

with

$$n=0, \pm 1.$$

Thus g_{11} and A_{11} can be determined in the same manner as they would be using the approximation of Bleaney.²⁵ Similarly, g_{\perp} can be determined at $\theta=90^\circ$ from the location of the nearly isotropic center line. However, diagonalization of the Hamiltonian matrix at $\theta=90^\circ$ shows that there is no simple relationship between A_{\perp} and the minimum splitting when the contribution due to A_{\perp} is less than the contribution due to A_{11} in second order. In order to determine A_{\perp} , the matrix was numerically diagonalized at $\theta=90^\circ$ for a series of values of A_{\perp} using a digital computer, and then by graphical interpolation it was found that an A_{\perp} of 21 G corresponded to 3-G minimum separation. These values of the g and A tensors are listed in Table I; from them transition energies were computed as a function of angle and plotted as the solid lines in Figs. 1-3. The computed energies are shown to be in good agreement with the experimental data.

For regions like L of Fig. 1, the detailed experimental angular variation showed the presence of two extra lines. Since in the neighborhood of this accidental degeneracy the eigenfunctions are linear combinations of the unperturbed basis functions, the selec-

tion rule $\Delta m_T=0$ no longer applies, and it is possible to observe transitions which would normally be forbidden. These are shown as the dashed lines labeled F in Fig. 2. A mixing of states also occurs at $\theta=90^\circ$, and it is expected that forbidden transitions may occur near this angle; however, because of the large overlap of the lines at $\theta=90^\circ$ no extra lines could be observed. In contrast to the spin resonances in KHF_2 , forbidden transitions were observed by Woodruff and Kanzig⁷ for the V_K center in LiF at $\theta=90^\circ$ rather than $\theta=81^\circ$ since their A_{\perp} was larger, giving a greater resolution of lines at $\theta=90^\circ$ and an absence of degeneracy near $\theta=81^\circ$.

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Positron Lifetimes in Metals*

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Positron decay curves in various metals have been measured, using careful sample preparation techniques and a delayed-coincidence system with 0.30-nsec (full width at half-maximum) prompt time resolution and $10^4:1$ peak-to-background ratio. Evidence was found that the annihilation in pure metals under ideal conditions is characterized by a single exponential decay, the second lifetime usually observed being an artifact of sample preparation. In the case of Mg with Na^{22} produced *in situ* by the (p,α) reaction, a single exponential decay over approximately four decades was observed. In a plot of annihilation rate versus conduction electron density, the observed rates for the nearly-free-electron metals fell close to the theoretical curve of Kahana, approaching the spin-averaged positronium rate at low densities. Compared with these rates, annihilation rates at a given valence-electron density were found to be higher in the transition metals and lower in Be, Bi, and in the semiconductors Si and Ge, in agreement with qualitative ideas about the one-positron many-electron system in real metals. Within the experimental error ($\pm 2.5\%$), no difference in lifetime was observed between intrinsic and heavily n -type Si, and similarly for Ge.

I. INTRODUCTION

THE lifetime of slow positrons annihilating in a metal is determined by the average density of electrons at the site of the positron in the ground state of the one-positron many-electron system.^{1,2} Because of

its charge, the positron is repelled from the positive ions at the lattice sites; thus it annihilates mainly with the electrons in the conduction band and, to a lesser extent, with core electrons. Simple one-electron calcu-

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¹ For early review articles on positron annihilation in solids, see S. Berko and F. L. Herford, *Rev. Mod. Phys.* **28**, 299 (1956);

R. A. Ferrell, *ibid.* **28**, 308 (1956); L. Simons, in *Handbuch der Physik* edited by S. Flügge (Springer-Verlag, Berlin, 1958), Vol. 34, p. 139; P. R. Wallace, *Solid State Physics* (Academic Press Inc., New York, 1960), Vol. 10, pg. 1.

² For up to date review articles, see *Proceedings of the Conference on Positron Annihilation* (Academic Press Inc., New York, 1966).

lations of the positron and electron wave function³⁻⁶ have succeeded in giving momentum distributions that are in reasonable agreement with those measured in annihilation gamma angular-correlation experiments. These calculations show that in many metals, for example in Al, nearly all the annihilation takes place with conduction electrons, and that a simple electron-gas model is adequate to describe these electrons; in other metals, for example in Cu, the fraction of core annihilations is higher and the importance of the lattice cannot be so easily neglected.⁶ The same one-electron model, however, is itself incapable of providing correct lifetime predictions; since it neglects the effects of electron-positron correlations, it gives lifetimes which are too long, and vary too much with electron density.^{1,2} To obtain reasonable agreement with experiment, the methods of many-body theory are required, taking full account of electron-positron forces, electron-electron forces, and the Pauli principle. Such many-body calculations have been carried out in various forms,^{1,7-10} but with one recent exception¹¹ they have only treated the electron-gas model. The absence of theoretical work on positron lifetimes in real metals may be attributed both to the added computational difficulties introduced by the lattice, and to the lack of experimentally measured lifetimes accurate enough to test the theoretical work.

We have remeasured lifetimes in a number of metals, including those in which lattice effects and core annihilation are known to be important, in order to test existing models used to describe positron decay in metals and to stimulate new theoretical efforts. Two secondary aims of our work were (1) to resolve the discrepancies among existing lifetime measurements by different observers; and (2) to study the complex decay (double lifetime) which has been reported in recent experiments in order to determine whether or not it is a real effect of positron decay in a pure metal under ideal conditions.

