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Applications of positron-lifetime measurements to the study of defects in metals*

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We describe in detail the data-analysis techniques which we have developed for obtaining information about defect properties from positron-lifetime measurements. These techniques eliminate many of the incorrect assumptions usually made in analyzing positron-lifetime data to obtain defect parameters. Some specific features of the data analysis are the use of an improved form for the instrumental resolution function, the use of a model which allows for the presence of several types of defect traps, and the inclusion of the possibility of temperature dependence in the specific positron trapping rate (defined as the positron trapping rate per unit defect concentration). These techniques were used to analyze data from heated specimens of pure aluminum, pure gold, and aluminum–1.7-at.%-zinc, in which the equilibrium concentration of vacancies was high enough to alter positron lifetimes. Analysis of data from lifetime measurements on pure aluminum at temperatures between 200 and 400 °C, and on pure gold at temperatures between 360 and 760 °C yielded monovacancy formation energies of $E^F_{1V} = 0.62 \pm 0.02$ eV for aluminum and $E^F_{1V} = 0.98 \pm 0.03$ eV for gold assuming no temperature dependence in the specific positron trapping rate. The fit to the data was significantly improved by assuming a temperature dependence in the specific trapping rate of $T^{1.2\pm0.3}$ for aluminum and $T^{0.5\pm0.2}$ for gold. The best-fit formation energies corresponding to these temperature dependences were $E^F_{1V} = 0.69 \pm 0.03$ eV for aluminum and $E^F_{1V} = 1.00 \pm 0.03$ eV for gold. Equilibrium measurements between 200 and 400 °C in aluminum–1.7-at.%-zinc yielded a value for the binding energy of vacancies to impurities $E^B_{VP} = -0.09 \pm 0.03$ eV assuming no temperature dependence in the specific trapping rate. The fit was improved by assuming a temperature dependence in the specific trapping rate of $T^{1.1\pm0.2}$, corresponding to a best-fit value for the binding energy of $E^B_{VP} = +0.04 \pm 0.07$ eV. From our results we conclude that there is a positive temperature dependence in the specific positron trapping rate and that vacancies are not strongly bound to zinc impurity atoms in aluminum.

I. INTRODUCTION

The use of positron-lifetime measurements to study defects in metals has grown rapidly in recent years.[1] The technique holds much promise as a tool for defect studies since the behavior of a positron in a metal is quite sensitive to the presence of vacancy-type defects. In addition, the method eliminates some of the problems of other techniques for studying defects.

Positron measurements can be performed with the specimen in thermal equilibrium, thus eliminating the problem of defect clustering which occurs with quenching techniques.[2] Moreover, since the positrons are sensitive to low vacancy concentrations, the measurements can be performed at relatively low temperatures. This reduces the problem of divacancy and trivacancy formation which occurs in high-temperature equilibrium experiments such as simultaneous length-change–lattice-parameter measurements.[3]

At the present time the principal problem with using positron measurements to study defects is the question of how to extract the defect properties of interest from the positron-lifetime data. We have found that from a single experiment a number of different answers for a given quantity may be obtained depending upon what type of data analysis is used. In the course of our work, we have made an extensive study of the methods of analyzing the data. We have found that relatively sophisticated data-analysis techniques are required before self-consistent results can be obtained.

The sequence of events in our positron-annihilation experiments is shown in Fig. 1 and may be simply described. The decay of ^{22}Na to ^{22}Ne produces a positron and simultaneously a γ ray of energy 1.28 MeV. This γ ray is detected and signals the creation of the positron. The positron enters the metal specimen, is quickly thermalized, and either drifts through the metal lattice or becomes trapped in a vacancy-type defect. In both cases it eventually annihilates with an electron, most often producing two γ rays of 0.511 MeV. One of these 0.511-MeV γ rays is detected and signals the annihilation of the positron. The time difference between the 1.28- and the 0.511-MeV γ rays is measured electronically and stored for analysis in the form of a histogram which represents the number of events as a function of the time difference.

In 1967 MacKenzie, Khoo, McDonald, and McKee[4] reported that the positron lifetime showed a reversible increase with increasing temperature which, they suggested, might be caused by thermally induced vacancies. Their results were explained in terms of Brandt's[5] "trapping model" by Bergersen and Stott[6] and independently by Connors and West.[7] The theory which they developed is based on two simple assumptions: The first assumption is that the annihilation lifetime of a positron trapped in a monovacancy, τ_V, is longer than the lifetime of a positron in the lattice, τ_L, because the electron density is lower in a vacancy than in the lattice. The second assumption is that positrons become trapped at a rate $\mu_{1V}c_{1V}$ which is proportional to the monovacancy concentration c_{1V}. Here μ_{1V} is the specific positron trapping rate, which is defined as the positron trapping rate per unit vacancy concentration. The monovacancy concentration as a function of temperature is given by[8]

$$c_{1V}(T)=e^{S^F_{1V}/k}e^{-E^F_{1V}/kT}, \tag{1}$$

where S^F_{1V} is the monovacancy formation entropy, E^F_{1V} is the monovacancy formation energy, and T is the absolute temperature.

If $n_L(t)$ and $n_{1V}(t)$ are the fraction of free and trapped positrons, respectively, as a function of time we can write a set of simple equations for their time rate of change:

$$\frac{dn_L(t)}{dt}=-\frac{n_L(t)}{\tau_L}-\mu_{1V}c_{1V}(T)n_L(t),$$

$$\frac{dn_{1V}(t)}{dt}=-\frac{n_{1V}(t)}{\tau_{1V}}+\mu_{1V}c_{1V}(T)n_L(t).$$

That is, the change in the fraction of positrons in the lattice per unit time is determined by the fraction lost through annihilation and the fraction lost through trapping; and the change in the fraction of positrons trapped in vacancies per unit time is given by the fraction lost through annihilation plus the fraction gained through trapping. If we assume that initially no positrons are trapped we have for the observed rate of annihilation as a function of time and temperature

$$\begin{aligned}P(t,T)&=\frac{d}{dt}[n_L(t)+n_{1V}(t)]\\&=\frac{\tau_L\mu_{1V}c_{1V}(T)}{[\tau_{1V}-\tau_L+\tau_{1V}\tau_L\mu_{1V}c_{1V}(T)]}e^{-t/\tau_{1V}}\\&\quad+\frac{(\tau_{1V}-\tau_L)[1/\tau_L+\mu_{1V}c_{1V}(T)]}{[\tau_{1V}-\tau_L+\tau_{1V}\mu_{1V}c_{1V}(T)]}\\&\quad\times e^{-[1/\tau_L+\mu_{1V}c_{1V}(T)]t}.\end{aligned} \tag{2}$$

This is a sum of two exponential components whose decay rates and intensities depend on τ_L, τ_{1V}, and $\mu_{1V}c_{1V}(T)$.

