

TABLE III. Parameters (A_s and Z_s) and combining coefficients (C_{ij}) defining the Hartree-Fock orbitals for Cu^+ .

j	A_j	Z_j	$C_{1s,j}$	$C_{2s,j}$	$C_{3s,j}$
1	0	84.8828	0.00037044	-0.00036468	-0.00038449
2	0	30.4491	0.91205876	-0.27950925	0.10652016
3	1	26.9961	0.10841891	-0.16245115	0.04976048
4	1	14.1023	-0.00647884	0.64460027	-0.21227812
5	2	13.3297	0.00561417	0.46415723	-0.38260515
6	2	8.5681	-0.00204424	0.06610429	0.17263958
7	2	5.0982	0.00065755	-0.00454834	0.94245212
8	2	2.8171	-0.00016921	0.00134453	0.07547339
			$C_{2p,j}$	$C_{3p,j}$	
9	0	34.5244	0.00103326	0.00096650	
10	0	18.9852	0.13481246	-0.05841121	
11	0	11.6372	0.84951100	-0.29915630	
12	1	10.8502	0.02041835	-0.11625686	
13	1	6.8083	0.02746109	0.54128259	
14	1	3.9668	-0.00525461	0.63298421	
15	1	2.2563	0.00172020	0.02228438	
			$C_{3d,j}$		
16	0	1.6956	0.19657400		
17	0	2.4954	0.25771318		
18	0	4.2881	0.46579549		
19	0	7.5015	0.24455545		
20	0	13.0768	0.02287090		

were obtained, normalized such that

$$\int_0^\infty |U_i(r)|^2 dr = 1. \quad (\text{A2})$$

TABLE IV. One-electron energies for Cu^+ in atomic units (1 a.u. = 2 Ry).

$\epsilon_{1s} = -329.11$	$\epsilon_{2p} = -35.928$
$\epsilon_{2s} = -41.127$	$\epsilon_{3p} = -3.641$
$\epsilon_{3s} = -5.324$	$\epsilon_{3d} = -0.8099$

The basis functions, R_j , are of the form

$$R_j(r) = N_j r^{(l+A_j+1)} e^{-Z_j r}, \quad (\text{A3})$$

where N_j is a normalization constant and is expressible in terms of the other parameters, i.e.,

$$N_j = [(2Z_j)^{2l+2A_j+3} / (2l+2A_j+2)!]^{1/2}. \quad (\text{A4})$$

$U_i(r)$ of common l value are constructed from a common set of $R_j(r)$'s. Z_j 's, A_j 's and combining coefficients (C_{ij} 's) are listed in Table III; the one-electron energies are given in Table IV. The C_{ij} 's define orthonormal functions to the number of digits reported but have by no means been uniquely determined to that number of digits. The total energy for the ion is -1638.724_5 a.u. as compared with -1638.705 a.u. obtained in a previous calculation.¹³ The improvement is primarily associated with the greater variational freedom allowed to the outer parts of the $3s$ and $3p$ shells; repercussions on the $3d$ shells were small.

Positron Mean Lives in Scandium, Yttrium, and the Rare-Earth Metals*

J. L. RODDA AND M. G. STEWART

Institute for Atomic Research and Department of Physics, Iowa State University, Ames, Iowa

(Received 21 February 1963)

Positron mean lives relative to that in aluminum are reported for scandium, yttrium, and all of the stable rare-earth metals. An automatic cycling procedure allows these relative measurements to be made with an accuracy of $\pm 3 \times 10^{-12}$ sec. The average positron lifetime in the trivalent rare earths and in yttrium is 0.675×10^{-10} sec longer than the positron lifetime in aluminum, with an average deviation of $\pm 0.035 \times 10^{-10}$ sec. The positron lifetimes in the divalent rare earths (europium and ytterbium) are appreciably longer, while the lifetime in scandium is somewhat shorter. The experimental results indicate a correlation between the positron lifetime and the conduction electron density, and they show that the $4f$ electrons do not participate in the annihilation process.

I. INTRODUCTION

IF a positron is injected into a metallic sample with an energy of a few hundred kilovolts, it will be able to penetrate to the interior of the sample. There it will be thermalized in about $1/3 \times 10^{-12}$ sec via collisions with conduction electrons, and it will become part of the electronic system. Some time later the positron will annihilate with an electron, producing (usually) two

0.511-MeV annihilation gamma rays. These relatively high-energy gamma rays can then bring information about the annihilation process out of the sample with negligible attenuation or scattering. Thus, the investigation of the positron annihilation in a metal should provide some information on the electronic structure of the metal.

