Double Vacancies in the K Shell Associated with K-Electron Capture in A^{37}†

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The pulse-height spectrum produced by the decay of A^{37} in a proportional counter was analyzed to determine the probability, per K-electron capture, for the production of a double vacancy in the K shell. The double vacancy is produced by promotion of the second K electron to a bound state or to the continuum. In these experiments both processes could be observed; the measurements included events in which the kinetic energies of the promoted electrons were in the range zero to 4.0 kev. Seventy-three percent of the theoretically predicted total effect should occur in this energy interval. The data, appropriately corrected, give for the probability of double K-vacancy production per K capture, in the energy interval investigated, $3.9\pm0.7\times10^{-4}$. The result is substantially in agreement with the value calculated from theory.

INTRODUCTION

THE atomic excitation and ionization which accompany change of nuclear charge in radioactive decay have been the subjects of considerable theoretical and some experimental investigation.[1–12] It may be calculated from a relation given by Serber and Snyder[9] that the average electronic excitation produced by beta decay at $Z=18$ is 64 ev; the probabilities for excitations sufficiently great to create vacancies in the K shell are finite. Calculations by various workers[1–6] show that in negatron decay the probability of K-vacancy creation is approximately $0.5/Z^2$. For levels of higher principal quantum number, the probability of vacancy creation increases because of the decrease in the effective value of Z due to the shielding effect of the inner electrons. The effects to be expected in K-capture decay are somewhat different.[6] The probability of removal of the remaining K electron is calculated to be $0.125/Z^2$, and the probability of vacancy creation in levels of higher principal quantum number is smaller because, for these electrons, the electrostatic potential from the nucleus Z shielded by two K electrons is nearly the same as that from the product nucleus Z-1 shielded by one K electron.

In the case of K capture in Fe^{55}, a search has been made by Porter and Hotz[7] for orbital electrons ejected with energies in the range 30 to 205 kev. The upper limit resulting from this experiment, 0.6×10^{-6} electron ejections per disintegration, was considered to be not in disagreement with the value 3.6×10^{-6} derived from theory. G. Charpak,[12] using proportional counters and an Fe^{55} source, searched for the x-x coincidences which must accompany K-electron ejection. The effect observed did not exceed a few percent of the accidental coincidence rate; the result was interpreted to be in agreement with theory.

This paper reports measurements on the production of double K-shell vacancies in 35.0-day A^{37}, which decays 92 percent by K capture and 8 percent by L capture.[13]

EXPERIMENTAL METHOD

The pulse-height spectrum from a small proportional counter containing A^{37} consists mainly of one peak, centered at 2.83 kev, the K binding energy of chlorine. This peak is produced by the 89 percent[14] of the K-capture events in which the orbital vacancy is filled by Auger processes; in the case of the counters described below, it may be calculated that a relatively small contribution to the peak, less than 1 percent, is made by a fraction of the K fluorescence processes in which the x-ray is absorbed in the counter gas. A second small broad peak centered at about 200 ev results about equally from L capture and from those K-capture-fluorescent events in which the K x-ray is not absorbed. Whenever a K-capture event is accompanied by removal of the remaining K electron, the pulse corresponds to an energy of at least 5.76 kev if both K vacancies are filled by Auger processes. The pulse size corresponds approximately to 5.76 kev if the second K electron is promoted to a bound state; when the K electron is ejected from the atom the resulting pulse is larger than 5.76 kev by the amount of the kinetic energy of the electron. The value 5.76 kev for the double K vacancy with promotion to bound states has been taken to be somewhat larger than twice the K binding energy of chlorine, because one of the vacancies is filled in an atom which has no K electrons. Analysis of the pulse spectrum in the region of 6 kev and a comparison of the intensity in this region with that in the neighborhood of 3 kev, therefore, should give information about the probability

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of double-vacancy creation and about the kinetic energies of the ejected electrons.

The counters used for these measurements are similar to those described by Bernstein and Ballantine,[15] except for their size, which was made quite small (1-cm diameter, 4-cm length) in order to reduce background. One of the two counters was made with glass sleeves to define the central wire length; in the other counter metal sleeves, connected to the central wire, were used for this purpose. The counter gas mixture consisted of tracer amounts of A^{37} and a 60–40 mixture of argon and methane, at a total pressure of one atmosphere. The resolution of the two counters was the same. The operating characteristics of these tubes proved to be reproducible and stable over times of the order of months.