The earliest measurements of positron lifetimes in metals¹² showed that the mean lives in various metals are all of the order of 2×10^{-10} sec, thus establishing the importance of correlation effects in determining positron lifetimes. Limitations of time resolution in the early experimental work were such that lifetime values had to be determined by the centroid-shift method, with its large systematic errors, rather than by the

inherently more reliable slope method.¹³ Thus the early measurements could not determine the lifetime variation from metal to metal accurately enough to study its dependence on the conduction-electron density and on other parameters of the metals. A number of further centroid-shift measurements with comparable or slightly better time resolutions¹⁴ were subsequently reported. Agreement among various reported values for each metal was rather poor. More recently, workers in two different laboratories¹⁵ measured lifetimes in many metals using the centroid shift method but with improved time resolution and with special care to minimize various systematic errors. Agreement between their two sets of measured values was fair; however the errors were still such that one was unable to make significant new theoretical comparisons. In particular the centroid-shift measurements only gave the mean lives relative to that in Al, the absolute magnitude of which was poorly known.

At about the same time, Bell and Jorgensen¹⁶ measured lifetimes in Al and the alkali metals with considerably improved accuracy, using the slope method. Their data demonstrated conclusively the dependence of the lifetimes on the conduction-electron density in the metals studied, all of which have small core-annihilation fractions. The slope measurements of Bell and Jorgensen,¹⁶ which were absolute rather than relative measurements, were found to be in good agreement with the most recent many-body electron gas calculations.⁸ Recently, lifetimes in Sc, Y, and trivalent rare earths were reported,¹⁷ also with improved accuracy. No comparably accurate measurements existed, however, for the metals in which core annihilation are important.

In the measurements performed with improved time resolution, a complex decay (second lifetime) has been observed. Two studies of this second lifetime have been reported. In the first,¹⁶ it was shown that the second lifetime was apparently not an effect of pile-up or other electronic anomalies, and was present even with sources of a tenth the usual strength. In the second,¹⁸ however, it was found that the intensity and slope of the second lifetime depend somewhat on sample preparation techniques, suggesting that the second lifetime may be entirely an anomaly of sample preparation, involving positrons which come to rest in the region of the surface

³ S. DeBenedetti, C. E. Cowan, W. R. Konneker, and H. Primakoff, *Phys. Rev.* **77**, 204 (1950).

⁴ G. Lang and S. DeBenedetti, *Phys. Rev.* **108**, 914 (1957).

⁵ A. T. Stewart, *Can. J. Phys.* **35**, 168 (1957).

⁶ S. Berko and J. S. Plaskett, *Phys. Rev.* **112**, 1877 (1958).

⁷ S. Kahana, *Phys. Rev.* **129**, 1622 (1963); J. P. Carbotte and S. Kahana, *ibid.* **139**, A213 (1965).

⁸ A. J. Zuchelli and T. G. Hickman, *Phys. Rev.* **136**, A1728 (1964).

⁹ C. K. Majumdar, *Phys. Rev.* **140**, 227 (1965).

¹⁰ For further references and a critical review see Birger Bergersen, Ph.D. thesis, Brandeis University, 1964 (unpublished).

¹¹ J. P. Carbotte, *Phys. Rev.* **144**, 309 (1966).

¹² S. DeBenedetti and H. J. Richings, *Phys. Rev.* **85**, 377 (1952); R. E. Bell and R. L. Graham, *ibid.* **90**, 644 (1953).

¹³ For a review of delayed coincidence techniques, see, for example, A. Schwarzschild, *Nucl. Inst. Meth.* **21**, 1 (1963); G. Present *et al.*, *ibid.* **31**, 71 (1964).

¹⁴ A. T. G. Ferguson and G. M. Lewis, *Phil. Mag.* (7) **44**, 1339 (1953); George H. Minton, *Phys. Rev.* **94**, 758 (1953); T. R. Gerholm, *Arkiv Fys.* **10**, 523 (1956); G. Jones and J. B. Warren, *Can. J. Phys.* **34**, 1033 (1956); Nicole Longeque, *Compte Rend.* **251**, 1376 (1960); Teuvo Kohonen, *Ann. Acad. Sci. Fennicae A.* **VI**, 92 (1961).

¹⁵ A. Bisi, G. Faini, E. Gatti and L. Zappa, *Phys. Rev. Letters* **5**, 59 (1960); G. Jones and J. B. Warren, *Can. J. Phys.* **39**, 1517 (1961).

¹⁶ R. E. Bell and M. H. Jorgensen, *Can. J. Phys.* **38**, 652 (1960).

¹⁷ J. L. Rodda and M. G. Stewart, *Phys. Rev.* **131**, 255 (1963).

¹⁸ Teuvo Kohonen, *Ann. Acad. Sci. Fennicae A.* **VI**, 130 (1963).

of the metal or in the radioactive source itself. Positrons in a metal are usually considered to be free, i.e. not bound to any particular valence electron or lattice site.^{1,2} Thus one expects a single exponential decay in the annihilation time distribution. In analogy with the situation with plastics and liquids,^{1,2} however, one may invoke the formation of a positronium-like bound state to account for the double lifetime. However, the most recent theoretical work¹⁹ suggests that such a bound state, defined as a discrete level in the energy spectrum of the one-positron, many-electron system, will not exist at electron densities corresponding to real metals.

Section II of this paper describes the experimental techniques used in our work. Section III discusses source and sample preparation and gives experimental results on the nature of the second lifetime component. Section IV contains our measured lifetime values. In Sec. V our results are compared with various theoretical predictions, and suggestions are made for further experimental and theoretical work.

II. EXPERIMENTAL TECHNIQUES AND ANALYSIS OF DATA

The standard positron lifetime measurement technique was used: A Na²² positron source was surrounded by samples of the metal in which the annihilation is to take place; the spectrum of time delays between the 1.27-MeV prompt nuclear gamma ray and one of the 0.51-MeV annihilation gamma rays was recorded in a multichannel delayed coincidence system.²⁰ Positron lifetimes are typically 0.2 to 0.4 nsec; compared with this, the mean time between the Na²² beta decay and the subsequent emission of the 1.27-MeV Ne²² gamma ray is 0.003 nsec.²¹ Thus the measured delayed coincidence curve is closely equal to the ideal positron time-decay curve folded into the instrumental time resolution of the system.

