Measurements of the vacancy formation enthalpy in aluminum using positron annihilation spectroscopy

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The temperature dependence of positron annihilation in aluminum has been investigated over the range 20–435°C by simultaneous measurements of positron lifetime and Doppler broadening of the annihilation spectrum. The analyses of lifetime data are critically examined, especially with respect to the effects of instrumental resolution-function uncertainties. The lifetime and Doppler-broadening data have been analyzed in terms of the two-state trapping model. Application of this model to the measurement of the vacancy-formation enthalpy E_v^F in aluminum is discussed in light of the observation of a strong temperature dependence of the apparent positron lifetime in the bulk or lattice state above 370°C. The monovacancy formation enthalpy in aluminum, $E_{1v}^F = 0.66 \pm 0.02$ eV, was determined for temperatures below 372°C. This is compared with values previously reported.

I. INTRODUCTION

The two-state trapping model[1-3] has served for some time as the primary description of the behavior of the positron in metals containing vacancies, which act as traps for the positron. With this model it has been possible to proceed in developing positron-annihilation spectroscopy (PAS) as a technique for determining the temperature dependence of equilibrium vacancy concentrations in metals and, hence, their vacancy formation enthalpies. However, the way in which the trapping model is applied depends on the type of positron experiment which is undertaken. In particular, both peak-counting angular correlation experiments and Doppler-broadening experiments, which measure properties of the momentum distribution of the annihilating positron-electron pairs, require a number of assumptions which are not inherent to a corresponding positron lifetime experiment.

The present investigation[4] was carried out in order to study the temperature dependence of positron annihilation in well-annealed polycrystalline aluminum. Although previous positron-annihilation experiments[5-10] have been done on aluminum, in the present work Doppler-broadening and lifetime experiments were performed on the same sample at the same time so as to determine if these momentum and lifetime techniques, each with their own inherent experimental and analysis problems, would in fact result in the same quantitative determination of the vacancy-formation enthalpy in aluminum. A detailed treatment of lifetime-analysis uncertainties has been undertaken, particularly with regard to the problem of uncertainties in the instrumental resolution function. The lifetime spectra were analyzed extensively and the temperature dependences of the positron lifetimes in the positron bulk and vacancy states were determined.

II. EXPERIMENTAL METHOD

A. Sample and source

The positron source and sample configuration used was the well-known "sandwich" type. The source was prepared by deposition of ~50 μCi of $Na^{22}Cl$ on 1 mg/cm^2 rolled Ni foil (~1 μm thick). An envelope was formed by folding the Ni foil in such a way that the source was covered from both sides by only one layer of Ni. This source resulted in a peak-to-background ratio of ~630. The source was deposited from a neutral water solution in such a way as to minimize the areal density of the dried salts. The source correction (2% intensity) was similar to that obtained with weaker sources deposited by the same technique. The count rate depends on both source strength and geometry factors. The sample chamber permitted the detectors to be placed a minimum distance of ~1.75 cm from the sample. The singles count rate (~30 kHz) was measured by observing the rate of discriminator events from the Argonne constant-fraction units. These discriminators, the so-called "arming levels" of the constant fraction units, were adjusted to be just above the noise level of the anode output of the photo tubes. A number of possible count-rate problems were considered. It is important to note that the count rate remained constant throughout the experiment, thus eliminating the effects of many possible problems. In addition, electronic studies of the resolution properties of the time-to-amplitude converter showed no measurable broadening at these count rates. Moreover, the instrumental resolution function eventually determined for our equipment

with this source was in agreement with the resolution function obtained with sources of about half of this strength. Pile-up rates at the fast discriminators were calculated and found to be negligible, based on an anode pulse width of ~12 nsec measured at 10% maximum of the peak. Pulse pile up at the side-channel discriminator system was minimized by using delay-line shaped pulses of width ~300 nsec measured from 10% of peak height to the crossover point.