The solution can be expressed in terms of the mean positron lifetime defined as $\bar{\tau}(T)=\int_{-\infty}^{\infty}tP(t,T)\times dt$. Substituting $P(t,T)$, from Eq. (2), we obtain

$$\bar{\tau}(T)=\tau_L\left(\frac{1+\tau_{1V}\mu_{1V}c_{1V}(T)}{1+\tau_L\mu_{1V}c_{1V}(T)}\right). \tag{3}$$

We see that at low temperature when $\mu_{1V}c_{1V}(T)$ is small compared to $1/\tau_{1V}$ and $1/\tau_L$, $\bar{\tau}$ approaches τ_L, the lifetime of positrons in the lattice. Similarly at high temperatures when $\mu_{1V}c_{1V}(T)$ is large, $\bar{\tau}$ approaches τ_{1V}, the lifetime in the vacancy. At intermediate temperatures $\bar{\tau}$ takes some value between the two extremes. This is qualitatively the experimentally observed behavior as seen in Fig. 2. By inverting Eq. (3) we obtain the concentration of vacancies

$$c_{1V}(T)=\frac{\bar{\tau}(T)-\tau_L}{\mu_{1V}\tau_L[\tau_{1V}-\bar{\tau}(T)]}. \tag{4}$$

To deduce the monovacancy formation energy from positron-lifetime experiments we can make use of this equation and Eq. (1) in the following way: First we can make measurements at low temperatures, where there is little trapping, to obtain τ_L; next we can make measurements at high temperatures, where most of the positrons are trapped, to obtain τ_{1V}; and finally, we can make measurements at intermediate temperatures to obtain $\bar{\tau}(T)$. From the slope of a semilogarithmic plot of the quantity $[\bar{\tau}(T)-\tau_L]/[\tau_{1V}-\tau(T)]$ as a function of $1/kT$ we should obtain the monovacancy formation energy E^F_{1V}.

The foregoing procedure for obtaining the monovacancy formation energy is based upon several assumptions, some of which require further examination: (i) Those which are quite reasonable and which are supported by experimental evidence: (a) Positrons become trapped in vacancy-type defects. (b) The lifetime of a trapped positron is

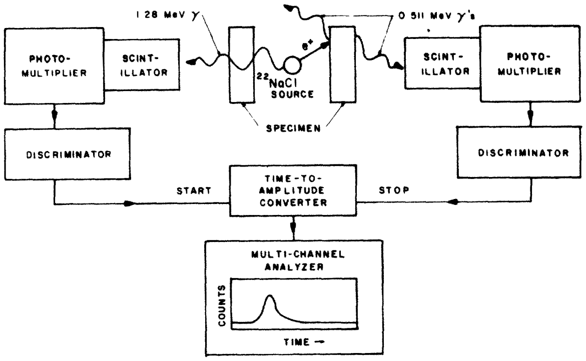

FIG. 1. Simplified schematic of the experimental apparatus.

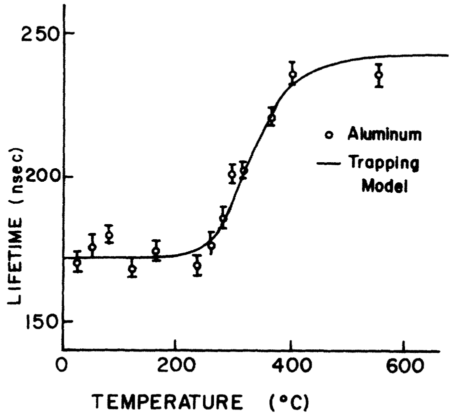

FIG. 2. Lifetime vs temperature in pure aluminum.

different from the lifetime of a positron drifting freely through the lattice.[5-7] (ii) Those which require further investigation: (a) The specific positron trapping rate, μ_{1V}, is a constant independent of temperature.[1] (b) No detrapping of positrons occurs, i.e., that once a positron is trapped it stays trapped until annihilation.[1,9,10] (iii) Those which are commonly made in this type of analysis but which are incorrect: (a) The mean lifetime $\bar{\tau}$ may be obtained by fitting the data with a single exponential component. (b) The lifetime in the lattice, τ_L, may be obtained by fitting data from low temperatures. (c) The lifetime in the vacancy trap, τ_{1V}, may be obtained by fitting data from high temperatures. In addition there are errors associated with commonly used methods of taking the instrumental resolution into account when extracting lifetimes from real experimental data.

This paper is principally concerned with the results of our efforts to investigate the validity of the assumptions outlined above. Heretofore, we have reported our results primarily in letters and at conferences. In this report our aim is to provide a fuller discussion of our apparatus, data analysis, and conclusions, with particular emphasis upon the details of analysis which have been lacking in previous publications. Our research has enabled us to determine defect properties with increased accuracy, and to obtain new information about the interaction between positrons and vacancy-type defects.

Section II contains some of the details of experimental procedure which are relevant to the analysis of the lifetime data. In Sec. III we discuss the evolution of the data-analysis techniques starting at the level described previously and leading to the more sophisticated analysis finally developed. Section IV contains the results of this analysis using the data obtained from equilibrium measurements on pure aluminum, pure gold, and aluminum-1.7-at.%-zinc.

II. EXPERIMENTAL

In this section we will briefly describe the preparation of the samples from the specimen material, and the electronic apparatus used to measure the positron lifetimes. For a more detailed description of the sample preparation see Ref. 11, and for a detailed description of the lifetime apparatus see Ref. 12.

Table I lists some information about each of the specimens. Small drops of ^{22}NaCl in neutral solution were dried onto two pieces of specimen material. The two pieces were clamped together and electron-beam welded around the edges. A chromel-alumel thermocouple for temperature measurement was fastened to each specimen and the specimen was then lowered into a quartz furnace where it rested on a piece of asbestos as shown in Fig. 3. A temperature-control thermocouple threaded through an alumina tube was held in place against the outside of the quartz furnace by nichrome heater wire wrapped around the outside.

The electronic apparatus used to measure the positron-annihilation lifetimes is basically a high-resolution timing device. The elements of this apparatus are shown in block form in Fig. 1. Although the principles of operation of this equipment are basically simple, the high degree of precision necessary for the measurement of positron lifetimes in metals containing defects requires that every element be performing at its optimum. When we started our work there were several sources of systematic errors of order 0.050 nsec in the electronic timing which prevented us from making reliable lifetime measurements. We have been able to reduce those systematic errors introduced by the lifetime apparatus to 0.005 nsec or less so that they have essentially no effect on the measurements. The details of these improvements are described in Ref. 12. Some of the more important features of our electronic apparatus described there are the following: (i) The use of an integrated-circuit constant-fraction timing discriminator which is thermoelectrically cooled to stabilize it against long-term temperature drift. (ii) The use of fast energy discrimination and the use of a polystyrene time-to-amplitude conversion capacitor to minimize rate-dependence problems. (iii) The use of a carefully optimized voltage-divider base for the photomultiplier tubes to allow the best time resolution to be obtained.

The data are accumulated in a multichannel analyzer in the form of a histogram of the number of events as a function of time. For measurements on a metal this is the sum of the exponential com-

TABLE I. Specimens.

Material	Size (mm)	Supplier	Measurement temperature (°C)	Preanneal temperature (°C)	Vacuum (Torr)
99.9999% Al	25×25×0.75	Cominco	20–400	550	2×10^{-6}
99.9999% Au	25×25×0.25	MRC	20–760	760	none
Al–1.7-at.%-Zn	25×25×1.00	MRC	20–400	550	2×10^{-6}

ponent corresponding to annihilations in the metal and the exponential component corresponding to annihilations in the sodium chloride source. These exponential components are folded with the resolution of the instrument. A good estimate of the resolution may be obtained by substituting a ^{60}Co source in place of the sample to be measured. Since ^{60}Co emits two γ rays within ~0.005 nsec of each other, the measured time spectrum will be essentially the resolution of the instrument. Such a time spectrum for ^{60}Co and a time spectrum for pure gold at low temperature (20 °C) are shown in Fig. 4. A constant background due to random coincidences has been subtracted from the data.

III. DEVELOPMENT OF THE DATA-ANALYSIS TECHNIQUES

We now discuss the development of the data-analysis techniques starting at the level described previously in the Introduction, and culminating with the analysis finally used. In this work our goals were to eliminate the incorrect assumptions of other data-analysis techniques and also to extract the maximum amount of information from the lifetime data.