The high-voltage power supply used in these measurements has been described.[16] Counter pulses, after amplification by a linear, nonoverloading amplifier,[17] were measured with a single-channel analyzer. A nominal channel width of two volts, equivalent to approximately 250 ev, was used in all measurements. Corrections were made to the observed spectrum for a small variation of channel width with channel position. Good electrostatic shielding and careful treatment of insulating surfaces made it possible to reduce the effects of electrical leakage pulses to a fraction of one percent of the smallest measured rates. The distribution of the time intervals between pulses at the low count rates give no evidence for nonstatistical fluctuations. The over-all gain was monitored by observation of the location of the peak at 2.8 kev. Corrections were made for the small gain drift which occurred in one of the experiments.

In the energy region above the principal 2.8-kev peak there are four possible sources for pulses in addition to background and double-vacancy production. These are (a) inner bremsstrahlung, (b) statistical spread of the 2.8-kev pulse distribution, (c) accidental pulse addition, and (d) possible radioactive impurity.

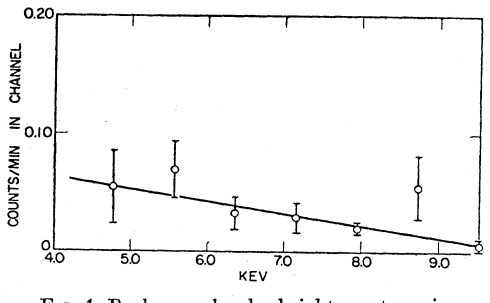

FIG. 1. Background pulse-height spectrum in small proportional counters.

(a) The energy distribution of the inner bremsstrahlung of A^{37} has recently been measured,[18] and the results are in agreement with theory.[19,20] The probability per K capture for the emission of a photon in the energy region of interest should be approximately 10^{-7}, or less than 0.1 percent of the expected double-vacancy effect.

(b) The statistical spread of the 2.8-kev peak was observed to give it a full width at half-maximum intensity of 30 percent. If the peak shape is assumed to represent a Gaussian distribution, it may be estimated that the area under the curve from 5 kev to infinity is 10^{-7} of the total area. Analysis of the peak shape, with allowance for accidental addition, showed that the distribution fell off on the high-energy side more rapidly than a Gaussian of equal width at half maximum.

(c) Pulses of size larger than those corresponding to 2.8 kev are produced whenever two 2.8-kev events occur within a sufficiently short time interval. The magnitude of this effect, which is proportional to the time duration of the pulses and to the square of the count rate, was made reasonably small by the avoidance of high rates and by the use of a short clipping-time constant ($\sim$0.3 μsec) in the amplifier; and it was evaluated by spectrum measurements made on samples of different strengths. The sample strengths, R and nR, were determined by measurement of the areas under the 2.8-kev peaks. In the spectral region between 4.5 kev and 10 kev the count rates, at any energy E, of the samples are

$$\text{for sample } R: \quad W_E = k_E R + c_E R^2,$$

and

$$\text{for sample } nR: \quad S_E = k_E nR + c_E (nR)^2,$$

where k_E is the factor for the double-vacancy production and c_E the factor for accidental pulse addition.[21] Then

$$W_E - S_E/n^2 = (n-1)k_E R/n.$$

The desired quantity $k_E R$ is thus evaluated because all other quantities in this relation are experimentally determined.

(d) Because small amounts of radioactive impurities in the A^{37} could produce pulses in the energy region of interest, complete sets of measurements were made with sources prepared in two different ways. In the first preparation the A^{37} was produced by neutron irradiation of calcium metal sealed in vacuum. Before irradiation the metal was cleaned and outgassed in vacuum at 600°C. The A^{37} was released by vacuum fusion of the calcium and was further purified by the

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[21] The factor c_E is energy-dependent because the pulse shape is not square and because all pulses under the 2.8-kev peak are not of one size.