Two polycrystalline aluminum samples with dimensions of $2.5 \times 1 \times 0.05$ cm were prepared from nominally 99.9995 wt.% pure Al supplied by the Materials Research Corporation. The samples were chemically etched in concentrated NaOH, rinsed, and annealed on quartz flats at 7×10^{-7} Torr at 500 °C for 20 h and then slowly (over ~8 h) cooled to room temperature under vacuum. The Ni source envelope was placed between the two Al samples and the entire sandwich was clamped at one end between two halves of a solid Cu cylinder such that the source was ~1 cm from the end of the clamp. The entire assembly was then placed in a high vacuum chamber and subsequently annealed *in situ* at 435 °C for 23 h. The sample remained in the vacuum chamber, at pressures $<10^{-7}$ Torr, for the remainder of the experiment. The temperature of the sample was continuously monitored, and was maintained at each measurement temperature to better than ±1 °C.

B. Counting systems

The Doppler-broadening measurements were made with an intrinsic germanium detector, with resolution of ~1.1-keV FWHM (full width at half-maximum) at 514 keV. Signals were passed to a main amplifier and a gated biased amplifier, both of which were maintained at constant temperature (±0.1 °C) during the experiment. The lifetime system was of the fast-slow coincidence type using 1.9-cm-diam. by 1.9-cm-thick Pilot-U plastic scintillators[11] coupled to fast high-gain phototubes. Suitable shaping of the anode signals was used to provide amplitude risetime compensation (ARC) to the constant-fraction discriminators. Side-channel selection was derived from delay-line-shaped dynode signals using modified Ortec delay-line amplifiers. The side channel windows were operated at ~70% of their maximum width. The ability to operate with wide windows while achieving good resolution, ~244-psec FWHM, was a result of the ARC along with the high gain of the phototubes. As with the Doppler-broadening measurements critical components (fast discriminators and the time-to-amplitude converter) were maintained at constant temperature.

C. Data acquisition

Data from both the lifetime and Doppler-broadening apparatus were digitized in analogue-to-digital converters coupled to a digital computer. At each sample temperature histograms were constructed in the computer core. At the end of a short time interval (200 sec for the lifetime and 300 sec for the Doppler broadening) the histograms, identification information, sample temperature, and the temperature of the electronic components were dumped to magnetic tape. The information from these microscopic experiments was subsequently used to correctly stabilize the total experiment against temperature and pulse-electronic instabilities. Data points reported represent a range of total counts accumulated from ~50 000 to ~500 000.

III. DATA TREATMENT

The presentation of the data treatment falls naturally into two parts, one devoted to the treatment of the lifetime data, and the other to the treatment of the Doppler-broadening data. Since the results observed in the present work with respect to the lifetime data were unusual and unexpected, it is necessary that the details of the data analysis should be described.

The most important problem in the interpretation of an observed positron lifetime spectrum arises from the fact that the FWHM of the instrumental resolution function is comparable to the FWHM of the annihilation spectrum itself. It is therefore natural to raise the question of the resolution-function dependence of the results finally obtained. The focus of the following is on this resolution-function dependence, since it can dominate when compared to other possible errors.

A. Lifetime analysis

In the conventional lifetime spectrum analysis one fits the data to a particular physical model, with variable parameters, which is then convoluted with a proposed resolution function. The proposed resolution function is often obtained from experiments which are performed independently of the actual lifetime experiment under study. It is therefore an obligation to prove experimentally that the proposed resolution function is in fact suitable for deconvoluting the data at hand. The χ^2 sum of the fit is commonly used as the test criterion for the validity of both the physical model and the resolution function, and it should consequently be asked which other resolution functions would also be acceptable from a χ^2 sum point of view. This set of possible resolution functions is thus defined by the actual lifetime data themselves

and not by the knowledge of the proposed resolution function. Since the χ^2 sum is the test criterion in this procedure, the uncertainty on the actual resolution function should be taken large enough to raise the χ^2 sum to the significance level of rejection. This latter has been taken as two standard deviations in the present work. The effects of these large uncertainties were incorporated in the final analysis of the results. However, it should be realized that the current procedure leads to an overestimate of the actual resolution-function uncertainties. In the future it should be possible to reduce these uncertainties by a simultaneous fitting of the positron lifetime and resolution-function parameters.