We will first review some aspects of the method of nonlinear-least-squares analysis that will be useful in understanding what follows. We then describe the methods used by other workers and originally used by us to obtain defect parameters. We trace the development of our techniques using pure aluminum as an example. The final results of the data analysis are discussed in Sec. IV.

All data were analyzed using the nonlinear-least-squares method. The reader will recall that the method of nonlinear least squares starts with a data set containing experimental values for the dependent variable y_i and its uncertainty σ_{y_i} as functions of an independent variable x_i. A functional form $f(x_i, a_j)$, where a_j is the set of parameters to be adjusted, is chosen. The quantity

$$\chi^2=\sum_i\left[\frac{y(x_i)-f(x_i,a_j)}{\sigma_{y_i}}\right]^2 \tag{5}$$

is minimized using standard computational techniques to obtain the best-fit values a_j^* of the variable parameters as well as their uncertainties.[13] The agreement between the experimental values y_i and the best-fit function $f(x_i, a_j^*)$ can be evaluated by examining the values of χ^2/ν, where ν, the number of degrees of freedom, is defined as the total number of data points minus the total number of fitted parameters. For a good fit χ^2/ν should be of order 1. If a large value is obtained it indicates poor agreement between theory and experiment.

In general, if the fitting function is the true parent function of the data, least-squares analysis will give the best possible estimates of the fitted parameters. In developing our data-analysis techniques we have attempted to make use of the current understanding of the behavior of positrons in metals containing defects to choose the best form of the fitting function.

A. Original method

The original method of data analysis was based on the mean lifetime of the positron in the metal,

$$\bar{\tau}(T)=\int_{-\infty}^{\infty} tP(t,T)\,dt, \tag{6}$$

where $P(t, T)$ is the time distribution of the annihilation at temperature T. As outlined in the

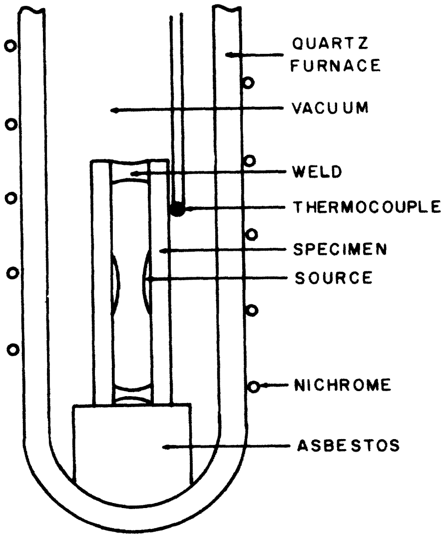

FIG. 3. Furnace for equilibrium measurements.

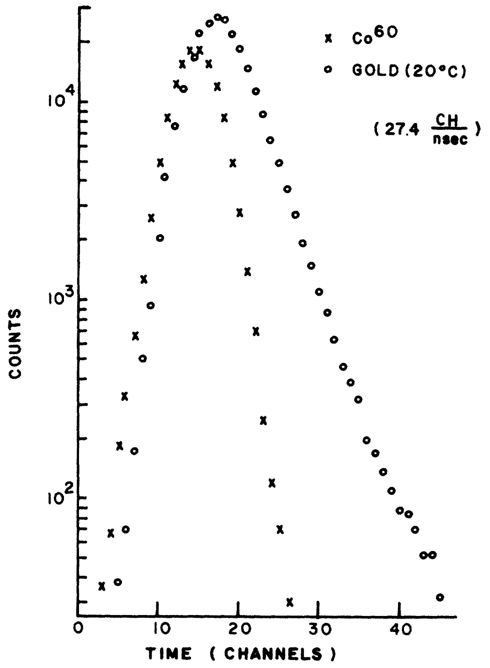

FIG. 4. Time spectra for ^{60}Co and pure gold.

Introduction, the formation energy for monovacancies was obtained as the slope of a semilogarithmic plot of the quantity $[\bar{\tau}(T)-\tau_L]/[\tau_{1V}-\bar{\tau}(T)]$, where $\bar{\tau}(T)$ is the mean lifetime as a function of temperature. Lifetime data obtained from measurements at low temperatures were analyzed to obtain τ_L by fitting an exponential decay to that part of the data which corresponds to times long compared to the resolution of the instrument.[14] It was also necessary to allow for a small-intensity, long-lifetime component which corresponded to annihilation in the ^{22}NaCl positron source. Data from high-temperature measurements were analyzed similarly to obtain τ_{1V}. At intermediate temperatures the component due to the source was subtracted and $\bar{\tau}(T)$ was obtained from a single-exponential fit to the data. The formation energy E_{1V}^F was determined from an Arrhenius plot of the quantity $[\bar{\tau}(T)-\tau_L]/[\tau_{1V}-\bar{\tau}(T)]$ [see Eq. (4)].

We found that using this scheme to analyze data on pure aluminum our results were not reproducible from one run to the next. Although some of the difficulties were caused by experimental problems which were later overcome by improvements in the lifetime-measurement system, the method of analysis as we have outlined it so far was oversimplified to such an extent that it could not give accurate results.

The details of the improvements in the data analysis that were necessary to eliminate these difficulties will be described below. Briefly they are as follows: First, the commonly used technique of fitting data only for times that are long compared to the resolution time of the instrument was eliminated. This necessitated taking the resolution of the instrument into account. Second, the assumption that $\bar{\tau}(T)$, the mean lifetime at intermediate temperatures, could be obtained by a single-component fit was eliminated by a reparametrization of the fitting function so that $\kappa_{1V}(T) = \mu_{1V}c_{1V}(T)$ rather than $\bar{\tau}$ became the independent parameter at intermediate temperatures. Finally, the assumptions that the lifetime in the lattice, τ_L, and the lifetime in the vacancy, τ_{1V}, could be obtained by single-component fits to the high- and low-temperature data, respectively, were eliminated by the development of a technique which fit the defect parameters of interest to the data from all temperatures simultaneously. Use of this technique allowed us to include in our analysis the effect of several types of defect traps as well as the effect of temperature dependence in the specific trapping rates.

B. Fitting the entire time spectrum

Although the method of fitting a single exponential to the data for times that are long compared to the resolution time is valid when there is only one lifetime component in $P(t, T)$,[14] it is not valid when there is more than one component. When there are two components in $P(t, T)$, as predicted by the trapping model, the fitted lifetime will be an arbitrary function of the two lifetime components which depends upon what range in the time spectrum was used in the fitting. Therefore, if we are to obtain a unique result from a given set of data, when fitting it with a single lifetime component, it is necessary to fit the entire time spectrum. To do this we must fold the time distribution of the annihilations, $P(t, T)$, with a function representing the resolution of the instrument.

The form for the resolution function was at first taken as a Gaussian,

$$G(t') = (4\ln 2/\pi)^{1/2}\, W_{1/2}^{-1}\, e^{-[4\ln 2(t'-t_0)^2 W_{1/2}^{-2}]}, \qquad (7)$$

where $W_{1/2}$ is the full width at half-maximum and t_0 is the centroid. In analyzing positron-lifetime data on deformed aluminum, Hautojärvi *et al.*[9] used the values of $W_{1/2}$ and t_0 that they obtained by measuring the resolution function using a ^{60}Co source which emits two nearly simultaneous γ rays. They suggested that their high values of χ^2/ν (~1.3) might be the result of fixing $W_{1/2}$ and t_0 incorrectly, but our own experience with analysis of data on aluminum indicates that even when these parameters are least squares adjusted separately for each data set, the fit is not significantly improved. In addition to giving a poor fit, the use of the Gaussian function was found to induce systematic errors in the fitted lifetimes. When data on a specimen of well-annealed pure aluminum were analyzed to obtain τ_L, the mean lifetime in the perfect lattice, we found that our results were not reproducible from one run to the next as shown in Fig. 5.

