Test of Invariance of the Ionization-Energy Threshold Value with Ejection Energy*

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High-energy inner-shell ionization processes generate a spectrum of lower-energy shake-up lines and shake-off band satellites of a main electron energy peak, corresponding to excitations and multiple ionizations of the daughter ion. Such satellite final states give reduced screening for the ejected inner electron, and consequently the observed rise in binding energy. Experimentally we here verify the conventional view that the effective binding energy corresponding to the main peak is independent of transition energy in such fast ionizations; four transitions in $^{241}_{95}$Am, one only 7 keV above the K binding energy of 125 keV, gave (L_1-K) internal-conversion electron energy differences of ~101 keV, constant within 5 eV, over an electron energy range from 7 keV ($v/c=0.14$, nearly adiabatic) to 450 keV ($v/c=0.85$). This implied invariance of the K main-line binding energy within 5 eV is contrasted to a calculated rearrangement energy value of 88 eV from a Dirac-Hartree-Fock (DHF) "frozen-orbital" eigenvalue minus the full atom-ion DHF "adiabatic" energy difference. Further, the main peak binding energy should be the threshold, adiabatic value; comparison of our (L_2-K) electron energy difference, 102.031 ±0.005 keV, with the $K\alpha_2$ x-ray energy, 102.033 ±0.010 keV, verifies this to 12 eV. The displacement of the centroid of the satellite spectrum from the main peak, i.e., the mean increase in binding energy averaged over this spectrum as the transition energy increases infinitely above threshold, should equal the rearrangement energy of the ion. Based on β-decay shake-off intensity predictions for all shells of Carlson, Nestor, Tucker, and Malik, and on our experimental results for K and L shells at lower Z, we calculate a centroid shift of 89 ±10 eV for Am.

I. INTRODUCTION

A. The Conventional Wisdom

A number of theoretical treatments[1,2] of the question of inner-electron ionization energy in non-adiabatic, i.e., not infinitely slow, processes are all in essential agreement on the behavior of the whole atom system during the event. We preface the quantum-mechanical description with a "classical" picture, for didactic illustration. In actually more or less fast ionization processes, the residual electron cortege is classically unable to rearrange adiabatically so as to maintain an essentially equilibrium configuration with the ejected electron. The orbitals cannot shrink fast enough to that configuration characterizing the ground state of the daughter inner-vacancy ion. The relatively "frozen neutral-atom orbital" electron density distribution provides less screening for the electron being ejected than would the daughter-ion ground-state orbitals. Classically, this necessarily results in a small *increase* E_R in the ionization energy BE_{K-A} associated with very high transition energy [see Fig. 1(a)].

In quantum-mechanical terms, the daughter system must exist in an allowed stationary state; the sudden transition can only result in the formation of a daughter ion in either its ground state or in one of the allowed excited "shake-up" or multiply-ionized "shake-off" states. This spectrum of possible final states is populated with a probability distribution which depends on wave-function overlap integrals[1,3] between initial and final states and, near threshold, strongly on the energy available for the ionizing process.[4] As this energy increases to exceed the adiabatic or threshold ionization energy, which can generate only the daughter-ion ground state, the probability increases for the formation of allowed excited but bound shake-up states and doubly or multiply ionized shake-off states with increasingly larger excitation and ionization energies. Such excitation and additional ionization energy effectively increases the *average* ionization energy for the process.

This increase is seen experimentally as an increasing relative displacement to lower kinetic energy of the centroid of the distribution of shake-up line and shake-off continua companion satellites from the main ground-state ion line, the satellites appearing and saturating in intensity and more energetically displaced ones appearing with increasing available energy [see Fig. 1(b)]. In the limit of infinite avaiable energy for the ionization process when the electron is ejected with velocity c, the displacement of this centroid (calculated including the main line) from the main line should equal the "rearrangement" energy, i. e., that small negative component of the adiabatic binding energy corresponding to the difference between "frozen-parent-orbital" eigenvalue and the difference in total energy of atom and ion. This is the small component of binding energy ignored in the