TABLE I. Analysis of pulse-height spectrum representing events of energy between 4.5 kev and 10 kev from A^{37}. In column 7, n^2 represents the square of the ratio of the disintegration rate of Sample 2 on 11–21–53 to the disintegration rate of Sample 1 at the times listed in column 3. Column 11 is column 10 divided by $(n-1)/n$. All rates are given in counts/minute.

1[a]	2	3	4	5	6	7	8	9	10	11	12
Energy (kev)	Bkg rate	Sample 1 Date	Sample 1 Obs rate	Sample 1 Net rate	Sample 2 Net rate 11–21–53 0:00	n^2	Column 6 / Column 7	Net Sample 1 corrected Col. 3 – Col. 8	Col. 9 corr. for decay to 11–6–53, 14:00	Col. 10 corr. for excess accidental subtraction	Col. 11 corr. for channel width variation
4.62	0.058±0.02	11–9–53 10:30	(0.80)[b]	(0.74)[b]	(3.88)[b]	13.4	(0.29)[b]	(0.45)[b]	(0.48)[b]	(0.66)[b]	(0.68)[b]
4.78	0.056±0.02	11–9 10:30	0.47 ±0.05	0.414±0.05	2.69±0.3	13.4	0.201±0.02	0.213±0.06	0.226±0.06	0.311±0.08	0.32±0.08
5.10	0.052±0.02	11–10 14:00	0.301±0.03	0.250±0.04	1.53±0.2	14.0	0.109±0.01	0.141±0.04	0.152±0.04	0.208±0.06	0.22±0.06
5.41	0.049±0.02	11–10 13:00	0.268±0.03	0.219±0.03	0.97±0.1	14.0	0.069±0.007	0.150±0.03	0.162±0.04	0.221±0.05	0.23±0.05
5.73	0.046±0.02	11–11 13:00	0.224±0.03	0.178±0.03	1.07±0.1	14.6	0.073±0.007	0.105±0.03	0.116±0.03	0.157±0.05	0.17±0.05
6.05	0.042±0.01	11–12 15:00	0.226±0.03	0.184±0.03	0.93±0.09	15.2	0.061±0.006	0.123±0.03	0.137±0.03	0.185±0.05	0.20±0.05
6.37	0.039±0.01	11–13 01:30	0.194±0.01	0.155±0.02	0.87±0.08	15.4	0.056±0.005	0.099±0.02	0.113±0.02	0.152±0.03	0.16±0.03
6.69	0.036±0.01	11–16 11:30	0.194±0.02	0.158±0.02	1.02±0.1	17.8	0.058±0.005	0.100±0.02	0.122±0.03	0.160±0.04	0.17±0.04
7.00	0.033±0.01	11–17 00:00	0.153±0.01	0.120±0.01	1.06±0.1	18.1	0.059±0.006	0.061±0.015	0.075±0.017	0.098±0.02	0.10±0.02
7.32	0.029±0.01	11–14 23:00	0.142±0.01	0.113±0.01	0.79±0.08	16.5	0.048±0.005	0.065±0.015	0.077±0.017	0.102±0.02	0.11±0.03
7.64	0.026±0.01	11–12 03:00	0.143±0.01	0.117±0.01	0.68±0.07	14.9	0.046±0.005	0.071±0.015	0.079±0.016	0.107±0.02	0.12±0.02
7.96	0.022±0.01	11–10 01:00	0.117±0.01	0.095±0.01	0.53±0.02	13.8	0.039±0.001	0.056±0.014	0.060±0.015	0.082±0.021	0.09±0.02
8.75	0.014±0.01	11–14 02:00	0.072±0.008	0.058±0.01	0.34±0.02	16.2	0.021±0.001	0.037±0.012	0.043±0.014	0.057±0.019	0.06±0.02
9.55	0.006±0.005	11–16 01:00	0.063±0.006	0.057±0.008	0.22±0.02	17.5	0.013±0.001	0.044±0.008	0.053±0.009	0.070±0.012	0.08±0.01

[a] The uncertainty in the energy values is about 2 percent.
[b] Values based on interpolation.

use of barium "getter" and by passage through a liquid-nitrogen-cooled trap. This material was six months old when used in the experiments. For the second preparation calcium fluoride, in the form of cleaned optical crystal material, was irradiated in vacuum. The irradiated material was transferred to a tantalum crucible and melted in vacuum, and the A^{37} was removed via a liquid-nitrogen-cooled trap. This A^{37} was used soon after preparation. Considerations of the purity of materials irradiated, of the nature of the purification process, and of the half-lives of possible products make it very unlikely that there was any measurable contribution by impurities to the observed pulse spectrum. Possible interference by 265-year A^{39} is ruled out because the results obtained from the two preparations are the same even though the A^{39}/A^{37} ratio was 30 times as large in the first preparation as it was in the second.