Our delayed coincidence system was basically a conventional fast-slow system, with a number of refinements included to improve the performance. With modern fast electronics, time resolution is mainly determined by scintillator, light collection, and photomultiplier performance. In our system the photomultipliers were 10-stage RCA 7746 types, operated at 2500 V. The scintillators were 1-in.-diam × 1-in.-long Naton 136, painted with white reflective coating and mounted directly on the photomultipliers. With narrow ($\Delta E/E \approx 20\%$) energy selection windows set near the Compton edge of the Co⁶⁰ spectrum, we obtained a prompt Co⁶⁰ resolving time of 0.22-nsec full width at half-maximum (FWHM). This resolving time is close

to the value of 0.21 nsec reported¹⁸ with Radiotechnique-type XP1020 photomultipliers, a value which is thought to be the best attainable with currently available components.

The anode pulses were fed through 50- Ω cables to the electronic system. Coaxial attenuators at the photomultipliers brought the signal level to a value suitable for triggering the tunnel-diode circuitry, and at the same time served as back terminations for the line, eliminating the possibility of spurious effects caused by reflections. The photomultiplier signals drove conventional tunnel-diode univibrators, which trigger at the 20-mV level. We found that the resolving time is quite insensitive to the triggering level, and that no improvement occurs with zero crossing triggering; in practice we triggered at the 5% level of the initial (negative) rise of the anode pulse.

The signals from the tunnel-diode input triggers were fed to a tunnel-diode time-to-pulse-height converter, which has been described elsewhere.²² This circuit has an inherent time resolution (with both start and stop signals obtained from the same photomultiplier) of 0.04 nsec, and has a single-valued input time versus output pulse-height relationship, which reduces the accidental background by a factor of 2 over that obtained with the usual double-valued circuits. The time-to-pulse-height converter output is digitized by a multichannel analyzer whose coincidence gate is obtained from a conventional (slow) energy selection coincidence system.

For obvious reasons, it is necessary to eliminate pile-up effects, which would introduce a spurious "tail" in the resolving curve. Thus our system included a pile-up detector circuit, described elsewhere.²³ Furthermore, in order to permit wide energy selection windows without degrading the resolving time, pulse height compensation was used: To compensate for the time shift with pulse height, appropriate fractions of the (slow) energy signals were analog added or subtracted to the time-to-pulse-height converter output.

In order to stabilize the over-all system, ac line voltage regulators were used, the laboratory temperature was held constant to 1°C, and the tunnel-diode circuitry was thermally isolated and temperature regulated to a fraction of a °C. Typical residual drift was 0.015 to 0.030 nsec per 48 h.

The prompt resolving time (FWHM) under typical experimental conditions was 0.30 nsec, and the peak-to-background ratio was 10⁴:1 [see Fig. 2(a)]. With a typical source strength of 2 μ Ci, singles counting rates (without energy selection) were approximately 4 kc, and the coincidence rate was 3 cps.

To reduce further the effects of drift, data were taken alternately from prompt (Co⁶⁰) and delayed sources. The sources were mounted on a wheel which

¹⁹ A. Held and S. Kahana, *Can. J. Phys.* **42**, 1908 (1964); H. Kanazawa *et al.*, *Phys. Rev.* **138**, A1155 (1965).

²⁰ For details see H. Weisberg, Ph.D. thesis, Brandeis University, 1965 (unpublished).

²¹ *Nuclear Data Sheets*, compiled by K. Way *et al.* (Printing and Publishing Office, National Academy of Sciences—National Research Council, Washington 25, D. C.) NRC 59-4-16.

²² H. Weisberg, *Nucl. Instr. Methods* **32**, 133 (1965).

²³ H. Weisberg, *Nucl. Instr. Methods* **32**, 138 (1965).

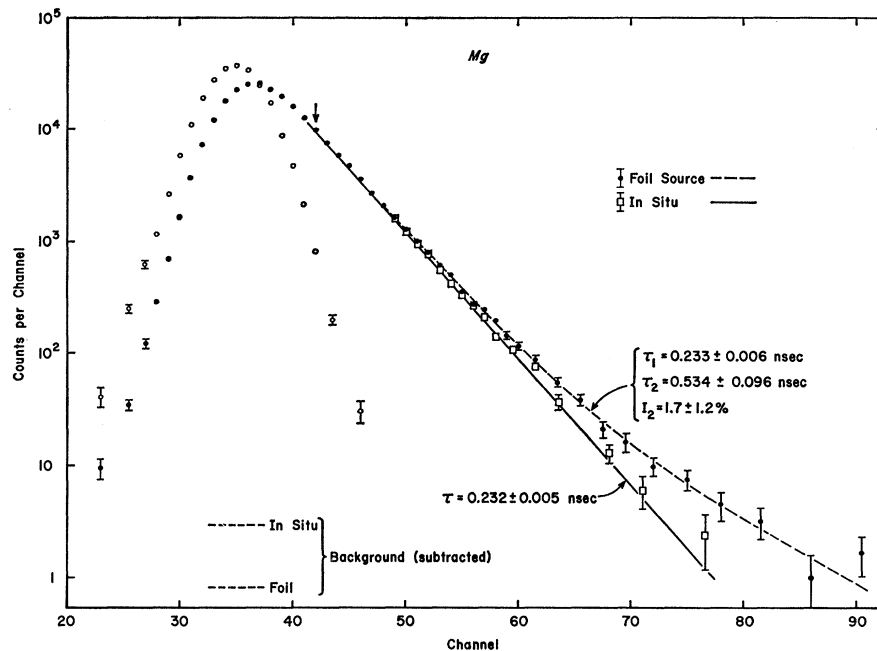


FIG. 1. Decay curves in Mg with foil deposited source (Run 225) and *in situ* source (Run 223). Arrow on top of curves points to the starting channel used to fit exponentials. Horizontal scale is 16.6 channels/nsec.