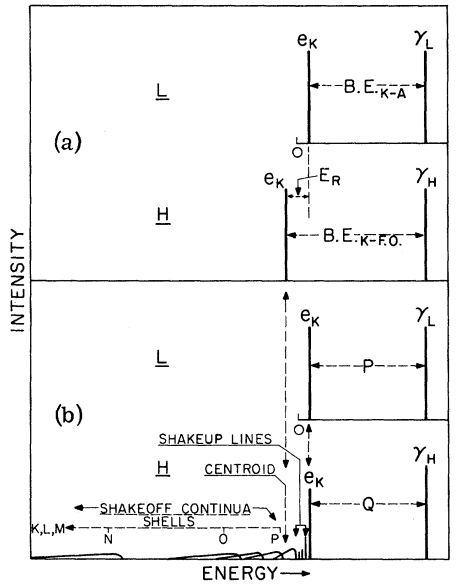

FIG. 1. Schematic representation of K internal-conversion spectra of low-energy (L; near ionization threshold) and very high-energy (H) transitions according to classical (a) and quantum-mechanical (b) views. Discrete lines shown without natural width at infinite resolution; shake-off satellite continua shapes grossly exaggerated in intensity for visual clarity, K, L, M shake-off continua far off scale to left. Sections of the energy scales are shifted so that transition energies (γ_L, γ_H) are aligned vertically for comparison of relative displacements of electron spectra. 0 denotes approximate zero of energy scale. e_K = main K conversion line. $(BE)_{K-A}$ = K binding energy, adiabatic value. $(BE)_{K-FO}$ = K binding energy, frozen-orbital value. E_R = rearrangement energy. Centroid of shake-up–shake-off satellite plus e_K spectrum displaced by E_R from e_K. *Purpose of this experiment is verification of* $P = Q = (BE)_{K-A}$.

Koopmans's theorem approximation.[2]

Theoretically,[3] even in the high-energy limit, the main line is strongly populated.

B. Supporting Evidence

The identification of shake-up and shake-off satellites in photoelectric[5,6] and internal-conversion[7,8] ionization processes is well established, and the agreement of their intensities, continuum spectrum shapes and energies is in fair accord with theoretical predictions.[3,7,9] Moreover, in the photoionization of the 1s electron in Ne the satellite centroid shift observed was 22 eV,[5,6] compared to 24 eV calculated[1] for the rearrangement energy. These experimental data support the view of the process depicted above.

In the 122- and 136-keV transitions in ^{57}Fe following ^{57}Co electron-capture decay, and in the 661-keV transition in ^{137m}Ba, the L shake-off companion satellite continua have been observed[7] to have about the expected intensities and displacements from the main K conversion line. Thus, the sudden process is an accurate description for the relativistic range of ejected-electron velocity.

This evidence also lends indirect support to the tacit assumption that the main conversion line seen in these cases and in all internal conversions corresponds to the formation of the daughter ion in its ground state, and thus necessarily is characterized by the threshold adiabatic binding energy. Further support is derived from the agreement observed between nuclear transition energies calculated from the sum of high-energy conversion lines plus tabulated shell binding energies and precisely measured γ-ray energies; such agreement is occasionally accurate to the order of 20 eV in the intermediate Z range in which the rearrangement energy is calculated to be ~ 50 eV. This agreement says that the ionization energy of the main line is the adiabatic value, if the tabulated binding energies are threshold values. That the tabulated inner-shell values are indeed threshold binding energies is supported by their being mainly based on low energy, ~ 1 keV, photoelectron spectroscopy [electron spectroscopy for chemical analysis (ESCA)] measurements of outer-shell electrons combined with inner-shell x rays, and by the agreement of some ESCA[6] binding energies in Ne and Ar with ionization threshold values.[10] However, the photoelectron values are all from low-energy excitations, and do not directly bear on the question of the *effective* binding energy for *high energy*, e.g., internal-conversion, processes.

C. Variants on Model

Although there is no evidence that the *main internal-conversion line* is other than that corresponding to the ionic ground state, one could hypothesize that the line carrying the highest intensity might instead progressively shift downward in energy through the spectrum of available shake-up and shake-off states as the energy available for ionization is increased. To do so would be at variance only with the predictions of the probability distribution calculations from the wave-function overlap integrals, but not with the basic quantum-mechanical requirement that the final state be stationary.