Background rates were measured when the counters were filled with inactive gas. The gas gain in the background measurements was made to equal that of the A^{37} measurements by adjustment of the high voltage; the pulse spectrum of an external Cd^{109} source was used as a monitor. The backgrounds of the two counters used, which were the same within the statistical errors, are shown in Fig. 1.

RESULTS AND DISCUSSION

In Table I are given the data and corrections obtained from the experiment with A^{37} produced from irradiated calcium fluoride. The data obtained with A^{37} from irradiated calcium metal were similar. Final results (column 12) are shown graphically in Figs. 2 and 3. The errors indicated in the table are derived from the counting statistics.

In the region below 5.5 kev the rates change so rapidly with energy that an energy uncertainty of a

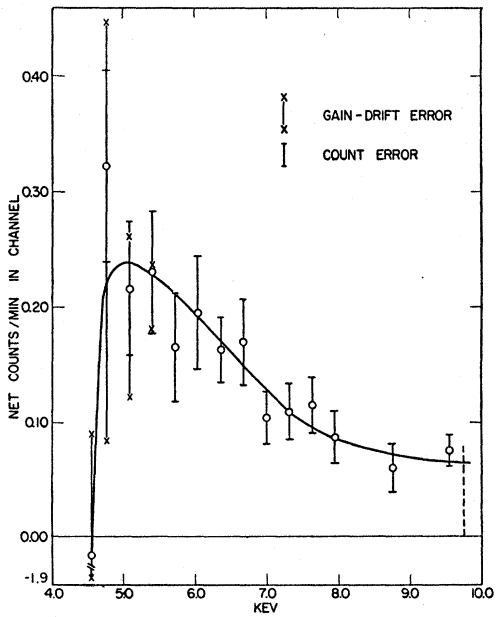

FIG. 2. Pulse-height spectrum representing events of energy 4.5 kev to 10 kev in the decay of A^{37}. (CaF_2 source).

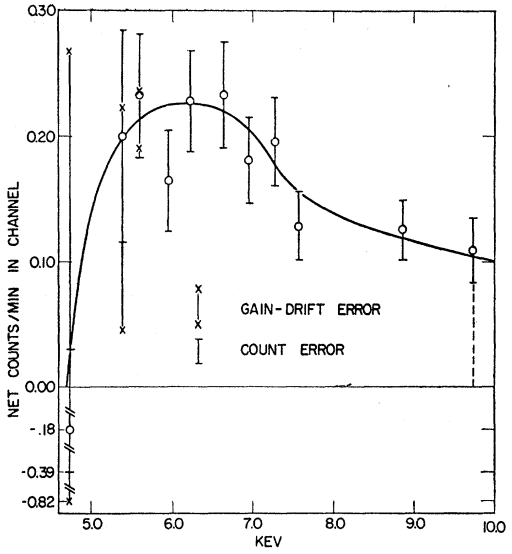

FIG. 3. Pulse-height spectrum representing events of energy 4.5 kev to 10 kev in the decay of A^{37}. (Ca metal source).

few percent, because of the subtraction which is involved in the calculation of column 9, gives rise to uncertainties larger than those shown in the table. Whenever the errors from this source become comparable with the tabulated errors, both are indicated in the figures. In the calculation of the errors caused by energy uncertainty, a 3 percent relative gain drift was assumed.

A smooth curve has been drawn through the experimental points (Figs. 2 and 3); and it has been made to reach the zero ordinate at approximately 4.7 kev rather than at the theoretical value 5.76 kev because of the finite energy resolution of the counters. Because of the large experimental uncertainty in the region below 5.4 kev, only the data for energies between 5.4 kev and 9.7 kev are used in the calculations.