To eliminate the problems associated with the use of the Gaussian resolution function we developed what we call the slope-sided resolution function $R(t')$, which is the convolution of a Gaussian with a double-side exponential,

$$R(t') = \int_{-\infty}^{0} G(t'' - t')\, e^{t''/\tau_-}\, dt'' + \int_{0}^{\infty} G(t'' - t')\, e^{-t''/\tau_+}\, dt'' , \tag{8}$$

where τ_- and τ_+ characterize the left- and right-hand sides of the resolution function, respectively. Comparison of Figs. 4 and 6 shows that the function $R(t')$ is a better approximation to the instrumental resolution function as obtained from measurements of ^{60}Co γ rays than is the Gaussian function. This is because the straight sides on $R(t)$ are similar to the sides of the measured time spectrum. (This form is not to be confused with the double-sided exponential used by Lichtenburger *et al.*[15] which has a sharp peak and is a poor approximation to the experimentally observed resolution function.) Results of the determination of the lifetime in pure aluminum at low temperature using this method are shown in Fig. 7. The parameters characterizing the resolution function, $W_{1/2}$, t_0, τ_-, and τ_+, as well as the lifetime, were adjusted for each data set. Here we see that the lifetime is always reproducible within its uncertainty. Typical values of $\chi^2/\nu \sim 1.1$ indicated a significant improvement in the fit.

To see what systematic errors could be caused by using a Gaussian resolution function we devised the following test: First, we generated synthetic data which had an exponential-sided resolution function folded with a single lifetime component. We then fit these synthetic data with a single exponential component folded with a Gaussian resolution function. We found that the best-fit lifetime was not equal to the true lifetime of 0.164 nsec which had been synthesized into the data. In fact, the deviation was a monotonic function of the difference of the quantities τ_- and τ_+ which had been used in generating the synthetic data. This monotonic behavior for the synthetic data is shown by the solid line in Fig. 8.

To test this correlation for real data it was necessary to fit data sets obtained from pure aluminum at room temperature first using the slope-sided resolution function folded with a single exponential component, and then using a Gaussian resolution function folded with a single exponential component. We then plotted the best-fit lifetime

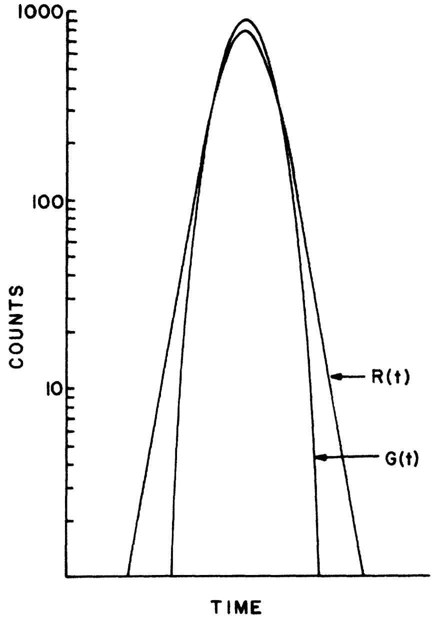

FIG. 6. Comparison of Gaussian, $G(t)$, and exponential-sided resolution function, $R(t)$. Note that the straight sides on $R(t)$ are similar to the sides of the ^{60}Co time spectrum, shown in Fig. 4.

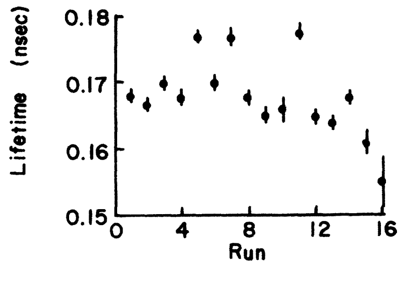

FIG. 5. Lifetime vs run using a Gaussian resolution function showing lack of reproducibility.

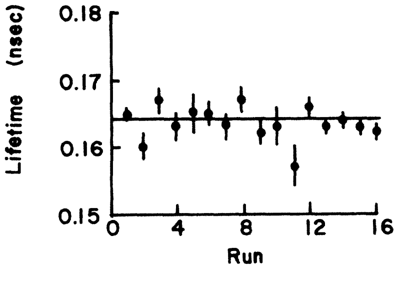

FIG. 7. Lifetime vs run using an exponential-sided resolution function. Note that the lifetime is reproducible within the uncertainty.

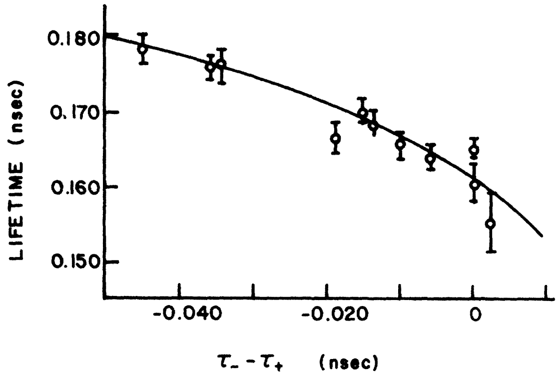

FIG. 8. Lifetime obtained using Gaussian resolution function vs the quantity $\tau_- - \tau_+$ showing that lifetime varies systematically with the shape of resolution function. Data points are for pure aluminum; solid line is synthetic data.

obtained when the Gaussian was used in analyzing the data as a function of the quantity $\tau_- - \tau_+$ which was obtained when the slope-sided resolution function was used instead. The results are indicated by the circular data points in Fig. 8. Again we see that the fitted lifetime using a Gaussian is a monotonic function of $\tau_- - \tau_+$, and that in fact the data points lie exactly along the solid line obtained by analyzing synthetic data.

We can thus see that the large deviations in the measured lifetimes are explained by changes in the quantities τ_- and τ_+ from one run to the next. These changes in τ_- and τ_+ occurred because the data were obtained using nonstabilized electronics. It is important to note that even if the electronic apparatus had been more stable, there would still have been a systematic error in the deduced lifetime except in the fortuitous case that τ_- and $\tau_+ = -0.005$ nsec.

The values obtained for τ_- and τ_+ using the system employed in the gathering of the data on the aluminum were 40 ± 4 and 55 ± 5 psec, respectively. The system used in obtaining the results for the gold gave 40 ± 04 and 50 ± 5 psec, respectively, for τ_- and τ_+. These same values were obtained when the spectrum of ^{60}Co was fitted in the case where a ^{60}Co specimen was substituted for a test specimen, indicating that the program was successfully fitting the resolution function under the data and not generating spurious results. The fit of the synthetic data discussed earlier bears this out. Parenthetically, this points out that the specification of τ_+, and the stability of the electronics, are probably the best measure of the resolution of a lifetime instrument since we are, after all, making a slope-determination analysis.

These results lead to the conclusion that the use of a Gaussian resolution function can introduce systematic errors of the order 0.010 nsec in the deduced lifetimes, and that it should not be used if accurate values of the lifetimes are desired. Furthermore, we believe that failure to take into account the shape of the resolution function is *one* reason that the values of positron lifetimes in pure metals quoted in the literature vary widely.