Alternatively, the main line could hypothetically correspond to leaving the ion always in its ground state, but with some part of the excess available energy always appearing concurrently as low-energy electromagnetic radiation that escapes observation. This latter would be represented by

$$E_{\text{kinetic}} = E_{\text{avail}} - (BE)_{\text{thres}} - E_{\text{rad}} ,$$

where $(BE)_{\text{thres}}$ is the adiabatic binding energy and E_{rad} is a small increment of lost radiation in amount

determined uniquely by the excess available energy, i.e., by the suddenness of the ionization process. Such radiation is analogous to inner bremsstrahlung, but is here regarded as having a discrete rather than continuous distribution consistent with the observation of possibly shifted but not further broadened main lines. One would then observe, in normal (i.e., no shake-up or shake-off) internal ionization processes, and increasing difference $(E_{\text{avail}} - E_{\text{kinetic}})$ with increasing E_{avail} depending on the exact form of the dependence of E_{rad} on the excess of available energy. If a constant loss E_{rad} occurred at all practically observable energies above threshold, the main-line displacement from E_{avail} would be constant, but larger than $(BE)_{\text{thres}}$. In such a model, the alternative modes of inner-shell ionization associated with shakeup and shake-off are regarded as independent phenomena not directly associated with rearrangement processes.

Experimentally, both of these variant models yield a main-line position shifted at least partly in the direction of the classical model, so we shall refer to such line behavior in subsequent discussion as "classical" shifts.

We certainly do not imply that these models are very reasonable alternatives; clearly both are subject to easy criticism. However, until accurate experimental proof verified all even very plausible aspects of the conventional theory, the correct model must remain to some extent an open question.

D. Experimental Tests

In view of the possibilities suggested above and the experimental uncertainties indicated in Sec. IB, it appeared worthwhile to extend and make more accurate the verification that the binding energy *corresponding to the main line alone* is independent of the available energy over a wide energy range, up into the relativistic region, and down at least as far as would make deep inner-shell shake-off energetically impossible. We chose to check this constancy, therefore, at high Z where inner binding energies are large and where K-rearrangement energies of ~100 eV are large compared to our attainable accuracy. Our procedure was to measure the energies of K and L_1 conversion lines of a number of transitions in a single isotope, some of quite high energy and some low enough in energy to be as little above the K binding energy as we could find favorable cases for, yet whose associated L_1 line would still be fairly relativistic in energy. A comparison of the $L_1 - K$ line energy differences at high and low energy would yield the desired information.

A second test is a comparison of the $L_2 - K$ difference, if it is independent of transition energy, with the measured $K\alpha_2$ x-ray energy. On the assumption that the x-ray energy is equal to the difference between the total electronic binding energies of the $1s$ and $2p_{1/2}$ ion hole states, i.e., that neither "inner-bremsstrahlung"-like losses nor multiple-ionization effects in the initial vacancy states significantly shift x-ray energies, the energy is the adiabatic difference (see discussion of this point in Sec. IV). Agreement of the $L_2 - K$ difference with the $K\alpha_2$ energy would verify that the main-line binding energy is the adiabatic value and would rule out the last described model of a constant E_{rad} loss.

The virtue of the former ($L_1 - K$ difference constancy) test is that spectrometer calibration uncertainties tend to cancel in comparing two such differences, whose constancy rather than absolute value is of primary interest. The $L_2 - K$ vs $K\alpha_2$ x-ray comparison relies on absolute accuracy of completely independent measurements.

II. EXPERIMENTAL

The tests were applied to a set of transitions in ^{241}Am populated in the electron-capture decay of $33d$ ^{241}Cm. This isotope was generated by $(\alpha, 2n)$ reaction on a ^{239}Pu-Al alloy. After chemical separation[11] from Pu, Am, and fission products, ^{241}Cm ions were deposited on a 1-mil Al target foil in the Argonne electromagnetic isotope separator. The 50-keV ions were decelerated to 100 eV before impact. At this energy the ions cannot penetrate even one atom layer into the aluminum oxide surface film, so they remain surface bound as an oxide. A 1-mm-diam mask hole defined the deposition area. Mass density of the invisible sample was ≤ 1 $\mu g/cm^2$ estimated from separator beam-current limits and separation time. Sample intensity was $\sim 5\times 10^5$ dis/min.