automatically interchanged them at set time intervals; correspondingly, the time signals were routed to alternate halves of the multichannel analyzer memory. Using this method, centroid shifts of a few times 0.001 nsec could be detected. However, the centroid-shift measurements still contain a number of systematic errors, including failure to reject all prompt events, variable amounts of annihilation in the source, and time-of-flight errors resulting from differences in the geometrical position of prompt and delayed sources (0.5 mm could easily be detected). Thus we analyzed our data by the slope method. Data were used only from channels above a cut-off delay value, below which the decay curve departs from a simple exponential behavior. The cut-off channel was determined by inspection of a plot of the derivative of the logarithm of the decay curve. At large positive delays, where there were only a few counts per channel, counts from adjacent channels were averaged together. These modified data were then fit, using computer programs, by a standard iterative least squares procedure, to a theoretical curve consisting of the sum of a constant background plus a maximum of three exponential decays of arbitrary intensities and decay constants. The background was determined from the measured singles counting rates and time calibration factors, and was typically 1 to 2 counts per channel. Background values determined experimentally from the measured counts at large delays agreed with those determined from the singles rates to within a few tenths of a count per channel; our final results are unaffected, within statistical error, by background uncertainties of this magnitude.

Time calibration was by means of fixed and variable

coaxial delay lines (General Radio 874 series) inserted between the photomultipliers and the tunnel diode univibrators. Comparable results were obtained by two different methods: (1) Centroid shift of prompt curves at different delays (with a 10 μ Ci source a statistical accuracy of 0.005 nsec could be attained after a few minutes counting); (2) channel versus delay measurements with a split signal from a single photomultiplier. Based on the linearity and reproducibility of such time calibrations, we assigned an expected error of $\pm 2\%$ to the time calibration factors entering into the quoted lifetime values in Sec. IV.

III. SAMPLE PREPARATION AND THE SECOND LIFETIME

Ideally one would like a massless positron source imbedded in an otherwise homogeneous, pure metal sample. For the special case of Mg, such a source could be experimentally obtained: Na^{22} activity was produced *in situ* by irradiation. The solid curve in Fig. 1 is the positron-decay curve obtained in a piece of Mg which was activated by the $\text{Mg}^{25}(p,\alpha)\text{Na}^{22}$ process with 22-MeV protons at Oak Ridge. The Mg piece, which was 2 mm thick, was surrounded by nonirradiated Mg so that the positrons all stopped in Mg metal. The dashed curve was obtained with some of the same (nonirradiated) metal sandwiched in the usual way around a foil-deposited source (see below). These two curves are the best evidence that positron annihilation in a homogeneous metal is characterized by a single lifetime, and that the second-lifetime component which is usually found is an anomaly of sample preparation or is due to