C. Reparametrization in terms of the trapping rate

The next assumption eliminated was that the mean lifetime at intermediate temperatures $\bar{\tau}(T)$ could be obtained by fitting the data with a single exponential component of the form $Ae^{-t/\bar{\tau}(T)}$. We evaluated the effect of this assumption by generating synthetic data with two components determined from Eq. (2) for $P(t, T)$. We then fit the data with a single lifetime component. The values of the lifetime thus obtained varied by as much as 30% from the value of $\bar{\tau}(T)$ known from Eq. (3) to be synthesized into the data. From this result it is clear that fitting with a single lifetime component is unsatisfactory for determining $\bar{\tau}$.

We see from Eq. (2) that if τ_L and τ_{1V} are known, then $P(t, T)$ is a function only of the trapping rate $\kappa_{1V}(T) = \mu_{1V} c_{1V}(T)$ and time. Thus, if the parameters τ_L and τ_{1V} are obtained from single-component fits to low- and high-temperature data and are held fixed for the analysis of the intermediate temperatures, the data can be analyzed by fitting the function $P(t, T)$ folded with an instrumental resolution function and adjusting the single parameter $\kappa_{1V}(T)$. This type of analysis is similar to that developed independently by Hautojärvi, Tamminen, and Jauho[9] for analyzing data on deformed aluminum. Results using this technique on pure aluminum are given in Fig. 9, where we have plotted $\ln[\kappa_{1V}(T)]$ versus $1/kT$ in order to obtain the formation energy E^F_{1V} as the slope. We see that there is a curvature at the lower temperatures which makes the determination of E^F_{1V} ambiguous. The removal of this ambiguity is discussed in Sec. IV.

D. Simultaneous fitting of data from all temperatures and inclusion of more than one type of trap

The final assumptions to be removed from the basic fitting procedure were that τ_L and τ_{1V} could be obtained by single-lifetime-component fits to low- and high-temperature data. The assumption that the lifetime in the trap, τ_{1V}, could be obtained by a fit to the high-temperature lifetime data is at best an approximation. Even at the melting point, typically only 95% of the positrons are trapped. Although the assumption that τ_L can be obtained from low-temperature measurements seems at first reasonable, Fig. 9 gives evidence that this is not correct. The flattening off of this graph at

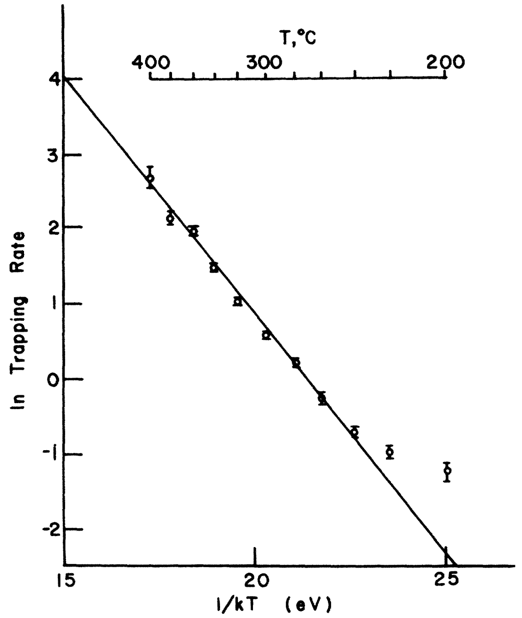

FIG. 9. $\ln[\kappa_{1V}(T)]$ vs. $1/kT$. Note the flattening off at low temperatures.

low temperatures suggests that the trapping rate κ_{1V} is not purely exponential in $1/kT$, but rather has the form

$$\kappa_{1V} = \mu_{1V} e^{S^F_{1V}/k} e^{-E^F_{1V}/kT} + \kappa_D\,, \tag{9}$$

where κ_D represents the presence of temperature-independent defect traps. We have interpreted these temperature-independent defect traps as being associated with dislocations, although they may be some other type of temperature-independent traps such as might exist on the surface of the metal. It is known from work on deformed metals that positrons are sensitive to dislocations,[9,16,17] and it is also known that although annealing near the melting point can reduce the dislocation density, the positrons may be sensitive to those dislocations which remained in our samples even after they were annealed. Therefore τ_L cannot be obtained from a single-exponential fit to low-temperature data.

In order to eliminate the assumptions concerning τ_L and τ_{1V} we have developed the technique of simultaneously fitting data from all temperatures with an extension of the trapping model which allows for the presence of several types of defect traps. The trapping rate for each type of trap was taken as

$$\kappa_j(T) = \mu_j c_j(T) = \mu_j e^{S^F_j/k} e^{-E^F_j/kT}, \tag{10}$$

where $j = 1 \cdots m$ denotes the defect type, $\kappa_j(T)$ is the trapping rate, μ_j is the specific trapping rate, $c_j(T)$ is the concentration of defects, and S^F_j and E^F_j are the defect formation entropy and energy, respectively. With the trapping rates defined in this way the temperature-independent term may be represented by setting $E^F_j = 0$, for one particular value of j.

Assuming that a positron in trap type j has an annihilation rate λ_j $(=\tau_j^{-1})$, we write the rate equations for $n_L(t)$, the fraction of free positrons, and $n_j(t)$, the fraction of positrons trapped in defect type j, in the form

$$\begin{aligned}\frac{dn_L(t)}{dt} &= -\lambda_L n_L(t) - \sum_{j=1}^{m} \kappa_j(T)\, n_L(t)\,,\\ \frac{dn_j(t)}{dt} &= -\lambda_j n_j(t) + \kappa_j(T)\, n_L(t)\,.\end{aligned} \tag{11}$$

This set of differential equations can be solved for the time distribution of the annihilations,

$$\begin{aligned}P(t, T) &= -\frac{d\left(n_L(t) + \sum_{j=1}^{m} n_j(t)\right)}{dt}\\ &= \sum_{j=1}^{m} \frac{\lambda_j \kappa_j(T)}{s - \lambda_j}\, e^{-\lambda_j t} + s\left[1 - \sum_{j=1}^{m} \frac{\kappa_j(T)}{s - \lambda_j}\right] e^{-st},\end{aligned} \tag{12}$$

where

$$s = \lambda_L + \sum_{j=1}^{m} \kappa_j(T).$$

This is a sum of exponential terms, one term for each defect type j with decay rate equal to the annihilation rate λ_j, plus one additional term with a decay rate which is a function of both the annihilation rate in the perfect lattice and the trapping rates $\kappa_j(T)$.

The fitting function was formed by folding this $P(t, T)$ with the exponential-sided resolution function $R(t')$. The independent variables were taken as the time t and the temperature T and the dependent variable was taken as the experimentally observed number of annihilations as a function of time and temperature, $C(t, T)$. The parameters to be obtained by fitting are the annihilation rate in the lattice λ_L and the annihilation rate λ_j, the formation energy E^F_j, and the preexponential $\mu_j e^{S^F_j/k}$, for each trap type j. The four resolution-function parameters $W_{1/2}$, t_0, τ_-, and τ_+ for each data set (i.e., each temperature) were adjusted separately to allow for possible drift in the electronics.