Internal-conversion lines from transitions in ^{241}Am were measured in the Argonne iron-free double toroidal electron spectrometer.[12] With the two toroids operated in tandem, an instrumental resolution of 0.045% was obtained at a transmission of 4.4% of 4π Sr. Spectrometer current-supply stability and linearity are of the order of 1–2 ppm at currents corresponding to $\geq$ 40-keV electron energy; below this they correspond to $\leq$ 0.08-eV electron kinetic energy down to energies approaching 5 keV. Spectrometer calibration was based on the K line of the 122.060 ± 0.004-keV transition in ^{57}Fe at 114.939 ± 0.005 keV.[13] External magnetic fields are compensated[14] to 10^{-4} Oe, assuring that spectrometer calibration is constant to < 1 ppm down to below 1 keV. The detector was a bare cleaved NaI:Tl crystal.

III. LINE-SHAPE ANALYSIS

Fairly intense transitions at 471.81, 180.27, 165.05, and 132.40 keV,[15] mainly $M1$ multipolarity,

are all significantly converted in K and L_1 shells. These shell binding energies are 124.986 and 23.813 keV, respectively.[16] The K and L_1 lines of the 472- and 132-keV transitions, on which the principal conclusions are based, are shown in Fig. 2. Here the symmetric Lorentzian widening of the K lines (natural width ~115 eV) can be seen adding significantly to the instrumental linewidth even in the 347-keV K line where the instrumental width is ~190 eV. For the 7-keV K line of the 132-keV transition, the instrumental width of ~7 eV is unimportant compared to the natural width, but in this case particularly the asymmetric broadening to lower energies due to solid-source effects, backscattering, and to unresolved outer- and near-outer-shell shake-up and shake-off satellites is clearly seen.

Shake-up and shake-off of any orbital electron is

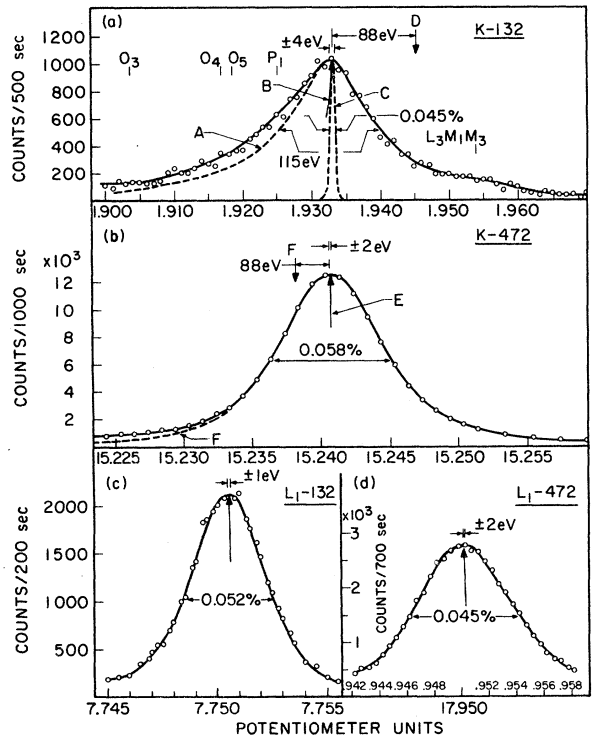

FIG. 2. K and L_1 conversion lines of the 132- and 472-keV transitions in ^{241}Am. The locus of line medians is shown as an upward arrow, e.g., B, E. Horizontal error bars mark the line-axis locations. On the 7-keV K-132 line, the instrumental resolution curve C is shown, A is the reflected upper part of the line, and the expected $0_{3,4,5}$ and P_1 shake-off satellite band-head positions are marked. D [and F] are the expected positions for the K-line axes that would correspond to the classical rearrangement model if the other three conversion lines in this figure occupy their experimentally found positions (see text). The expected position of the $L_3M_1M_3$ Auger line is marked in (a).

energetically allowed in each of these conversions except for the 7-keV K line of the 132-keV transition. There K and L shake-off are not possible and M shake-off is probably much reduced below usual intensity expectations.[3] This is because M-shell binding of 6.3 $\cdots$ 4.0 keV for $M_1 \cdots M_5$ subshells (in Cm) leaves only 1–3 keV to be shared by the M shake-off electron and the K (satellite) electron; consequently the sudden approximation condition is not realized and the shake-off probability expectation is lowered, in analogy to the low-energy electron-induced shake-off results of Carlson, Moddeman, and Krause.[4] However, shake-off and shake-up of outer shells are expected with intensities essentially independent of the conversion-line energy for the 7 keV and all higher-energy lines.

