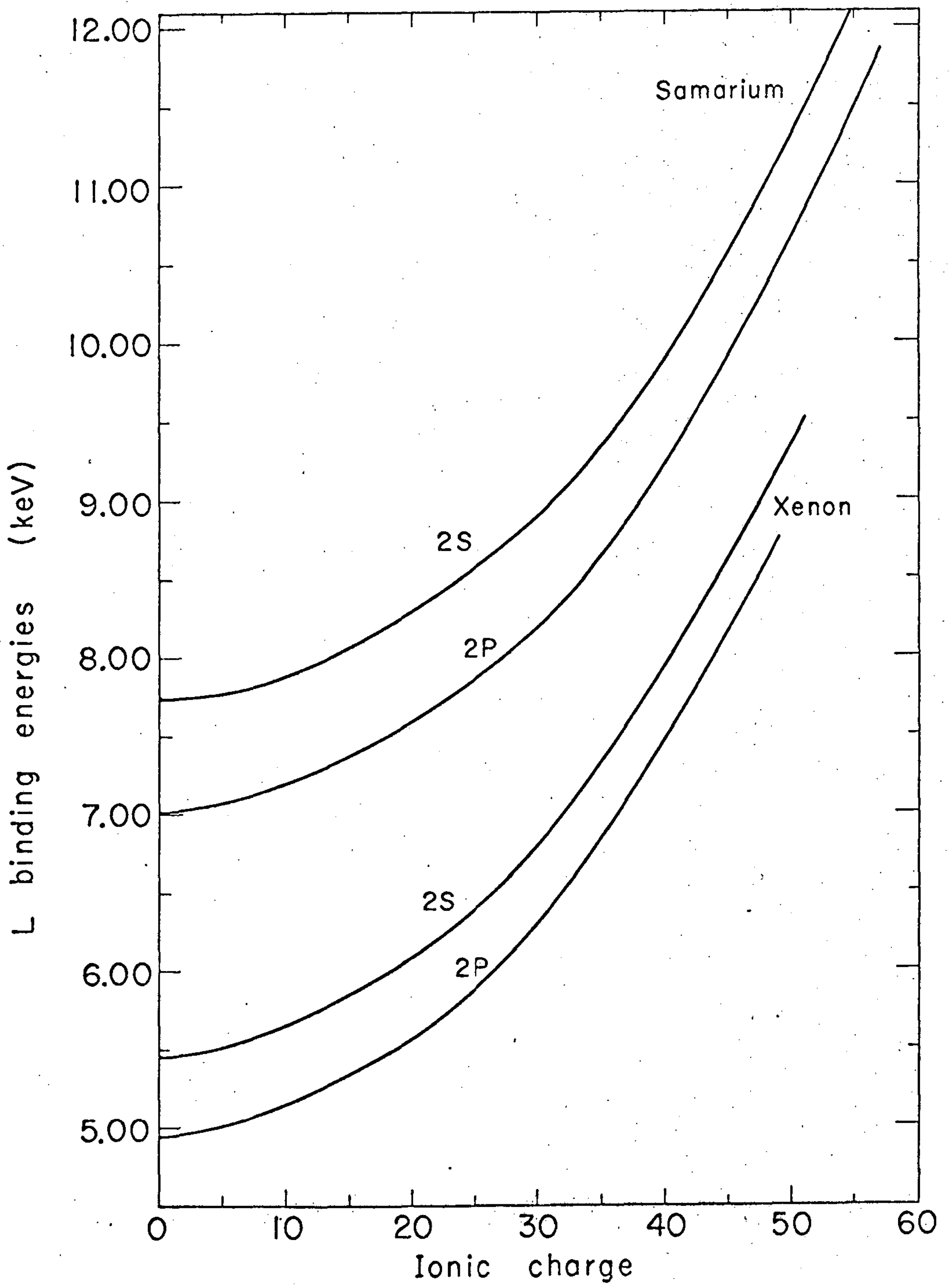

Samarium (Z = 62)
K binding energy (keV)
55.00
54.00
53.00
52.00
51.00
50.00
49.00
48.00
47.00
0
10
20
30
40
50
60
Ionic charge
MUB 13957