All the lifetime data in the present work were analyzed using the POSITRONFIT (extended)[12] computer program permitting a description of the resolution function as a sum of two Gaussians with FWHM of Γ_1 and Γ_2, relative intensities i_1 and i_2, and a relative centroid shift of t_s. Although the program does not permit fitting of the resolution function by itself, it was used to determine the proposed resolution function to be used in all subsequent analyses of the lifetime spectra. The resolution function was obtained by analyzing selected lifetime spectra for different choices of Γ_1, Γ_2, i_1, i_2, and t_s. It was concluded that good fits could be obtained by varying Γ_1 and Γ_2 when a suitable choice of i_1, i_2, and t_s was made. A subsequent search of the i_1, i_2, and t_s parameters within limited ranges yielded the same Γ_1 and Γ_2. Of course it would be desirable in the future to include directly the determination of the resolution parameters in the POSITRONFIT program. In the vicinity of its minimum the χ^2 sum has a quadratic form in Γ_1 and Γ_2, which was subsequently determined. The resulting proposed resolution function $R0$, is represented by the point in the center of the ellipse in the (Γ_1, Γ_2) plane shown in Fig. 1. The ellipse represents the boundary defined by the previously mentioned χ^2 sum rejection criterion with a rejection beyond two standard deviations. The resolution functions $R1$, $R2$, $R3$, and $R4$, whose representations are also shown in Fig. 1, can thus be considered as limiting cases for resolution function $R0$. All lifetime spectra were analyzed using these five proposed resolution functions.

As expected, $R1$ and $R3$ produced results almost identical to those of $R0$. Therefore, the results using $R1$ and $R3$ are not presented, and $R2$ and $R4$ will be considered to be the limiting cases in the subsequent presentation. It should be kept in mind that $R2$ and $R4$ are overestimates of the real resolution-function uncertainties, since they are based upon the χ^2 sum rejection criterion. This will be apparent from Figs. 5 and 6, where virtually all the points obtained by using $R0$ lie within the limits defined by $R2$ and $R4$. A somewhat smaller overestimate of the resolution-function errors can be deduced by considering the distribution of the χ^2 sums. The observed distribution is slightly broader than it ought to have been according to theory. By neglecting all other possible chance effects and associating all of the broadening with resolution-function errors alone, the uncertainty limits obtained are approximately a factor of 2 less than those found in Fig. 1.

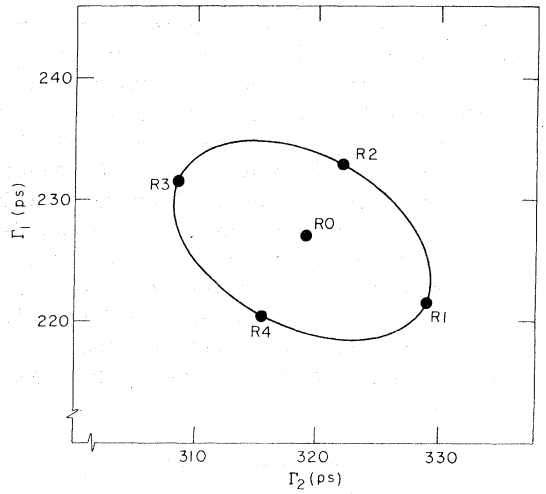

FIG. 1. Γ_1, Γ_2 plane illustrating the five resolution functions applied to the lifetime data. The ellipse represents the χ^2 sum rejection criterion.

While all of the results reported in this paper were from analyses of the entire positron lifetime spectra (full-peak analyses), "off-peak analyses" were also performed in order to serve as a verification of the full-peak results. In an off-peak analysis only a part of the observed spectrum is analyzed, while demanding that the total area of the fitted spectrum equals that of the observed spectrum. In the full-peak analyses the spectra were analyzed down to one standard deviation above the background. For both types of analyses backgrounds were determined from a region of ~8 nsec width on the "short-time side" of the peak. The validity of this background level was verified by suitable linearity checks of the system. In the off-peak analyses only that part of the lifetime spectrum which was approximately one FWHM of $R0$, i.e., ~230 psec or ~40% of the peak-count rate, greater than time zero was analyzed. The sensitivity to the resolution function was thereby reduced, but at the expense of an increased uncertainty in the results. Except for this increased uncertainty, off- and full-peak analyses led to the same results.