The theoretical energy distribution for the electrons ejected to the continuum in the decay of A^{37}, as calculated from Eq. (18a) reference 6, is shown in Fig. 4. The decay energy is taken to be 816 kev.[22] In Fig. 5,

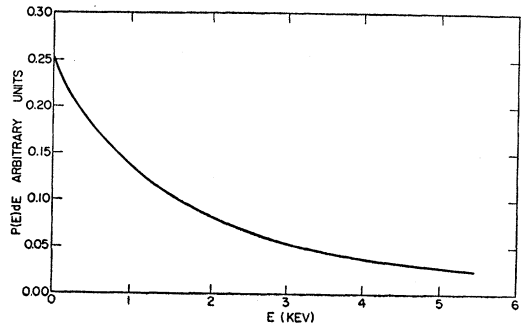

FIG. 4. Theoretical energy distribution of K electrons ejected in the decay of A^{37}.

[22] Richards, Smith, and Browne, Phys. Rev. **80**, 524 (1950).

Curve C shows this theoretical distribution as it appears when modified by the finite resolution of the counters and by the addition of the energy, 5.76 kev, derived from the filling of two K vacancies in chlorine. The energy of 5.76 kev appears only when both vacancies are filled by Auger cascades, for which the probability is $(0.89)^2$ or 0.79. Curve B is the pulse spectrum to be expected from the promotion of K electrons to bound states; the areas under B and C out to the end-point energy are normalized so that they are in the ratio 2:3, as given by reference 6, Eq. (17b) and Eq. (15) with the added factor $\frac{2}{3}$ as cited in the text. Curve A is the sum of B and C and represents the actual pulse-height distribution to be expected from the theory. In the calculation of B and C the resolution of the counter was computed from the observed resolution at 2.8 kev, with the assumption of an $E^{\frac{1}{2}}$ dependence.

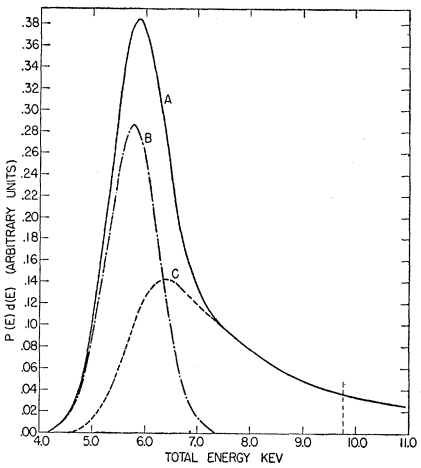

FIG. 5. Theoretical pulse-height distributions corrected for finite counter resolution. Curve C is the contribution of events in which the second K electron is ejected to the continuum. Curve B is the contribution of events in which the electron is promoted to a bound state. Curve A is the sum of B and C.

The vertical line at 9.73 kev, marking the high-energy limit of these experiments, corresponds to a kinetic energy for the ejected electron of 9.73–5.76 kev or 3.97 kev. From a graphical integration under the theoretical momentum-distribution curve it was found that 0.71 of all continuum-ejection events should be included in the experimental range 5.4 to 9.7 kev. Similarly 0.79 of the area under Curve B, Fig. 5, should be included. Thus the range of the measurements should include $(0.71)\frac{3}{5}+(0.79)\frac{2}{5}$ or 0.73 of all ejection and promotion events accompanied by double Auger cascade.

The final results are summarized in Table II. The various rates set down in Table II are obtained by division of the areas under the curves of Figs. 2 and 3 and under the 2.8-kev peaks by the channel width. The values given in column 5, however, do not depend on an accurate knowledge of this width.

A chlorine atom lacking two K electrons may complete its K shell in any of three ways: (a) double Auger process, probability $(0.89)^2$; (b) one fluorescent and one Auger process, probability $2(0.89)(0.11)$; and (c) double fluorescent process, probability $(0.11)^2$. The probability of completion of the K shell by path (b) is 25 percent as great as that by path (a), but the contribution by path (b) to the pulse distribution observed in these experiments is small, because the path (b) distribution has its maximum in the vicinity of 2.8 kev. Path (b) processes are estimated to contribute 8 percent of the areas under the curves of Figs. 2 and 3.