Fig. 5



MUB-10564

Fig. 6



MUB-10559

Fig. 7

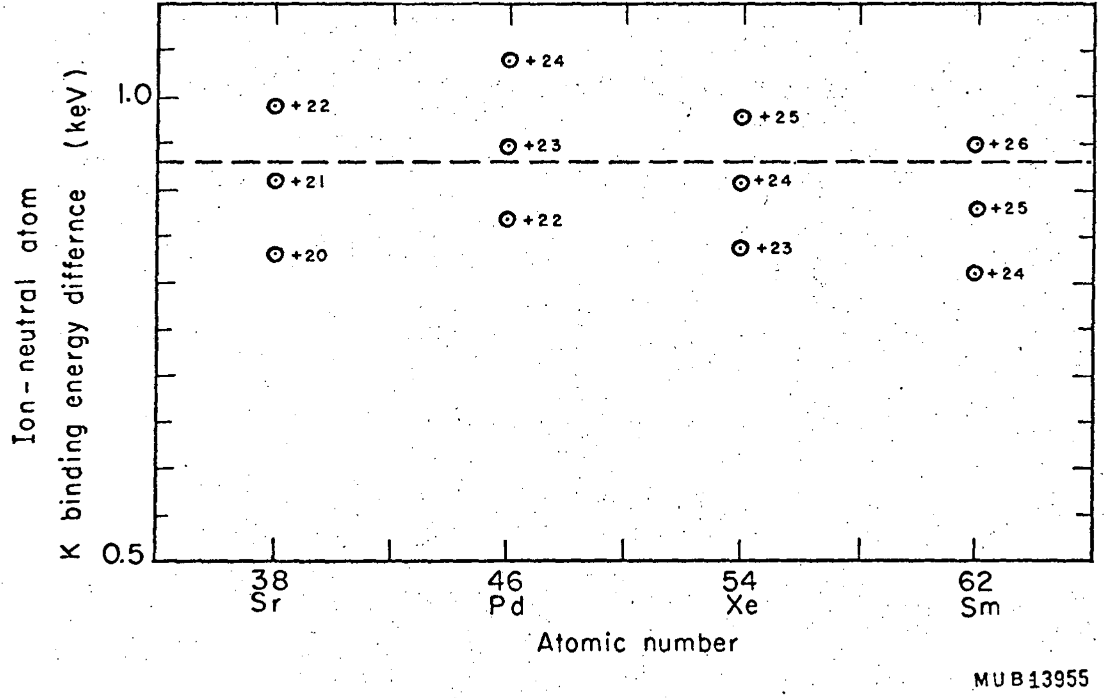
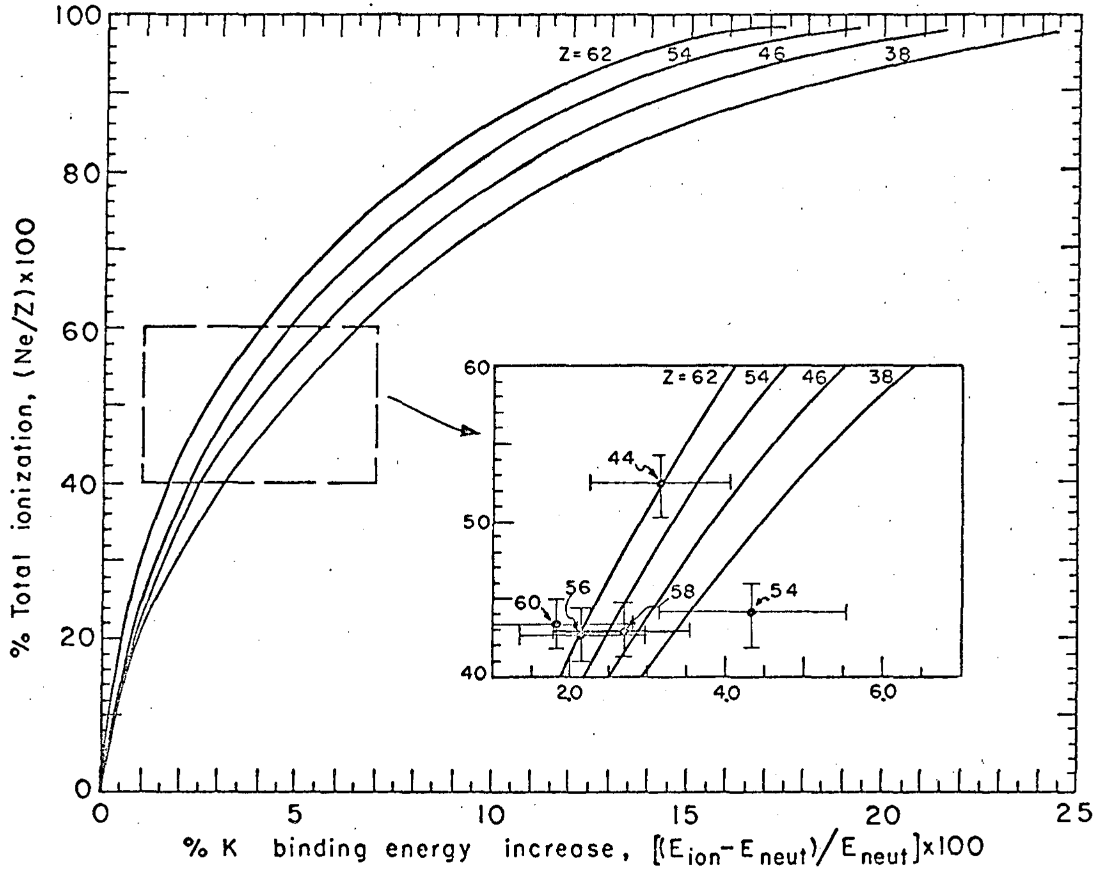

Ion-neutral atom
K binding energy differnce (keV)
1.0
0.5
+22
+21
+20
+24
+23
+22
+25
+24
+23
+26
+25
+24
38
Sr
46
Pd
54
Xe
62
Sm
Atomic number
MUB 13955

Fig. 8



MUB-13958

Fig. 9