E. Preliminary results using pure aluminum

The results of incorporating the improvements thus far obtained will now be discussed using, as an example, data from measurements on pure aluminum. We used the following functional forms for the trapping rates:

$$\kappa_{1V} = \mu_{1V} e^{S^F_{1V}/k} e^{-E^F_{1V}/kT} \quad \text{(isolated vacancy traps)} \tag{13a}$$

and

$\kappa_D = \mu_D c_D$ (temperature-independent traps). (13b)

Note that only the product $\mu_{1V} e^{S^F_{1V}/k}$ and the product $\mu_D c_D$ can be determined by least-squares fitting. In most of the analysis the lifetime in the temperature-independent defect was fixed at the value $1/\lambda_D = 0.245$ nsec, because the value $1/\lambda_D = 0.245 \pm 0.050$ nsec was obtained when this parameter initially was allowed to vary. This parameter was fixed because the magnitudes of the other parameters were found to be relatively insensitive to its value, and allowing it to vary only slowed the convergence of the fit. An additional exponential component with lifetime $1/\lambda_N$ and intensity I_N was incorporated in the fitting function to allow for annihilation of positrons in the sodium chloride source.

The results of using this method on pure aluminum are given in the first column of Table II. Data analyzed for the pure and alloyed aluminum were taken at room temperature and every 20 °C between and including 200 and 400 °C. We find that we have a good fit to the data as indicated by $\chi^2/\nu = 1.01$. The value of the formation energy of monovacancies, $E^F_{1V} = 0.62 \pm 0.02$ eV, is lower than any previously reported value, but not significantly different from the Seeger and Mehrer[18] value of 0.65 eV or the values obtained by the Kingston positron group.[19,20] The lifetime in the lattice was found to be $1/\lambda_L = 0.161 \pm 0.002$ nsec, which is lower than that obtained by other workers. We believe that our value is more nearly correct, and that the others have been shifted upward by the combined effects of ignoring the shape of the instrumental resolution function and of ignoring the temperature-independent defects. The lifetime in the monovacancy trap, $1/\lambda_V$, is found to be 0.243 ± 0.001 nsec, which is not inconsistent with the range of values obtained by other workers. Annihilations in the source produced a component with intensity $I_N = (4.7 \pm 0.3)\%$ and lifetime $1/\lambda_N = 0.560 \pm 0.010$ nsec.

To evaluate the trapping efficiency of monovacancies using Eq. (13a) we need the value of the monovacancy formation entropy S^F_{1V}. Using the relation $c_{1V} = e^{S^F_{1V}/k} e^{-E^F_{1V}/kT}$ and $c_{1V} \approx c_V = 6 \times 10^{-5}$ at 450 °C obtained from simultaneous length-change–lattice-parameter measurements on aluminum,[3] we deduce the value $S^F_{1V} = 0.2k$. Substituting in Eq. (13a) and solving for the monovacancy trapping efficiency we obtain $\mu_{1V} = 3.5 \times 10^5\ \text{nsec}^{-1}$.

In order to get a physical feeling for the magnitude of the temperature-independent trapping rate κ_D, we use a very simple model to obtain an equivalent dislocation density. If we assume that the specific trapping efficiency μ_D for sites associated with dislocations is approximately equal to μ_{1V}, we can estimate the fraction of sites associated with dislocations $c_D = \kappa_D/\mu_D \approx \kappa_D/\mu_{1V} = 1 \times 10^{-6}$. Multiplying by the number of sites per unit area ($1.5 \times 10^{15}\ \text{cm}^{-2}$) we obtain an estimated dislocation density $\rho_0 \sim 10^9\ \text{cm}^{-2}$. Alternatively, the value of the temperature-independent-defect term can be compared with results of experiments on deformed aluminum.[9] This comparison indicates that a value of $\kappa_D = 0.42\ \text{nsec}^{-1}$ corresponds to ~0.2% deformation. A third way of interpreting the magnitude of the temperature-independent-defect term is to say that the trapping rate for the temperature-independent defects is equal to the trapping rate of the monovacancy concentration thermally induced at 240 °C.

TABLE II. Preliminary results for pure aluminum.

	Allowing temperature-independent defects	Assuming no temperature-independent defects
E^F_{1V} (eV)	0.62 ± 0.02	0.62 ± 0.02
χ^2/ν ($\nu = 1223$)	1.01	1.06
$1/\lambda_L$ (nsec)	0.161 ± 0.002	0.167 ± 0.001
$1/\lambda_{1V}$ (nsec)	0.243 ± 0.001	0.238 ± 0.001
$\mu_{1V} e^{S^F_{1V}/k}$ ($10^5\ \text{nsec}^{-1}$)	5 ± 2	5 ± 2
κ_D (nsec^{-1})	0.41 ± 0.08	0 fixed
$1/\lambda_N$ (nsec)	0.560 ± 0.010	0.515 ± 0.005
1_N (%)	4.7 ± 0.3	6.4 ± 0.2

For comparison, the results of fitting pure-aluminum data assuming no temperature-independent defects are given in the second column of Table II. We see that χ^2/ν has increased, indicating a poorer fit to the data, but contrary to our expectations the best-fit formation energy was unchanged. The value of $1/\lambda_L$ was shifted upward to 0.167 ± 0.001 nsec. This can be interpreted in terms of the results, allowing for temperature-independent defects given in the first column, in the following way: Since the low-temperature region is now assumed to be defect free, one can think of the value of $1/\lambda_L$ as being forced to approximate the lifetime in the lattice (0.161 nsec) plus a small admixture of the lifetime in the dislocation traps (0.245 nsec). The value we have obtained assuming no temperature-independent defect traps is similar to the value 0.166 ± 0.002 obtained by Cotterill *et al.*[21] when fitting a single exponential component to low-temperature aluminum data. Hautojärvi *et al.*[9] and MacKenzie *et al.*[4] obtained an even higher value, suggesting that perhaps their specimens were not as well annealed or that failure to take the resolution function into account resulted in a further upward shift of the value. The downward shift in the value of $1/\lambda_{1V}$ can be thought of as resulting from the best-fit value being forced to compensate for the upward shift in $1/\lambda_L$ to approximately preserve the best fit in the intermediate-temperature region.

The improvements thus far described make the analysis consistent with the currently accepted version of the trapping model.

F. Temperature dependence in the specific trapping rate

Our final development in the data analysis was the inclusion of the possibility of temperature dependence in the specific trapping rate μ. At least three possible temperature dependences for μ have been proposed. Several groups have suggested that the specific trapping rate depends on how fast the positron can find a vacancy and is therefore proportional to the thermal velocity of the positron. This leads to the prediction that μ increases as $T^{1/2}$.[16] Stott disagrees,[22] arguing that the positron behaves as an extended wave packet which samples large areas of the lattice at all times so that the specific trapping rate is velocity independent and therefore temperature dependent. A third proposal, due to Seeger,[23] predicts a $T^{-1/2}$ dependence on the basis of positron-phonon scattering arguments.

Experimental evidence is sparse. Connors, Crisp, and West[24] obtained a result in cadmium supporting the $T^{-1/2}$ dependency, but they have since stated that they believe that their results may have been an artifact of their experimental procedure.[25] Some data[16,21] have been interpreted in terms of the $T^{1/2}$ dependence but the results were inconclusive. Recent results on quenched gold by McKee *et al.*[26] and Hall *et al.*[27] are contradictory, the former reporting negligible temperature dependence, the latter an approximate $T^{1/2}$ dependence. Most often, for simplicity, experimental results are interpreted assuming no temperature dependence in μ.

We assumed that the temperature dependence of the specific trapping rate could be described as some power x of the temperature so that the trapping rates are

$$\kappa_j(T) = (T/T_0)^x \mu_j e^{S_j^F/k} e^{-E_j^F/kT}, \tag{14}$$

where now μ_j is the specific trapping rate at T_0, an arbitrary scaling temperature.