Wave-function overlap calculations[3] predict that these outer-shell shake-off events will produce conversion-line satellites of (summed) relative intensity ~20% of the main line. These will form a series of lines and bands extending to lower energy starting just a few eV below the line. Though such close-lying structures could be resolved in very low-energy photoelectron spectroscopy of light noble gases,[5,6] our extensive attempts failed to resolve such expected structure from the smeared out backscattering tail of an approximately tenfold narrower (than K-132) 7-keV K conversion line in ^{57}Fe from an ultrathin solid source. For the ^{57}Fe line the observed resolution was only 0.075%, widened from the instrumental width of 0.052% (~7 eV) by a K-level natural width of ~1 eV, and by solid-state, backscattering, and shake-off effects. In the ^{241}Cm case also [Fig. 2(a)], solid-state effects and the much larger natural K width smear out the bumps that would be expected to be easily resolved and intense enough to see, e.g., the O-subshell shake-off threshold bandheads.

These unresolved asymmetric broadenings must be deconvoluted from the lines to determine the line momenta. Since the instrumental electron-optical line shape is a fairly symmetric peak as seen in the high-energy narrow L_1 lines [Fig. 2(d)], and the natural width broadening is also essentially symmetrical about the line axis, the fiducial point is chosen from the upper more nearly symmetrical quarter of the K-132 line (and of all other lines) as the intercept of the locus of line medians with the peak. This intersection tends to eliminate the biasing effect of the asymmetry.

Table I gives these line fiducial points and their assigned errors (marked on Fig. 2), and the deduced line energies. The contribution of the line-position errors to the error in the energy is given separately from the error due to the 5 eV uncertainty in the energy of the 114-keV ^{57}Co electron-energy standard, because this latter error gives a correlated contribution to the K and L lines of

TABLE I. Conversion-line energies in $^{241}_{95}$Am.

Conv. line	Line median (Potentiometer units)	Energy[a] (keV)	σ_1[b] (eV)	σ_2[c] (eV)
$472-L_1$	17.95016±5	447.991	2	18
$472-K$	15.24058±5	346.820	2	15
$180-L_1$	9.49815±5	156.464	2	7
$180-K$	5.3984±1	55.293	2	3
$165-L_1$	8.9656±1	141.237	3	7
$165-K$	4.5624±1	40.061	2	2
$132-L_1$	7.75059±5	108.598	1	5
$132-K$	1.9332±5	7.424	4	0.5

[a]Includes 4 eV for spectrometer work function.
[b]σ_1 (standard deviation) from line-median error only.
[c]σ_2 from uncertainty in calibration-standard energy only.

each transition and thus does not fully contribute to the error of their L_1-K differences.

At this point to clarify the goal of succeeding discussion, we digress to note that our experimental results fully support the quantum-mechanical view depicted in Sec. I A, i.e., that the ionization energy of the main line is always the adiabatic value, independent of the available energy. Thus, we emphasize below those experimental factors and analytical judgements that lead to the contrary "classical" result (that higher available energy will correspond to higher effective binding energy), in order to show the inconsistency of this conclusion with the data.

Although the unfolding of the asymmetrical tail of the 7-keV K-132 line involves a greater degree of arbitrariness than for any of the higher-energy lines, the resulting error in the main-line axis position is only 4 eV because of the very low line energy. This lowest-energy conversion is the most nearly adiabatic of these ionizations and as such would be expected to include the largest rearrangement energy component, i.e., the associated binding energy would be least, and thus the "line" energy would be highest with respect to the transition energy. Were more of the low-energy asymmetrical bulge included in the line in determining its centroid, its energy would be lowered, and it would then appear to be associated with a higher binding energy and thus be *less* adiabatic than the higher-energy ionizations. Since the hypothesis being tested is that *the higher-energy ionizations might involve larger effective ionization energies in these main lines*, lowering the 7-keV-line centroid would compensate and thus conceal such an effect in the comparison. This argument shows rather, that the critical judgement of the 7-keV-line centroid is instead that it not be chosen unreasonably high for such a choice could simulate that a lower binding energy is indeed associated with the main line of this more adiabatic ionization. The vertical arrow on Fig. 2(a) shows where the line axis would be located if the 7-keV main-line binding energy were effectively lower than that for the other three lines by the full calculated[17] rearrangement energy of Am, 88 eV, i.e., were the classical model valid.