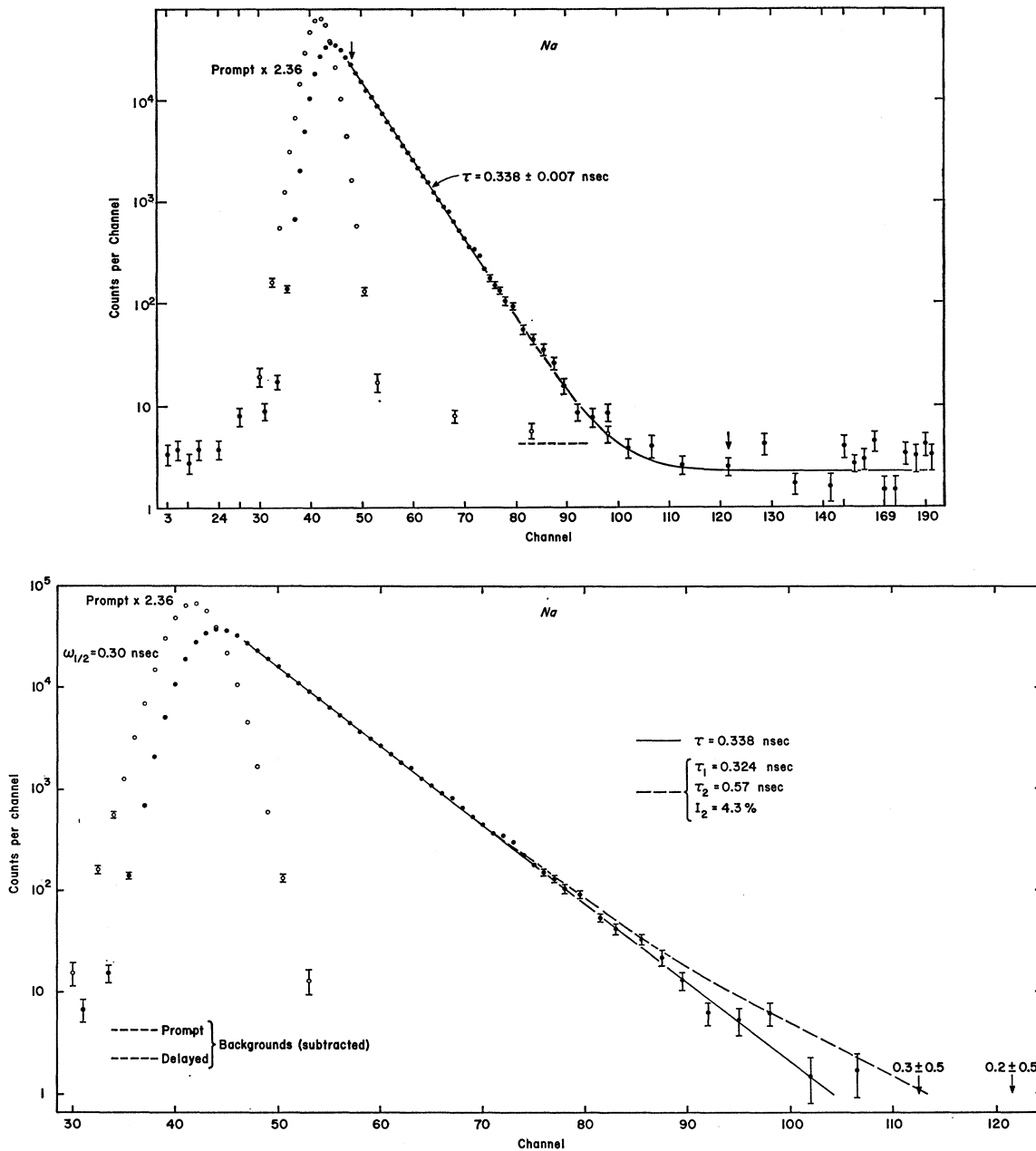


FIG. 2. (a) Measured decay curve for Na (Run 263) with background not subtracted. The solid line consists of a constant background, calculated from the measured singles rates, plus a single exponential decay. The arrows indicate the upper and lower limits of the fit; the dashed line indicates the calculated prompt background. Note that the time scale has been compressed below channel 30 and above channel 130. Horizontal scale is 16.5 channels/nsec. (b) Decay curve for Na, as in Fig. 2(a), but with background subtracted. The dashed line is the "fit" obtained for two exponentials, with the long component constrained to have the τ_2 and I_2 values found by Bell and Jorgensen. (Ref. 16.) The shape of the measured curve in Na is representative also of the curves obtained for K, Rb, and Cs.

surface effects. Schwarzschild²⁴ has obtained analogous results for Al in a piece of Duraluminum alloy which was activated by long exposure to 28-GeV protons. Unfortunately the *in situ* technique is only applicable to such special cases as Mg and Al.

²⁴ A. Schwarzschild (private communication).

The Na, K, Rb and Cs samples were prepared in glass ampoules. The activity for each was deposited from aqueous solution (NaCl in neutral aqueous solution, 1 μ Ci Na²² per μ g NaCl) on a thin (0.5-mg/cm²) Ni foil, which was then covered with a second foil; the foils were supported by an Al ring. The ring was held inside an ampoule with its geometrical location well

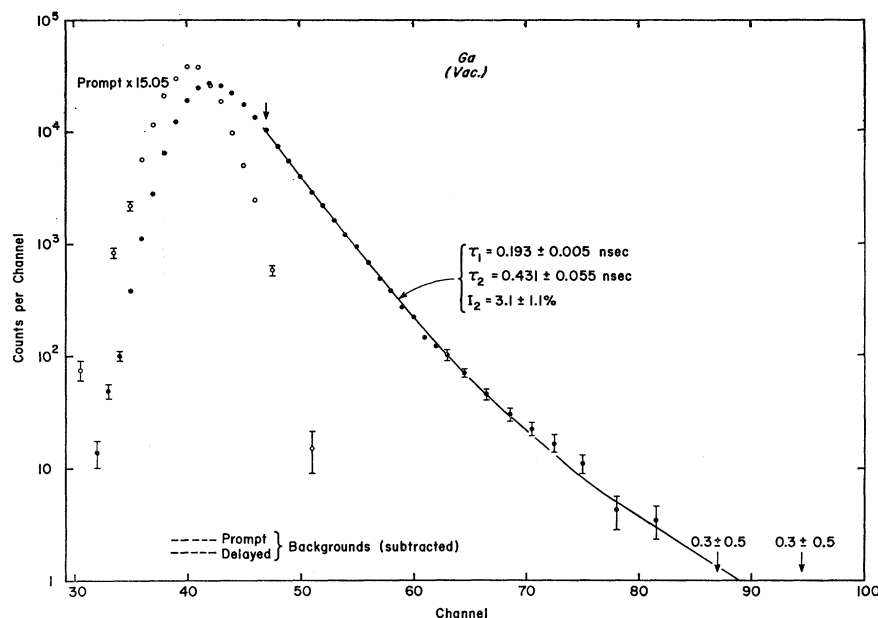


FIG. 3. Positron decay curve in Ga (Run 275), with metal poured in vacuum. This curve is representative of the results obtained in all metals except for the alkalis, Mg with *in situ* source, and Al, Fe, Bi, and Be. Horizontal scale is 16.3 channels/nsec.

determined. The metals used were vacuum distilled, of 99.9+ purity, and the pouring of the metals into the ampoules was done entirely under less than 10^{-5} -mm vacuum in clean glassware.

Figures 2(a) and 2(b) show the measured decay curve for Na (without and with the background subtracted). This curve is very well fitted by a single exponential, in disagreement with the results of Bell and Jorgensen¹⁶ (see Table II). However, we cannot rule out the presence in the curve of a second lifetime component of reasonably shorter lifetime and smaller intensity than that found by Bell and Jorgensen, since it would be effectively masked by the main component and background. The measured curves for K, Rb, and Cs have the same appearance as the one for Na. The lifetimes measured are in good agreement with Bell and Jorgensen's τ_{1s} .

The second lifetime component, if present, should show up most clearly in a metal in which the main component is short lived. The alkali metal with the shortest positron lifetime is Li, but since molten Li reacts with glass, we could not use the vacuum distillation and melting method of sample preparation. Instead we sandwiched a foil deposited between two blocks of the metal and sealed the source by dipping in paraffin, following Bell and Jorgensen.¹⁶ With this sample, we obtained a weak, long-lived second component, of which at least part could have perhaps been eliminated by better sample preparation.

Since Ga has a short positron lifetime and can easily be melted in glass, a Ga sample was prepared following exactly the same procedure that was used for Na, K, Rb, and Cs. The metal was degassed by baking overnight under vacuum before filling the ampoule and sealing. The measured decay curve, shown in Fig. 3,

has a 3% second lifetime-component intensity. The results obtained in this Ga run are quite similar to those obtained with most of the other metals when the simple source-foil-metal sandwich sample preparation technique is used.