The data were analyzed with x fixed at several different values and the resulting values of χ^2 were plotted as a function of the value of x. A polynomial curve was drawn through these points and the value of x at the minimum of the curve was taken as the best-fit value. The uncertainty σ_x was obtained using the formula $\sigma_x = 2/(\partial^2\chi^2/\partial x^2)$, where $\partial^2\chi/\partial x^2$ is the second derivative of the polynomial curve at the minimum.[13] This formula is equivalent to the statement that if χ^2 is approximately a parabolic function of the parameter x, then χ^2 will increase by 1 when x is shifted 1 standard deviation from its best-fit value. That is, if x^* is the best-fit value, then

$$\chi^2(x^* \pm \sigma_x) = \chi^2(x^*) + 1.$$

The results of this analysis of data for pure aluminum and pure gold, and the results of similar analysis of data for Al–1.7-at.%-Zn are given in Sec. IV.

IV. RESULTS OF EQUILIBRIUM MEASUREMENTS ON ALUMINUM, GOLD AND Al-1.7-at.%-Zn

We now discuss the results of data analysis on pure aluminum, pure gold, and an aluminum-zinc alloy. Section IV A gives the results obtained on the pure metals using the methods outlined in the data-analysis section. In Sec. IV B these methods are extended to take into account the presence of impurities.

A. Pure metals

The trapping rates were taken as

$$\kappa_{1V} = (T/T_0)^x \mu_{1V} e^{S_{1V}^F/k} e^{-E_{1V}^F/kT} \quad \text{(for monovacancy traps)} \tag{15a}$$

and

$$\kappa_D = (T/T_0)^x \mu_D c_D \quad \text{(for temperature-independent defect traps).} \tag{15b}$$

1. Pure aluminum

The results of this analysis on pure aluminum for temperature dependence between T^{-1} and T^{+3} in the specific trapping rate are given in Table III. We see that the formation energy E_{1V}^F and the pre-exponential $\mu_{1V} e^{S_{1V}^K/k}$ depend on the temperature dependence assumed in the specific trapping rate. The other fitted parameters did not vary significantly when temperature dependence in the specific trapping rate was assumed, but remained essentially at the values obtained when no temperature dependence was assumed. These values were as follows: The lifetime in the lattice $1/\lambda_L = 0.161 \pm 0.001$ nsec, the lifetime in the vacancy trap $1/\lambda_{1V} = 0.243 \pm 0.001$ nsec, the temperature-independent defect trapping rate $\kappa_D = 0.41 \pm 0.08$ nsec^{-1}, the intensity of the source component $I_N = (4.7 \pm 0.3)\%$, and the lifetime in the source $1/\lambda_N = 0.560 \pm 0.010$ nsec.

We observe χ^2/ν has a minimum value of 1.00 near T^{+1} and that for $T^{1/2}$ and T^2 temperature dependences χ^2/ν has increased to 1.01, correspond-

TABLE III. Results for aluminum with temperature-dependent trap efficiency. ($T_0=473$ °K).

Temperature dependence	E_{1V}^F (eV)	χ^2/ν ($\nu=1223$)	$\mu_{1V}e^{S_{1V}^F/k}$ (10^5 nsec^{-1})	S_{1V}^F [a] (k)	μ_{1V} (10^5 nsec^{-1})
T^{-1}	0.63 ± 0.03	1.06	8 ± 4	0.4 ± 0.5	5 ± 2
T^{0}	0.62 ± 0.02	1.02	5 ± 2	0.2 ± 0.4	4 ± 2
$T^{1/2}$	0.65 ± 0.03	1.01	8 ± 3	0.7 ± 0.4	4 ± 2
T^{1}	0.69 ± 0.03	1.00	12 ± 7	1.4 ± 0.5	3 ± 2
T^{2}	0.69 ± 0.04	1.01	11 ± 7	1.4 ± 0.6	3 ± 2
T^{3}	0.68 ± 0.04	1.01	6 ± 4	1.2 ± 0.7	2 ± 1

[a] Assumes $c_v=6\times10^{-5}$ at 450 °C.

ing to an increase of χ^2 of 12, and indicating that this is a fairly sharp minimum. Using the procedure outlined in Sec. III F, in which a polynomial is fitted to the values of χ^2, we deduce that the best fit should be for a temperature dependence of $T^{1.2\pm0.3}$. By interpolating between those temperature dependences which were actually fitted we find this corresponds to $E_{1V}^F=0.69\pm0.03$ eV and $\mu_{1V}e^{S_{1V}^F/k}=(12\pm7)\times10^5$ nsec^{-1}.

2. *Pure gold*

Results of a similar analysis on pure gold are given in Table IV. Data analyzed were taken at room temperature and every 40 °C between and including 360 and 760 °C. Assuming no temperature dependence we obtain a value $E_{1V}^F=0.98\pm0.03$ eV with $\chi^2/\nu=1.048$. The lifetime in the lattice was $1/\lambda_L=0.121\pm0.001$ nsec and the lifetime in the monovacancy trap was $1/\lambda_{1V}=0.211\pm0.001$ nsec. The source component had an intensity $I_N=(0.51\pm0.06)\%$ and an associated lifetime $1/\lambda_N=0.800\pm0.050$ nsec. Using the value $c_{1V}=2.5\times10^{-4}$ at 900 °C, which is determined from simultaneous length-change–lattice-parameter experiments,[3] we obtain $S_{1V}^F=1.4k$ and $\mu_{1V}=3.5\times10^5$ nsec^{-1}. From the best-fit value of the temperature-independent defect trapping rate $\kappa_D=0.28\pm0.04$ nsec^{-1} we obtain $c_D\approx1\times10^{-6}$ and $\rho\sim10^9$ cm^{-2}.

When temperature dependence in the specific trapping rate is assumed, the best fit is estimated to be for a $T^{0.5\pm0.2}$ dependence corresponding to the values $E_{1V}^F=1.00\pm0.03$ eV, $\mu_{1V}e^{S_{1V}^F/k}=(16\pm5)\times10^5$ nsec^{-1}, and $\chi^2/\nu=1.041$. As in the previous case of aluminum, the parameters $1/\lambda_L$, $1/\lambda_{1V}$, I_N, $1/\lambda_N$, and κ_D for gold did not change appreciably when temperature dependence in the trap efficiency was allowed.

3. *Discussion of results for pure metals*

We see that the data obtained from equilibrium measurements on pure aluminum and pure gold are best fit by assuming a positive temperature dependence in the specific trapping rate. In aluminum the formation energy obtained ($E_{1V}^F=0.69\pm0.03$ eV) has increased from the value obtained assuming no temperature dependence ($E_{1V}^F=0.62\pm0.02$ eV) so that now it is within the range of values obtained by other workers.[28] In gold the formation energy appears to be less sensitive to assumed temperature dependence in the specific trapping rate. The value obtained assuming a temperature-dependent specific trapping rate, $E_{1V}^F=1.00\pm0.03$ eV, is slightly, but not significantly, higher than the range of values obtained by other

TABLE IV. Results for gold with temperature-dependent trap efficiency. ($T_0=673$ °K).