The first extensive measurements of positron mean lives in metals were made by Bell and Graham,² and

* Contribution No. 1280. Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

¹ G. E. Lee-Whiting, Phys. Rev. **97**, 1557 (1955).

² R. E. Bell and R. L. Graham, Phys. Rev. **87**, 236 (1952); **90**, 644 (1953).

since then numerous measurements have been made by these and other investigators.^{3,4} These measurements indicate that the positron mean life in a metal is on the order of 2×10^{-10} sec, and for most of the metals thus far investigated it is independent of the metal chosen to within about $\pm 25\%$. Thus, it is evident that in order to detect meaningful variations in positron lifetimes between various metals the lifetimes should be measured with a relative uncertainty approaching one percent. This then implies that the positron lifetimes in various metals must be made with a relative time uncertainty not much larger than $\pm 2 \times 10^{-12}$ sec.

At the time the present measurements were undertaken, the existing theories were not sufficiently accurate to make quantitative predictions of positron lifetimes in metals. This investigation was thus undertaken in order to make some of the more accurate measurements needed in order to point the way for refinements in the theory. The particular measurements reported here are for all of the stable metals in group III B of the periodic table. The relative lifetimes are believed to be correct to within $\pm 3 \times 10^{-12}$ sec.

II. EXPERIMENTAL METHOD

The experimental method is described in detail elsewhere,⁵ and thus it will only be briefly outlined here. A transistorized time-amplitude converter is used together with a conventional fast-slow coincidence system. An automatic cycling procedure makes it possible to use the centroid shift technique to measure positron lifetimes relative to the positron lifetime in aluminum with an accuracy of $\pm 3 \times 10^{-12}$ sec. Let τ_{Al} be the centroid shift between the aluminum positron time spectrum and a prompt time spectrum, and let $\Delta\tau$ be the centroid

shift between the positron time spectrum for the metal under investigation and the positron time spectrum for aluminum. Then the positron mean life in the metal sample is given by $\tau = \tau_{Al} + \Delta\tau$.

The 5–10 μCi positron source (Na^{22}Cl in distilled water; 1 $\mu\text{Ci}/\mu\text{liter}$) was deposited between two pieces of 0.25-mil aluminum foil and dried with a heat lamp. The source was then sandwiched between two polished pieces of the metal to be studied. The aluminum foil was necessary because some of the rare earths react quite strongly with water. It is estimated that no more than a few percent of the positrons annihilate in the aluminum, and this would cause an almost constant error of no more than one percent in the measured mean lives. Because it reacts rapidly with the atmosphere, the europium sample was prepared in a dry box which was evacuated and then filled with dry nitrogen. The finished sample was then sealed in paraffin to exclude the atmosphere.

TABLE I. The time differences, $\Delta\tau$, between the centroids of the positron time spectra for the metals of group III B and the positron time spectrum for aluminum.

Element	$\Delta\tau = \tau - \tau_{Al}$ (10^{-12} sec)
Sc	56 ± 3
Y	75 ± 3
La	74 ± 3
Ce	66 ± 3
Pr	60 ± 3
Nd	66 ± 3
(Pm)	...
Sm	68 ± 3
Eu	106 ± 3
Gd	71 ± 3
Tb	70 ± 3
Dy	62 ± 3
Ho	65 ± 4
Er	64 ± 3
Tm	68 ± 3
Yb	93 ± 3
Lu	69 ± 3

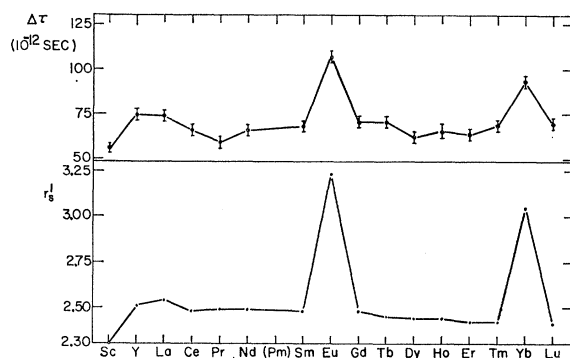


FIG. 1. The lower curve is a plot of the values of r_s' , the radius of the unit conduction electron sphere (corrected for the excluded volume of the ion) for Sc, Y, and the rare-earth metals. The upper curve is a plot of $\Delta\tau = \tau - \tau_{Al}$, the time difference between the centroid of the positron time spectrum in the group III B metal and the centroid of the positron time spectrum in aluminum.