The source correction (2% intensity, 480-psec lifetime) was determined from those spectra which contained only one lifetime in addition to the source term. These spectra were analyzed for two components (lifetimes); neither a source correction nor fitting constraints were imposed. The longer lifetime and its intensity were interpreted as originating from the source. In previous work[13] it has been shown that the source correction thus obtained is temperature independent over the entire temperature region investigated in the present work. When compared to the effect of the resolution-function uncertainty, it was found that the source correction uncertainties had a negligible effect on the results.

B. Doppler-broadening analysis

The treatment of the Doppler-broadening data was straightforward. The parameter chosen to describe the shape of the observed γ-ray spectrum of the annihilating positron-electron pairs was the peak-count parameter F, which was obtained from the number of counts in the three center channels (corresponding to ~7% of the FWHM) of the Doppler-broadened spectrum and normalized by dividing by the total number of counts in the spectrum. This choice of parameter is not in any way unique. However, it does simulate as closely as possible peak-counting experiments done by the angular correlation technique. Thus, F is the total probability that an annihilation of a positron will result in an event observed in the three center channels.

IV. RESULTS AND DISCUSSION

The discussion of the experimental results will be confined to a particular positron decay scheme called the two-state trapping model,[1-3] represented schematically in Fig. 2. In this model it is assumed that annihilation can only occur from one or the other of two states; the positron bulk state or the positron trap state. It is further assumed that the positron thermalization time is negligibly short. In Fig. 2 the parameters λ_b and λ_v are the 2γ-decay rates of the positron from the bulk state and the vacancy-trap state, respectively, and κ is the trapping rate of the positron from the bulk state to the vacancy state. The parameters F_b and F_v are the peak-count parameters characteristic of the positron's decay from the bulk state and the vacancy state, respectively.

For the purpose of completeness two additional complicating processes, also shown in Fig. 2, should be considered in this model. These are represented by the rate of thermal detrapping of the positron δ and the direct-trapping fraction α (i.e., the fraction of positrons in the vacancy-trap state at time zero). Thermal detrapping of a positron from a vacancy, while possible, has been recently considered[14] for Al and found to be a negligible effect. While the usual application of the two-state trapping model assumes that all positrons in the metal initially occupy the bulk state, the possibility of the necessity of inclusion of a direct-trapping term cannot *a priori* be excluded, particularly in the light of recent lifetime results for lead[15] and the subsequent interpretation of these results.[16] At least two different mechanisms could give rise to results which would appear experimentally as a population of the vacancy-trap state at $t=0$. One is capture of a positron by a vacancy prior to its thermalization, as suggested by Shulman and Warburton.[16] A second possibility could be a rapid depletion of the thermalized positron density around the vacancy, as suggested by Frank and Seeger.[17] Their formulas indicate that a quasistationary state would be reached within 10^{-13} sec, which would appear ex-

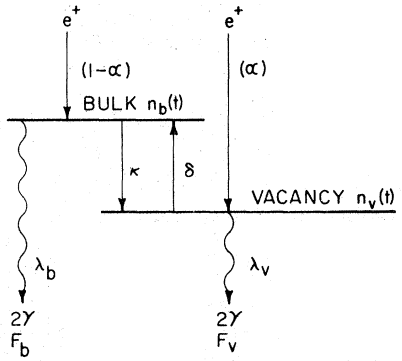

FIG. 2. Decay scheme of the positron two-state trapping model taking both detrapping and direct trapping (see text) into account.

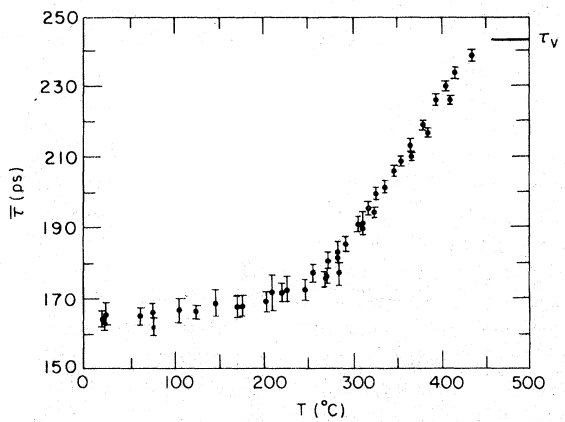

FIG. 3. Mean lifetime $\bar{\tau}$ of positrons in Al as a function of temperature T (°C). The value of the lifetime of the positron in a vacancy, $\tau_v = 244$ psec, is indicated.

perimentally as direct trapping. It should be pointed out that all the aforementioned parameters, λ_b, λ_v, κ, F_b, F_v, δ, and α, must be considered to be potentially temperature dependent.