Temperature dependence	E_{1V}^F (eV)	χ^2/ν ($\nu=2021$)	$\mu_{1V}e^{S_{1V}^F/k}$ (10^5 nsec^{-1})	S_{1V}^F [a] (k)	μ_{1V} (10^5 nsec^{-1})
T^{-1}	0.95 ± 0.01	1.090	12 ± 2	1.1 ± 0.2	4 ± 1
$T^{-1/2}$	0.97 ± 0.03	1.070	14 ± 5	1.3 ± 0.3	4 ± 1
T^{0}	0.98 ± 0.03	1.048	15 ± 5	1.4 ± 0.3	4 ± 1
$T^{1/4}$	0.99 ± 0.03	1.042	16 ± 5	1.5 ± 0.3	4 ± 1
$T^{1/2}$	1.00 ± 0.03	1.041	16 ± 5	1.6 ± 0.3	3 ± 1
$T^{3/4}$	1.00 ± 0.03	1.042	15 ± 5	1.6 ± 0.3	3 ± 1
T^{1}	1.00 ± 0.03	1.045	13 ± 5	1.6 ± 0.3	3 ± 1
T^{2}	0.95 ± 0.04	1.052	5 ± 3	1.1 ± 0.6	2 ± 1
T^{3}	0.93 ± 0.09	1.057	2 ± 1	0.9 ± 0.5	1 ± 0.5

[a] Assumes $c_v=2.5\times10^{-4}$ at 900 °C.

workers,[29] while the value obtained assuming no temperature dependence, $E_{1V}^F = 0.98 \pm 0.03$, is within that range.

We now have what we believe to be a good method for analyzing data on pure metals to obtain the monovacancy formation energy, the lifetime of the positron in the lattice, and the lifetime in a monovacancy trap. We have lowered the value of χ^2/ν and improved the precision of the fitted parameters by the use of the exponential-sided resolution function, and by simultaneously fitting the data for all temperatures with an extended trapping model which allows for temperature-independent defects as well as temperature dependence in the specific trapping rate.

B. Metals and impurities

To include the effects of impurities in face-centered cubic metals we use the following functional forms for the trapping rates[8,30]:

$$\kappa_{1V} = (T/T_0)^x \mu_{1V}(1 - 12i_0)\, e^{S_{1V}^F/k} e^{-E_{1V}^F/kT} \quad \text{(isolated monovacancy traps),} \tag{16a}$$

where i_0 is the impurity concentration,

$$\kappa_{VP} = (T/T_0)^x \mu_{VP} 12 i_0 e^{S_{VP}^F/k} e^{-E_{VP}^F/kT} \quad \text{(vacancy-impurity pair traps),} \tag{16b}$$

where S_{VP}^F and E_{VP}^F are the entropy and energy, respectively, for formation of a vacancy adjacent to an impurity atom, and

$$\kappa_D = (T/T_0)^x \mu_D c_D \quad \text{(temperature-independent traps).} \tag{16c}$$

In the analysis, those parameters associated with the isolated monovacancy traps, λ_{1V}, $\mu_{1V} e^{S_{1V}^F/k}$, and E_{1V}^F, were held fixed at the values obtained from the analysis of pure aluminum. When the lifetime in the Al-Zn lattice, $1/\lambda_L$, was allowed to vary, the fitted value was found to be exactly the same as the value of the lifetime in the pure-aluminum lattice, $1/\lambda_L = 0.161 \pm 0.001$ nsec. Therefore, throughout the remainder of the analysis on Al-Zn $1/\lambda_L$ was fixed at 0.161 nsec. Because the presence of the zinc did not affect the lifetime in the lattice and because theoretical calculations suggest that single substitutional metallic atoms do not trap positrons,[31] we did not include a term corresponding to positron trapping by the zinc impurity atoms.

The results for Al–1.7-at.%-Zn are given in Table V. We see for the case of no temperature dependence in the specific trapping rate that the vacancy-impurity binding energy

$$E_{VP}^B = E_{1V}^F - E_{VP}^F$$

is given by $E_{VP}^B = -0.09 \pm 0.03$ eV, with a corresponding value of χ^2/ν of 1.09. By fitting a polynomial to the values of χ^2/ν we estimate that the best fit is for a temperature dependence of $T^{1.1 \pm 0.2}$, corresponding to extrapolated values of $E_{VP}^F = 0.65 \pm 0.06$ eV, $E_{VP}^B = 0.04 \pm 0.07$ eV, $\mu_{VP} e^{S_{VP}^F/k} = (13 \pm 20) \times 10^5\ \text{nsec}^{-1}$, and $\chi^2/\nu = 1.08$. The lifetime in the vacancy-impurity pair trap, $1/\lambda_{VP} = 0.243 \pm 0.001$ nsec, was found to be equal to the lifetime in a monovacancy trap, $1/\lambda_{1V} = 0.243 \pm 0.001$ nsec, and like $1/\lambda_{1V}$ it did not change significantly for different temperature dependences. When the specific trapping rate is assumed to be temperature independent, the pre-exponential term $\mu_{VP} e^{S_{VP}^F/k}$ is much larger than the corresponding term for monovacancies. For the best-fit temperature dependence these terms are more nearly equal.

Our conclusion from this experiment is that there is essentially no binding between vacancies and zinc impurity atoms in aluminum. Comparison with the results of other methods gives support to the idea that the larger values of the binding energy sometimes obtained are in fact the result of clustering of the impurity atoms during the quench.[32,33]

V. CONCLUSIONS

We have used relatively sophisticated data-analysis techniques to obtain the values of several defect parameters associated both with pure metals and with metals containing impurities. In aluminum we have found the monovacancy formation energy to be $E_{1V}^F = 0.62 \pm 0.02$ eV when no temperature dependence in the specific trapping rate is assumed and $E_{1V}^F = 0.69 \pm 0.03$ eV when the optimum temperature dependence of $T^{1.2 \pm 0.3}$ in the specific trapping rate is assumed. These values are lower than the values obtained in the past by quenching experiments and simultaneous length-

TABLE V. Results for aluminum–1.7-at.%-zinc with temperature-dependent trap efficiency.

Temperature dependence	E_{VP}^F (eV)	E_{VP}^B (eV)	χ^2/ν ($\nu = 1380$)	$\mu_{VP} e^{S_{VP}^F/k}$ ($10^5\ \text{nsec}^{-1}$)
T^0	0.71 ± 0.02	-0.09 ± 0.03	1.089	28 ± 10
$T^{1/2}$	0.69 ± 0.02	-0.04 ± 0.04	1.082	27 ± 11
T^1	0.66 ± 0.6	$+0.03 \pm 0.07$	1.081	15 ± 18

change-lattice-parameter experiments, thus lending support to the current idea that the values obtained by those methods may have been shifted upward slightly by clustering effects.

We have made the first reported positron-lifetime measurements in pure gold as a function of temperature. We have found that the lifetime in the defect-free lattice is $1/\lambda_L = 0.121 \pm 0.001$ nsec and that the lifetime in a monovacancy trap is $1/\lambda_{1V} = 0.211 \pm 0.001$ nsec. If we assume no temperature dependence in the specific trapping rate we obtain the value of $E^F_{1V} = 0.98 \pm 0.03$ eV, while for the optimum temperature dependence of $T^{0.5\pm0.2}$ we obtain $E^F_{1V} = 1.00 \pm 0.03$ eV. These results are in substantial agreement with previous results of quenching experiments and simultaneous length-change-lattice-parameter experiments.

Our results for Al–1.7-at.%-Zn indicate that there is essentially no binding between vacancies and zinc atoms in aluminum, thus supporting the conjecture that the relatively large values sometimes obtained for this parameter are the results of impurity-impurity binding and vacancy clustering during quenching.

Our analysis has revealed that the vacancy-formation energy depends upon the temperature dependence of the specific trapping rate. Very little experimental evidence has appeared to define the proper choice of the exponent and theoretical treatments are not in agreement with one another. We believe that the ultimate success of the positron experiments in providing accurate formation energies will require a resolution of this problem.

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