³ R. E. Bell and M. H. Jorgensen, Can. J. Phys. **38**, 652 (1960).

⁴ See particularly: A. Bisi, G. Faini, E. Gatti, and L. Zappa, Phys. Rev. Letters **5**, 59 (1960); and G. Jones and J. B. Warren, Can. J. Phys. **39**, 1517 (1961).

⁵ J. L. Rodda, J. E. Griffin, and M. G. Stewart, Nucl. Instr. Methods (to be published).

III. EXPERIMENTAL RESULTS AND DISCUSSION

In the normal room temperature phase all of the group III B metals are trivalent except europium and ytterbium, which are divalent. The rare-earth metals have a core configuration consisting of the inert xenon configuration plus a number of 4f electrons (which varies from 0 in lanthanum up to 14 in lutetium). Scandium and yttrium have core configurations consisting of the argon and krypton configurations, respectively, and have chemical properties very similar to the rare earths.

The positron lifetime in a metal is expected to be a function of the density, n , of conduction electrons in the metal. Often the electron density is specified in terms of r_s , the radius of a sphere containing one conduction electron (the so-called unit conduction electron sphere). Thus, the volume per electron is $1/n = 4\pi(a_0 r_s)^3/3$, where the Bohr radius, a_0 , is included in the definition so that

r_s will be dimensionless. The lower curve in Fig. 1 shows the values of r_s' for scandium, yttrium, and the rare earths. (The r_s values have been reduced by 3 to 6% by subtracting the ionic volume, from which the positrons are assumed to be excluded, from the atomic volume, and thus they are relabeled r_s' .) It can be seen that r_s' is approximately constant ($\bar{r}_s' = 2.47$) for all of the trivalent rare earths, but it is appreciably larger for europium and yttrium. The value of r_s' is somewhat smaller for scandium because it has an appreciably smaller atomic volume than the trivalent rare earths.

The upper curve in Fig. 1 shows the experimental positron lifetimes measured with respect to the positron

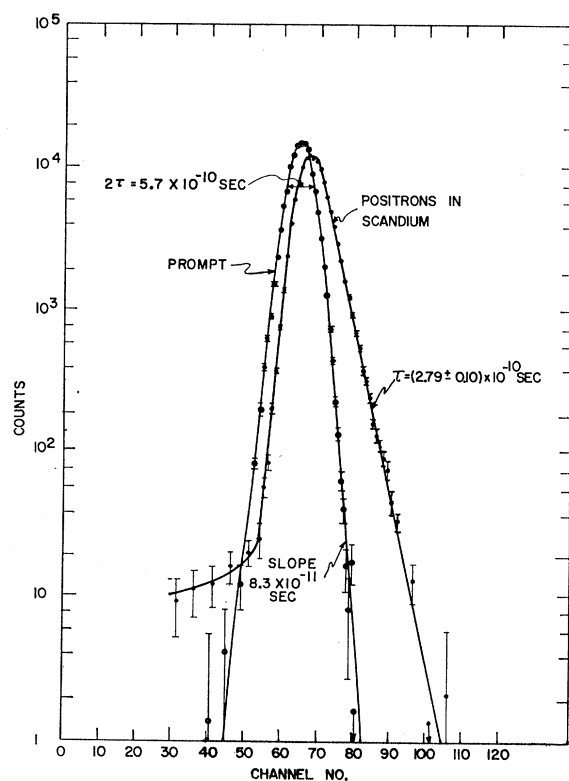


FIG. 2. Time spectrum of positron annihilation in scandium. The positron mean life obtained from the slope is $(2.79 \pm 0.10) \times 10^{-10}$ sec. The time calibration is 7.47×10^{-11} sec/channel. A prompt spectrum using Co^{60} is also shown.

lifetime in aluminum, and Table I gives a listing of these values.⁶ The trivalent rare-earth metals and yttrium all