With the usual sample preparation techniques, the dried activity does not form a uniform layer, but rather appears to form a ring of tiny crystals. Furthermore, even if the metal sample surfaces have been cleaned and etched, they may be subject to subsequent oxidation. A number of runs were therefore made in which it was attempted to obtain thin, uniform Na²² deposition and clean metal surfaces, both with foil deposited sources and with the activity deposited directly on the metal samples. Generally speaking, these attempts had little or no effect on the measured decay curves. In the most elaborate attempt, the activity was vacuum evaporated onto a foil from a small Ni crucible at 800°C. The source was assembled in a dry nitrogen atmosphere, pumped down, and sealed off. Thus the activity (which was invisible on the foil) formed a uniform layer, and was never exposed to water vapor. The metal pieces, which were freshly etched, were not exposed to air. This technique was used with Mg and Al samples (Runs 234 and 235, see Table I). The resulting decay curves were slightly straighter than those obtained with ordinary foil sources, although the difference was barely significant.²⁵ (The large I_2 value indicated in Table I for Run 235 is discussed in Sec. IV.)

Some experimentalists deposit the source directly on the surface of the metal to be studied. We have ob-

²⁵ Recently a measurement on Mg, Al, Cu, and Ni using sources prepared on gold foils indicated the absence of a second lifetime over three decades—see H. W. Kugel *et al.*, Phys. Letters **20**, 364 (1966).

TABLE I. Measured lifetimes and intensities.

Run	Metal	Source	τ_1 , nsec	τ_2 , nsec	I_2 , %
223	Mg	<i>in situ</i>	0.232±0.005	...	0
225	Mg	# 30	0.233±0.006	0.534±0.096	1.7±1.2
226	Al	# 30	0.199±0.006 ^b	0.39	11
234	Mg	# 32(V) ^a	0.230±0.004	0.874±0.252	0.4±0.2
235	Al	# 32(V) ^a	0.204±0.006 ^b	0.29	35
237	Cu	# 32	0.181±0.005	0.445±0.055	2.5±1.0
241	Ni	# 32	0.172±0.005	0.465±0.080	1.8±0.9
243	Fe	# 32	0.160±0.005 ^b	0.31	15
244	Co	# 32	0.162±0.004	0.577±0.051	1.2±0.2
246	Bi	# 32	0.243±0.008 ^b	0.38	20
247	Be	# 32	0.213±0.006 ^b	0.44	18
249	Ge(Int) ^e	# 32	0.226±0.005	0.480±0.063	2.2±1.1
250	Ge(N) ^d	# 32	0.227±0.006	0.455±0.055	3.2±1.6
251	Si(Int) ^e	# 32	0.222±0.005	0.508±0.094	1.0±0.7
252	Sn	# 32	0.202±0.005	0.521±0.050	2.0±0.6
255A	Al	# 32	0.198±0.011	0.32	30
257	Cd	# 32	0.185±0.004	0.526±0.041	1.6±0.4
258	Pb	# 32	0.201±0.005	0.477±0.048	2.7±1.0
263	Na	# 37(V) ^e	0.338±0.007	...	0
264	Ga	# 36	0.195±0.005	0.422±0.042	3.2±1.1
265	Hg	# 35	0.220±0.007	0.426±0.065	4.4±2.9
267	Be(X) ^f	# 38	0.150±0.004	0.422±0.042	9.9±1.0
268	Fe(X) ^f	# 38	0.185±0.004	0.509±0.113	3.2±0.7
269	Fe	# 38	0.160±0.005 ^b	0.45	7
270	Si(N) ^d	# 32	0.224±0.005	0.810±0.140	0.6±0.2
271	Cs	# 15(V) ^e	0.418±0.010	...	0
272	K	# 21(V) ^e	0.397±0.010	...	0
273	Li	# 39	0.291±0.006	2.780±0.252	0.6±0.1
275	Ga	# 40(V) ^e	0.193±0.005	0.431±0.055	3.1±1.1
276	Rb	# 20(V) ^e	0.406±0.010	...	0

^a (V)—Vacuum-evaporated source.

^b With I_2 constrained to be 5%; see discussion in Sec. IV.

^c (Int)—Intrinsic (40 Ω -cm Ge, 1000 Ω -cm Si).

^d (N)—Heavily N doped.

^e (V)—Foil source with metal poured in vacuum around it.

^f (X)—Single crystals.

served experimentally that using Na²² in HCl solution, with an HCl concentration equal to that which is often used to prevent chemical exchange with the glass storage bottle, the tail is considerably enhanced. Thus all sample preparations were done with Na²² in neutral aqueous solution.

The interpretation of our results could be as follows. When a deposited source surrounded by metal is used, a second lifetime component is found because some of the positrons come to rest and annihilate in regions other than the homogeneous interior of the metal. These regions may be either the source itself, the supporting foils (if used), or the surface oxide layer of the metal, as well as lattice defects on the surface of the metal.

In the Na, K, Rb, and Cs measurements, a small second lifetime component due to the source is also probably present but is obscured by the long-lived main component and by the background. In the other metals (except for Mg with the *in situ* source) one can fit the sum of two exponentials to the measured curve; the "true" lifetime (the one which would be measured under ideal conditions in a homogeneous metal) is then equal to the main (τ_1) component obtained from the fit.