According to Primakoff and Porter,[6] the total probability per K capture for double K-vacancy production is

$$p^{(2)} \cong (3/4Z^2)(1-\gamma)^2(\alpha), \quad (1)$$

where γ, a parameter, is given the value 0.50 to fit the electron space wave function used to that given by Hylleraas,[23] and α is a constant of value $\frac{2}{3}$ (but see below). For A^{37}, $p^{(2)}$ is calculated to be 3.86×10^{-4}; for comparison with the experiments this quantity is multiplied by 0.73 to give 2.82×10^{-4}. The value derived from the average experimental value (Table II, column 5), after correction for the path (b) contribution, is $3.9\pm0.7\times10^{-4}$.[24]

TABLE II. Summary of results for double K-vacancy production in A^{37}. In column 4 the rates of column 3 are corrected for fluorescence, factor $1/(0.89)^2$. Column 2 rates have been corrected for fluorescence, factor 1/0.89.

1	2	3	4	5
	K-capture rate (counts/min)	Rate of pulses in the interval between 5.38 kev and 9.73 kev (counts/min)	Column 3 corrected (counts/min)	Double K holes per K capture Col. 4/Col. 2
Exp. 1	6.65×10^3	2.35	2.97	4.47×10^{-4}
Exp. 2	5.26×10^3	1.66	2.10	3.99×10^{-4}
				av $4.2\pm0.7\times10^{-4}$ [a]

[a] The error value is estimated from a consideration of the possible sources of uncertainty; it is thought to be conservative.

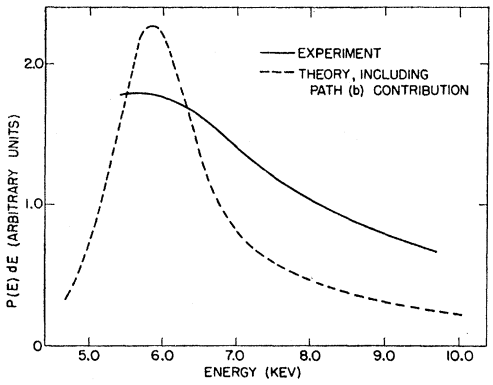

FIG. 6. Comparison of experiment and theory.

The probability per K capture for the ejection of the second K electron to the continuum as given in reference 6, Eq. (17b) is:

$$p_{\text{eject}} \cong 0.3(1-\gamma)^2/Z^2. \quad (2)$$

The probability for promotion of the second K electron to bound states is then the difference between Eqs. (1) and (2). There is sufficient uncertainty in the value of α in Eq. (1) to make p_{bound} uncertain by a factor of at least 3. A comparison of the average experimental spectrum with the theoretical one, Fig. 6, seems to indicate that the ratio of p_{bound} to p_{eject} is smaller than that calculated; and if the value of α were chosen to be not $\frac{2}{3}$ but $\frac{1}{2}$, as suggested by Levinger,[25] the fit of the calculated curve with the observed spectrum would be much better. This choice, however, would give $p^{(2)}$ the value 2.9×10^{-4}, and $0.73p^{(2)}$ then would be 2.1×10^{-4}.

It may be noted that the theory, which gives a result somewhat smaller than the experimental one here at energies small compared with the total energy available, gives a result larger than the experimental one obtained by Porter and Hotz[7] in their measurements with Fe^{55} at energies comparable with the total energy available.

The present state of the theory is such that an attempt to determine accurate values for the parameters α and γ is probably not justified.

The authors take pleasure in expressing their appreciation to Dr. Max Wolfsberg and to Dr. William Rubinson for helpful discussions and to Mr. Robert Chase for his electronics design work.

[23] A value of 0.4 for γ, as given by E. A. Hylleraas, Z. Physik **54**, 347 (1929), could be used instead of the value 0.5. The choice $\gamma=0.4$ increases both $p^{(2)}$ and p_{eject} by a factor 1.44.

[24] Levinger's[4] expression is $p^{(2)}=0.16/Z^2$, which for A^{37} becomes 5.0×10^{-4}. The calculation of Primakoff and Porter, however, includes factors omitted by Levinger.

[25] Reference 6, p. 934.