⁶ Note added in proof. The time calibration for these measurements was obtained using measured lengths of RG-62/U cable, but several of these measurements were recently repeated using an air-dielectric, 125-Ω trombone for calibration. In every case, the repeated measurements yielded lifetimes only 85% as long as the original ones. This systematic error in the original measurements was probably due more to the effect of attenuation in the calibration cable than to the use of an incorrect propagation velocity (0.81C) for the cable. Thus, all of the lifetimes reported here (including the aluminum lifetime) should be multiplied by a factor of 0.85. In Fig. 4 this correction will make the Al, Sc, and trivalent rare-earth points lie on Kahana's curve, while the Yb and Eu points now lie above the curve. The agreement between the two Na points is also improved.

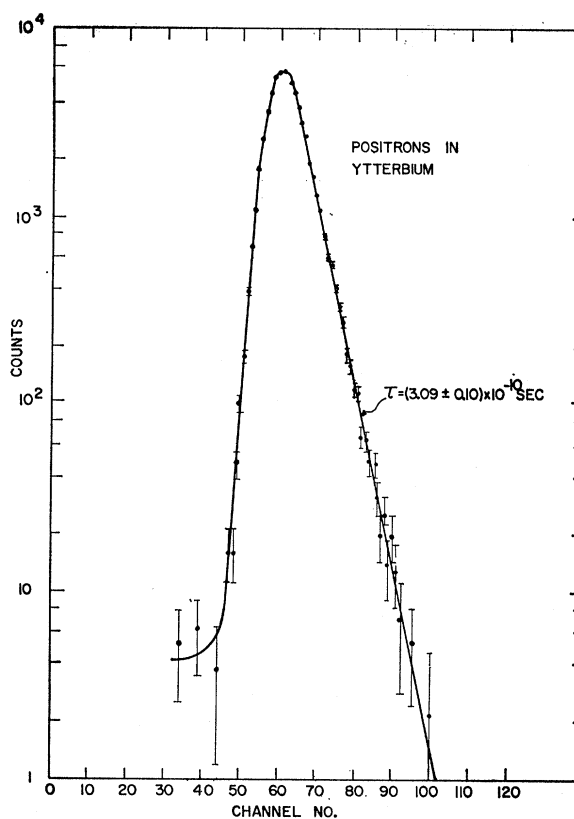


FIG. 3. Time spectrum of positron annihilation in ytterbium. The positron mean life obtained from the slope is $(3.09 \pm 0.10) \times 10^{-10}$ sec. The time calibration is 6.91×10^{-11} sec/channel.

have nearly the same r_s' value, and within statistics the measured positron lifetimes for these metals are also nearly the same. The average positron mean life for these trivalent metals is 0.675×10^{-10} sec longer than the positron mean life in aluminum, and the average deviation from this value is $\pm 0.035 \times 10^{-10}$ sec. The number of $4f$ electrons, however, varies from 0 in lanthanum (and yttrium) to 14 in lutetium, and thus one can conclude that the $4f$ electrons do not participate in the annihilation process. The much smaller density of the conduction electrons in the divalent rare earths, however, does give rise to an appreciably longer positron mean life, while the somewhat higher conduction electron density in scandium leads to a shorter positron mean life. In Figs. 2 and 3 are shown two typical time spectra that were obtained in these measurements. They are for scandium and ytterbium, respectively. A prompt spectrum using Co^{60} is also shown in Fig. 2.

In Fig. 4 the measured annihilation rates for aluminum and the group III B metals as well as Bell and Jorgensen's³ results for the alkali metals are plotted versus r_s' . Since the present set of measurements give only the relative lifetimes compared to aluminum, an absolute value for the positron lifetime in aluminum must be used in order to calculate the annihilation rates.