As can be seen in Fig. 2(b), the K-472 line is much more nearly symmetrically broadened (by natural width effects). Although shake-off satellites theoretically may contain ~20% of the unresolved line intensity, most of which should be well within about the left half-width of the line axis, there is little evidence of their presence. Except for an extended low-amplitude line tail that appears below 15.233 potentiometer units (i.e., above the reflected upper half of the line), no specific structure can be "resolved." This tail extends down about ten linewidths (~2 keV) where it sensibly merges with the background; it includes ~5% of the line intensity. Clearly, any closer-lying shake-off and shake-up structures, each component of which must have at least the natural width of the main K line, cannot be resolved, and we have no evidence, positive or negative, of their presence. The assigned line axis position may then be somewhat displaced to lower energy from the true main-line position owing to the presumed (~20%?) presence of such unresolved satellites. For this K line, such a displacement is in the direction to correspond to a *higher* effective binding energy for this very fast ionization, and thus will tend to support the aforementioned hypothesis to the extent of the possible shift. The arrow F in Fig. 2(b) shows the position that would fully support the hypothetical classical model.

Just as for the K-472 line, there was no evidence of shake-off structure on the L_1 lines of the 132- and 472-keV transitions though essentially the same relative shake-off intensities are expected for them as for the K-472, and they should appear as narrower, more easily seen, components since they have L-level widths rather than K. The enlarged width of L_1-132 (over L_1-472) is due to the natural L_1 width contribution of ~10 eV to the ~100-eV instrumental width.

The 165- and 180-keV lines are similar intermediate-energy examples.

IV. RESULTS

Table II gives the L_1-K energy differences for all four transitions. These differences are shown for the value of the spectrometer calibration constant corresponding to the best value of the ^{57}Co conversion-line energy standard and for a decrease in the value of the standard by one standard error (= 5 eV). Although the differences shift by 3–5 eV, their shift is correlated; the differences remain

TABLE II. (L_1-K) conversion-line energy differences in $^{241}_{95}$Am.

Transition keV	(L_1-K)[a] keV ± (eV)	(L_1-K)[b] keV ± (eV)
132	101.174(4)	101.169(4)
165	101.176(4)	101.171(4)
180	101.171(3)	101.167(3)
472	101.171(3)	101.168(3)
average	101.173(1.6)[c]	

[a]For best value of spectrometer calibration-standard energy.

[b]For best value of calibration-standard energy minus $\sigma_{std}=5$ eV.

[c]Close agreement of internal error (1.6 eV) and external error (1.2 eV) for the (L_1-K) differences indicates their consistency with energy independence. An increase in effective binding energy with transition energy would yield (L_1-K) differences increasing with energy. The range in this sense, from minimum low-energy difference (101.174 − 0.004 keV) to maximum high-energy difference (101.171 + 0.003 keV) is 4 eV. The actual listed (best) values show a 5-eV inverse trend. A specification of invariance within 5 eV thus appears conservative.

equal within a combined (line position uncertainty) error of 5 eV (see Ref. c, Table II).

The $\beta=v/c$ values for L_1-132, and all the higher-energy conversion lines, e. g., K-472 and L_1-472, range from 0.56 to 0.85; they are all fairly relativistic electrons whose velocities greatly exceed the average velocities of the electrons bound in the corresponding orbits. Classically, little rearrangement could occur during these ionizations. For the 7-keV K-132 electron, $\beta=0.14$; neither the remaining K nor any L electrons can be shaken off with it. In this sense and to this extent, it is a slower ionization, and at least the inner orbitals can "rearrange" during its emission. Yet, the constancy of the L_1-K differences implies that the *same binding energy is associated with both the fast and slow K conversion, and that any shift in the binding energy is no greater than* 5 eV, *compared to the full K rearrangement energy of* 88 eV.

As we have noted before, our lowest-energy line is not at zero energy, and in fact the 132-keV K conversion has full expectation for shake-off in N and higher shells. Thus a fairer comparison of our 5 eV uncertainty would be to the 56-eV "partial" rearrangement energy (= 88−32 eV, where 32 eV is the calculated centroid shift of the main line for a K conversion which can shake off only in N and higher shells).