IV. RESULTS

Table I lists our results for the two lifetimes, τ_1 and τ_2 , and the intensity I_2 of the second component, for

each experimental run. These values were obtained from a least squares fit of a double exponential curve to the appropriate part of the measured decay curve, as discussed in Sec. II. The data for Al, Fe, Bi, and Be require special comment. The measured decay curves were somewhat straighter in appearance than those for the other metals, although the difference was small. On the other hand, the least squares solutions for these metals gave rather large I_2 values and small τ_2 values, compared to those for the other metals. It was found, however, that nearly the same goodness of fit could be achieved with much smaller I_2 values, provided that the quantity $\tau_1 I_1 + \tau_2 I_2$ was kept constant. We believe that the large I_2 values are spurious and result from the ambiguity inherent in fitting sums of exponentials when the various components all have nearly the same lifetime. In particular the "second component" may not have a single lifetime, but instead may be a sum of components of different lifetimes, in which case a two-component fit could give a spuriously high I_2 value. Therefore, for these metals we give for τ_2 and I_2 the values obtained in the usual way by least squares fitting with τ_1 , τ_2 and I_2 allowed to vary; but for τ_1 , we give the values obtained with I_2 constrained to be 5%, and only τ_1 and τ_2 allowed to vary. The τ_1 values thus obtained are 0.01 to 0.02 nsec longer than those obtained with τ_1 , τ_2 and I_2 allowed to vary.

In Table II our values are compiled for each metal,

TABLE II. Slope measurements reported by various observers.

Z	Metal	τ_1 , nsec	τ_2 , nsec	I_2 , %	Reference
3	Li	0.29 ± 0.02	0.59	6.5	a
		0.291 ± 0.006	2.78 ± 0.25	0.6 ± 0.1	b
4	Be	0.213 ± 0.005 ^c	0.44	18	b
11	Na	0.315 ± 0.02	0.57	4.3	a
		0.338 ± 0.007	...	0	b
12	Mg	0.232 ± 0.005	...	0	b
13	Al	0.1	1.0 ± 0.2	30	d
		0.193 ± 0.02	0.39	6.5	a
		0.180	0.324	6	e
		0.21 ± 0.01	f
14	Si	0.201 ± 0.005 ^o	0.32	30	b
		0.222 ± 0.005	0.508 ± 0.094	1.0 ± 0.7	b
19	K	0.40 ± 0.02	...	0	a
		0.397 ± 0.010	...	0	b
21	Sc	0.238 ± 0.009	...	0	e
26	Fe	0.160 ± 0.005 ^o	0.38	15	b
27	Co	0.162 ± 0.004	0.577 ± 0.051	1.2 ± 0.2	b
28	Ni	0.172 ± 0.005	0.465 ± 0.080	1.8 ± 0.9	b
29	Cu	0.1	0.7 ± 0.06	20	d
		0.181 ± 0.005	0.445 ± 0.055	2.5 ± 1.0	b
31	Ga	0.194 ± 0.004	0.426 ± 0.048	3.1 ± 1.2	b
32	Ge	0.226 ± 0.005	0.480 ± 0.063	2.2 ± 1.1	b
37	Rb	0.406 ± 0.010	...	0	b
48	Cd	0.185 ± 0.004	0.526 ± 0.041	1.6 ± 0.4	b
50	Sn	0.202 ± 0.005	0.521 ± 0.050	2.0 ± 0.6	b
55	Cs	0.43 ± 0.02	...	0	a
		0.418 ± 0.010	...	0	b
70	Yb	0.263 ± 0.009	...	0	e
79	Au	0.1	0.66 ± 0.03	30	d
80	Hg	0.220 ± 0.007	0.426 ± 0.065	4.4 ± 2.9	b
82	Pb	0.201 ± 0.005	0.477 ± 0.048	2.7 ± 1.0	b
83	Bi	0.243 ± 0.008 ^o	0.34	20	b

^a Bell and Jorgensen (1960), Ref. 16.

^b This work.

^c With I_2 constrained to be 5%; see discussion in Sec. IV.

^d Longequeue (1960), Ref. 14.

^e Rodda and Stewart (1963), with all lifetimes multiplied by 0.85 to allow for the time calibration error reported in their footnote 6, Ref. 17.

^f Kohonen (1961), Ref. 14.

with suitable averaging for metals for which more than one run was taken. In addition, Table II summarizes the results of other experimenters who used the slope method.

We have also studied the agreement among all the data reported by different observers who used the centroid shift method.²⁰ It seems that the major discrepancies among the different quoted centroid shifts stems from the lack of agreement of the absolute value of τ_1 , in Al. Comparisons were also made between the quoted measurements of centroid shifts and the computed shift $\Delta_c = (1 - I_2)\tau_1 + I_2\tau_2$ ("S" values) from the direct measurements of τ_1 , τ_2 and I_2 . The unweighted average of all the centroid-shift measurements in Al relative to a prompt source and the "S" values is 0.203 ± 0.015 nsec, while the average of the "S" values alone²⁶ is 0.201 nsec.

V. DISCUSSION

It is to be noted that, in the two metals (Be and Fe) in which lifetimes in both polycrystalline and single-crystal samples were measured, small but significant differences were found. This effect merits further study,

²⁶ The recent values of Ref. 25 were not included in this average.

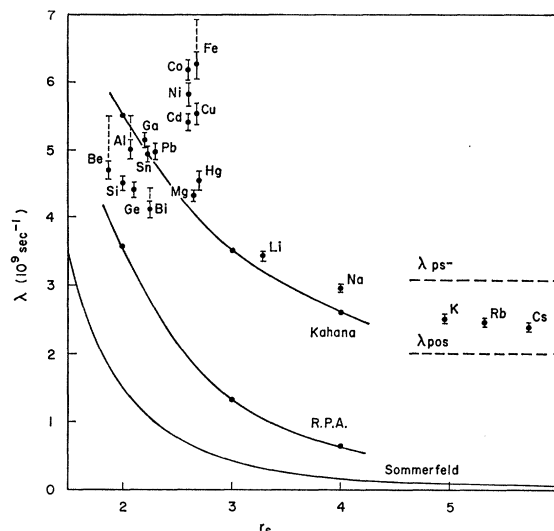


FIG. 4. Measured annihilation rates plotted against r_s . The dashed extensions on the error bars for Be, Al, Fe, and Bi indicate possible ambiguity in fitting the data due to the possible high second component intensity in those metals (see Sec. IV). Theoretical values indicated are: λ_{ps} , the spin averaged positronium annihilation rate; λ_{ps-} , the rate for the positronium negative ion; "Sommerfeld," the rate for a noninteracting electron gas; "R.P.A." the rate calculated in the random-phase approximation by Kahana, (Ref. 7), and "Kahana," the full many-body calculation of Ref. 7.

but in the subsequent discussion we shall confine ourselves only to the measured lifetimes in polycrystalline samples.