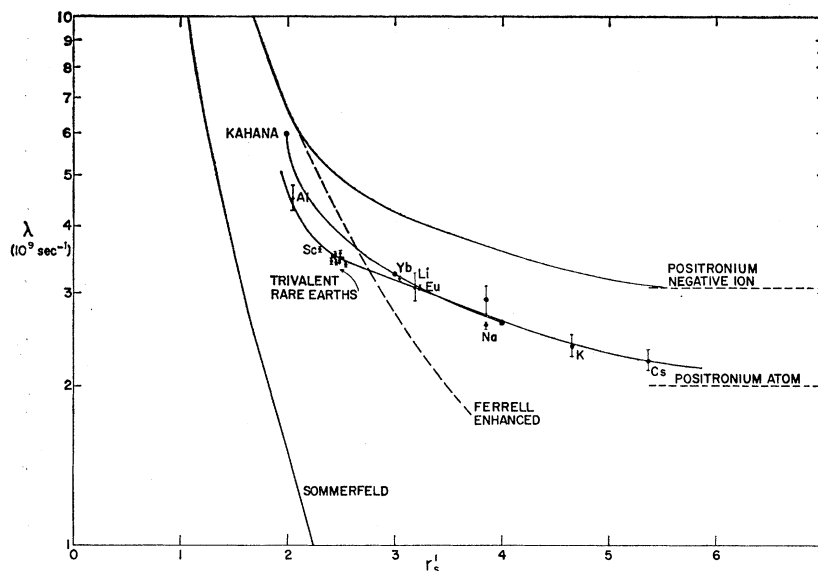


FIG. 4. Annihilation rate vs r_s' for Al and the metals of groups I A and III B. The annihilation rates for the alkali metals were taken from the work of Bell and Jorgensen (reference 3) and adjusted slightly as described in the text. The lower of the two points labeled Na is from the present investigation. A smooth curve is drawn through the experimental points, and various theoretical curves are shown for comparison.

For this purpose a value of $\tau_{Al} = 2.21 \times 10^{-10}$ sec was used⁵ with an estimated error of $\pm 0.12 \times 10^{-10}$ sec. It should be pointed out that there are two lifetimes in the aluminum positron time spectrum,^{3,5} and the value used here is the total centroid shift of the aluminum compared to a prompt source. Bell and Jorgensen's data were used to compute the composite lifetime $(1-f)\tau_1 + f\tau_2$, which would be measured in a centroid shift experiment for each of the alkali metals. (The fraction of the longer lived τ_2 component present is denoted by f .) These lifetimes were then normalized to a positron lifetime of 2.21×10^{-10} sec in aluminum, and the annihilation rates computed from these normalized lifetimes are the ones plotted in the figure. It should also be noted that the indicated errors for the group III B metals represent only the errors in the relative lifetime measurements and do not include the error associated with the measurement of τ_{Al} . The positron lifetime in sodium was also measured during the present investigation, and the result of this measurement is the lower one of the two points marked Na on the figure. (The sodium sample, being very reactive, was prepared in the same manner as the europium sample described previously.) Various theoretical curves are also included on the figure.

It can be seen that the experimental data lie on a fairly smooth curve, but both the Sommerfeld theory⁷ and the Ferrell theory⁷ predict a much stronger dependence of λ on r_s' than that found experimentally. Ferrell, however, expected his theory to hold only for high electron densities (small r_s'), and he expected that for low electron densities the annihilation rate would ap-

proach that of the positronium negative ion (two electrons bound to a positron). This is indicated in a qualitative manner by the solid curve which is arbitrarily drawn so as to be tangential to the enhanced curve at $r_s' = 2.5$ and to be tangential to the positronium ion rate at $r_s' = 5.5$. The theory recently published by Kahana,⁸ on the other hand, gives a fairly good description of the experimental results. However, this theory still predicts a somewhat stronger dependence of λ on r_s' than is found experimentally.

It should be noted that all of the theories of positron annihilation rates assume that annihilation takes place only with the valence electrons. It is known from the measurements of the angular correlation of annihilation photons, however, that some core annihilation does take place. The alkali metals, aluminum, scandium, and yttrium have only the valence electrons outside of an inert gas configuration, and the rare-earth metals have only the valence electrons outside of a core consisting of an inert gas configuration plus the well-shielded $4f$ electrons. Thus, the alkali metals, aluminum, and the group III B metals might be expected to have roughly the same amount of core annihilation, and perhaps this is why their annihilation rates do vary quite smoothly with r_s' .

ACKNOWLEDGMENTS

The authors would like to express their appreciation to Professor A. H. Daane and his group for providing the metallic samples, and to Wallace Souder for his aid in taking data.

⁷ Richard A. Ferrell, *Rev. Mod. Phys.* **28**, 308 (1956).

⁸ S. Kahana, *Phys. Rev.* **129**, 1622 (1963).