To obtain an absolute comparison with adiabatic binding energies, the L_2-K energy difference was obtained from the average L_1-K difference, and the 858 ± 1.4-eV difference of the L_1 and L_2 conversion lines of the 32.640-keV transition in the ^{241}Cm decay (Table III). The direct (L_2-K) conversion-line energy differences of three transitions are in excellent agreement with this value. These were not primary choices for obtaining this difference because of the low L_2 conversion intensity of these predominantly $M1$ transitions. The difference, 102.031 ± 0.005 keV is compared to the $K\alpha_2$ energy of 102.033 ± 0.010 keV, averaged from the crystal-diffraction results of Nelson, Saunders, and Salem[18] and the Ge-(Li) spectrometer data of Ahmad.[19] We conclude that *the K binding energy associated with the main conversion line has the adiabatic value within* 12 *eV.*

As noted in Sec. ID, this conclusion is founded on the assumption that the x-ray energy is given by the difference of adiabatic binding energies. Thus one must examine the magnitude of the effects arising from the spectrum distribution of *initial* ionic states preceding K x-ray emission on the x-ray energy. This array of states formed by the K-shell ionization is the composite of shake-up and shake-off ionic states in which at least about 70% of the intensity[3] is associated with the single K-vacancy ground state. Those ions doubly ionized in inner shells (KL) give rise, e. g., to the resolved x-ray satellites $K\alpha_3$ and $K\alpha_4$. A rough generalization verified in much ESCA work[6] is that chemical shifts in inner-shell binding energies are nearly independent in absolute value of the shell. Since such shifts are caused by displacements of valence electrons akin to outer electron ionization, it is reasonable to extend the generalization to the effects of outer-shell shake-off on inner-shell binding energies. From this one would expect much smaller shifts in x-ray energies, since a cancellation of binding-energy shifts occurs in their difference. In support of this judgement is the fact that the shifts from the $K\alpha_1$ x-ray peak that are observed, the $K\alpha_3$ and $K\alpha_4$ satellites, which arise from simultaneous initial ionization in K and L shells, are displaced from the main $K\alpha_1$ x-ray line by a small fraction of the displacement of L shake-off satellites in internal conversion. For example, for Mg, the $K\alpha_3$ displacement (seen in the photoelectron

TABLE III. (L_2-K) energy differences in $^{241}_{95}$Am.

Source	L_2-K[a] keV ± (eV)
$(L_1-K)_{av}+(L_2-L_1)_{32\ keV}$	102.031(5)
472-keV transition	102.030(6)
165-keV transition	102.032(7)
132-keV transition	102.032(7)
av	102.031(5)

[a]Error includes contribution of error in energy standard, which appears as a correlated contribution in average.

spectrum of neon excited by Mg, Ref. 6) is ~ 8 eV, compared to ~ 25 eV estimated (on the basis of the energy arguments of Ref. 7) for the shift of the L shake-off satellite edge from the L_3 binding energy in Mg. Thus even where the second vacancy is in the L shell itself, the effect on the KL_2 difference is greatly reduced. Outer-shell multiple ionization should give still smaller K-satellite shifts, probably less than a few eV at most for heavy elements, and would produce still smaller shifts in the position of the main x-ray peak from which they are not resolvable. Similar evidence is the much smaller chemical shifts of x rays than of ESCA lines.

It is noteworthy that the crystal-diffraction $K\alpha_2$ value,[18] 102.041 ± 0.006 keV was obtained from K vacancies generated with Am as an oxide fluoresced by ^{182}Ta γ rays, whereas the Ge(Li) spectrometer value,[19] 102.020 ± 0.010 keV, came from ^{241}Cm decay, where the K vacancies are produced by K capture and K internal conversion. This agreement within 20 eV in 10^5 is of about the same accuracy in verification of the independence of x-ray energy of mode of excitation as the results of Schnopper.[20] By crystal diffraction the ~ 5.8-keV $K\alpha$ x-ray energies of Mn excited by electron bombardment or by K-capture decay of ^{55}Fe were shown[20] to be identical within ~ 1 eV, ~ 20 in 10^5. Since K capture gives a much lower probability for producing shake-off than does ionization by electron bombardment, the agreement of x-ray energies from sources thus excited constitutes further evidence in support of the above judgement that the x-ray energy shifts due to unresolved initial multiple outer-shell shake-off satellites is very small. Note that the multiple outer-shell vacancies produced, in both cases, by the Auger cascade which follows K x-ray emission, are irrelevant to this consideration.