Figure 4 is a plot of our measured λ values, where $\lambda = 1/\tau_1$ is the annihilation rate, against r_s , the radius of a sphere containing one valence electron on the average. The valence values assumed in calculating r_s were as follows: 1 for the alkalis and the transition metals; 2 for Be, Cd, and Hg; 3 for Mg, Al, and Ga; 4 for Si, Ge, Sn, and Pb; and 5 for Bi.

It can be seen that the rates for the "nearly free electron" metals Al, Mg, Li, Na, K, Rb, and Cs fall on a smooth curve which is slightly above the theoretical curve of Kahana and approaches a value close to λ_{ps} , the spin-averaged positronium rate, at low densities. Furthermore, the rates for Be and Bi and the semiconductors Si and Ge are below the "nearly free" curve,²⁷ the rates for the transition metals and Cd are above it, and the remaining rates fall near it.

As far as positron annihilation is concerned, metals may be roughly classified according to the ratio A_g/A_p of the areas of the "Gaussian" and the "parabolic" parts of the two-photon angular-correlation curves⁴; in the nearly-free-electron metals, the measured shape and momentum cutoff of the parabola is in excellent agreement with simple noninteracting electron-gas theory. Furthermore, it has been shown⁶ that in metals

²⁷ In a recent measurement of the positron lifetime in Si by J. D. McGervey (preprint) a value of $\tau = 0.26$ nsec has been obtained, which is slightly larger than our measured value.

having large "Gaussians," much of the "Gaussian" part results from annihilation with core electrons. However, it is clear that there is not an exact correspondence between the parabolic part and conduction electron annihilation on the one hand, and the "Gaussian" component and core annihilation on the other. In particular, the measured rates in K, Rb, and Cs are already so close to the spin-averaged positronium rate that if we wish to avoid an electron-gas rate considerably below the spin-averaged positronium value, we must assign an appreciable part of the "Gaussian" component in these metals to conduction band annihilation. One indeed does expect higher momentum contributions from annihilation with the conduction band due to higher order Fourier components of the electron and positron Bloch functions.⁶ Thus the simple prescription used by Jones and Warren¹⁵ of multiplying the measured total rates by $(1+A_g/A_p)^{-1}$ to obtain "electron gas" values is of doubtful validity.

In a separate paper²⁸ we have investigated the extent to which a comparison of the annihilation rates with the two-photon angular correlation in alkali metals can be used to obtain separately the annihilation rates with the conduction electrons and the annihilation rates with the tightly bound core electrons. From this empirical study we can obtain evidence that the density "enhancement" factor due to the positron-electron interaction plays a smaller role in tightly bound electron annihilation than in conduction-band annihilation. This result is physically reasonable; it is to be expected that the stronger the interactions of electrons with the lattice field, the less polarizable the electrons are by the positron. When approximate correction is made for core annihilation in the nearly-free-electron metals, the partial annihilation rate due to only conduction electrons falls extremely close to Kahana's theoretical curve in the high- and medium-density region and approaches λ positronium for low densities (large r_s).

Next, we discuss the fact that our measured rates for the semiconductors Si and Ge fall below the "free electron" rates.²⁷ The angular correlation curves for these metals^{1,2} resemble those for nearly free metals quite closely, having small A_g/A_p values and well

defined parabolas cutting off at momentum values corresponding to the accepted valences. A theoretical calculation exists²⁹ of the annihilation rate, calculated in the random phase approximation, in a high-density electron gas with a phenomenological energy gap. For r_s values and energy gaps corresponding to those in Ge and Si, a decrease in rate is predicted of 0.8×10^9 sec⁻¹, in good agreement with our measured results. Finally, we note that the absence of an experimentally detectable difference between the decay curves for intrinsic and heavily *N*-type Ge and Si is evidence against the suggestion³⁰ that positrons may form a bound state with free electrons in *N*-type semiconductors.

The annihilation rates in the transition metals Fe, Co, Ni and in Cu appear above the "free-electron" curve; the two-photon angular correlation curves for these metals indicate that a considerable fraction of the total annihilation proceeds via core electrons,⁶ and we thus expect a large contribution to the annihilation rate due to those electrons. A simple computation based on treating the conduction electrons in the Wigner-Seitz approximation and the "*d*" band in the tight binding approximation indicates that for the "*d*" band one requires an enhancement factor of approximately half the enhancement required by the conduction band.³¹

From the above discussion it is evident that existing many-body computations of slow positron-annihilation rates in an electron gas, particularly the computations of Kahana,⁷ can account well for the observed annihilation rates in metals known to have nearly-free-conduction electrons and small contributions from core annihilation. It would be interesting if such computations could be extended to the low-density limit, in order to check whether the annihilation rates approach the spin-averaged positronium rate. More theoretical work along the lines outlined by Carbotte¹¹ is needed to provide quantitative predictions about annihilation rates with conduction band and core electrons in real metals, where the Bloch character of the positron as well as of the electrons must be taken into account.

²⁹ J. Reinheimer and W. Brandt, *Bull. Am. Phys. Soc.* **9**, 394 (1964).

³⁰ R. L. Garwin, *Phys. Rev.* **91**, 1571 (1953).

³¹ S. Berko and J. H. Terrell, *Optical Properties and Electronic Structure of Metals and Alloys*, (North-Holland Publishing Company, Amsterdam, 1966), p. 210.

²⁸ J. H. Terrell, H. L. Weisberg, and S. Berko, in *Proceedings of the Conference on Positron Annihilation* (Academic Press Inc., New York, 1966).