To be able to extend the range of this verification of the constancy of the binding energy to a significantly lower regime of ejected electron energy faces two difficulties. If it is to be attempted with internal conversion, one must seek a suitable high Z transition energy much nearer the K-ionization threshold; not many choices are available. One can extend the possibilities with external photoelectron emission, where the radiator Z can be chosen to obtain a closer match of γ ray and binding energies, but this needs many orders of magnitude more intense sources for the required very thin radiators. The second greater difficulty in attempting to reach below, say, $\frac{1}{2}$ keV emitted energy where N-shell shake-off would be energetically forbidden, is that of electron spectroscopy from solid sources at high resolution where the K-level width is ~ 100 eV. Thus, it is not likely that much gain can be made in this direction.

V. REARRANGEMENT ENERGY COMPARISON

The K-rearrangement energy for Am was estimated as 88 eV by interpolation of the results for Fm by Mann[17] and for W, Hg, Pb, and Rn by Desiderio and Johnson.[17] It sums three contributions: electrostatic, magnetic, and retardation. The latter two two terms account for the discrepancy of 22 eV with the approximate rearrangement calculation (electrostatic energy only) of Meldner and Perez,[1] 110 eV.

As noted in Sec. III, we have not resolved shake-off satellites for M and higher shells at high Z. Such satellites have been seen in photoelectron spectra at low Z,[5,6] and we have measured L shake-off continua[7] shapes in Fe and Ba. These were found to fit fairly well to theoretically predicted shapes[9,7] and intensities.[3] Based on this agreement for inner-shell shake-off at lower Z, we assume similar agreement for shake-off from all shells in Am. In calculating the centroid shift of the spectrum of final states from the main K line, we neglect the contribution of shake-up satellites.[1,21] We obtain the shake-off probabilities by extrapolation of the calculations of Carlson *et al.*,[3] except for K and L shake-off. Based on our K (and L) shake-off results and on the Slater screening constant of 1s electrons on each other (and on L electrons) we apply a factor $(\Delta Z_{eff})^2/(\Delta Z_\beta)^2 \approx 0.1\ (\approx 0.7)$ to the $1s(2s, 2p)$ predictions of Ref. 3. We assume a shake-off continuum shape similar to that found for L shake-off in Fe and Ba, but stretched or compressed in energy to be proportional to the shell binding energy. Following the calculation of average shake-off energy of Carlson *et al.*,[3] modified as indicated above, we obtained 89 ± 10 eV, to be compared to 88 eV from relativistic Hartree-Fock calculations. The agreement must, however, be regarded as tentative, in view of the evidence of disagreement of $L_1/(L_2+L_3)$ shake-off intensity ratios found for Fe,[7] and the lack of high Z, particularly M- and N-shell shake-off data. These shells give large contributions to the centroid shift.

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Angular Distributions of Secondary Electrons in the Dipole Approximation*

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A close relationship between the angular distributions of secondary electrons produced by photoionization and by impact of fast charged particles is pointed out. The dipole-interaction term in the charged-particle impact cross section [which has $(\ln T)/T$ dependence, T being proportional to the incident energy] has essentially the same angular dependence as the photoelectrons ejected by unpolarized light. An analysis of recent electron-impact data on He and N_2 indicates consistency with the present theory.

I. INTRODUCTION

Recently an increasing number of experimental data on the angular distribution of electrons ejected from atoms and molecules either through photoionization[1-3] or through ionization by charged particles[4-7] have appeared in the literature. This paper shows a simple relationship between the photoelectron data and the dipole-interaction part of the charged-particle impact data (referred to as the secondary-electron data for brevity as opposed to the photoelectron data).

Ionizing collisions between a fast charged particle and an atom or molecule[8] can be qualitatively classified into two parts: "soft" or glancing collisions with large impact parameters and small momentum transfers, and "hard" or close collisions with small impact parameters and large momentum transfers. The soft collisions, because of their large impact parameters, impart on the atomic electrons an impulsive force (= momentum transfer) nearly perpendicular to the path of the incident particle. The effect of such a force upon the atomic electrons is equivalent to that of light propagating in the direction of the incident particle[9]; the electrons experience a force along the direction of the polarization of the light. In short, ionization by soft collisions is equivalent to photo-