The positron decay scheme represented in Fig. 2 is described by two coupled first-order differential equations. The solution of these equations for the case $\alpha = 0$ has previously been discussed extensively in the literature (e.g., see the paper of Conners, Crisp, and West[18]). Despite the complexities of the decay scheme, a number of important properties can be derived without having to solve the differential equations. Consider the mean lifetime $\bar{\tau}$ of a positron given by

$$\bar{\tau} = -\int_0^\infty t \frac{d}{dt}[n_b(t)+n_v(t)]\,dt$$

$$= \int_0^\infty [n_b(t)+n_v(t)]\,dt$$

$$= \frac{1}{\lambda_b}\int_0^\infty \lambda_b n_b(t)\,dt + \frac{1}{\lambda_v}\int_0^\infty \lambda_v n_v(t)\,dt\,, \qquad (1a)$$

where $n_b(t)$ and $n_v(t)$ denote, respectively, the fraction of positrons present in the bulk and vacancy states at time t. Defining the positron lifetimes in the vacancy and bulk states as $\tau_v = 1/\lambda_v$ and $\tau_b = 1/\lambda_b$, respectively, the mean lifetime $\bar{\tau}$ can be expressed as

$$\bar{\tau} = (1-A_v)\tau_b + A_v\tau_v\,, \qquad (1b)$$

where $A_v = \int_0^\infty \lambda_v n_v(t)\,dt$ is the probability that the positron annihilates from the vacancy state. The mean lifetimes were determined from two-term fits to the data and are shown as a function of temperature in Fig. 3. Similarly, the total lineshape parameter F is the linear combination of the vacancy and bulk lineshapes,

$$F = (1-A_v)F_b + A_vF_v\,. \qquad (2)$$

Equation (2) follows simply from the principle of superposition of probabilities. It should be noted that Eqs. (1a), (1b), and (2) can be generalized as

$$\bar{\tau} = \sum_i A_i\tau_i \quad \text{and} \quad F = \sum_i A_iF_I\,, \qquad (3)$$

where $\sum_i A_i = 1$ for any multistate system. It is emphasized that the A_i and τ_i are not directly measured in a lifetime experiment.

The fraction of positrons $N(t)$ present in the system at time t is of the general form

$$N(t) = \sum_i I_i\, e^{-\Lambda_i t}\,, \qquad (4)$$

where $\sum_i I_i = 1$ and the Λ_i and I_i are the experimentally measured decay rates and intensities, respectively. For the two-state case shown in Fig. 2 the observable quantities I_i and Λ_i depend in a complicated way on the various physical transition rates. An important relationship between the experimentally observable quantities and the physical quantities is obtained by considering the positron 2γ-decay rate at $t = 0$,

$$-\left(\frac{\partial N}{\partial t}\right)_{t=0} = (1-\alpha)\lambda_b + \alpha\lambda_v = I_1\Lambda_1 + I_2\Lambda_2\,. \qquad (5)$$

Equation (5) has been derived previously[19] for the case $\alpha = 0$ (i.e., with no direct-trapping), while the $\alpha \neq 0$ case has recently also been considered.[16] A relationship coupling the two experimental quantities $\bar{\tau}$ and F is obtained by eliminating A_v between Eqs. (1b) and (2), giving

$$\bar{\tau} - \tau_b = \frac{\tau_v - \tau_b}{F_v - F_b}(F - F_b)\,. \qquad (6)$$

Equation (6) is noteworthy because it holds for any two-state model regardless of whether δ and α are zero or not.

The mean lifetime $\bar{\tau}$ is plotted versus the peak-count parameter F in Fig. 4. It has been commonly assumed[5-8,20-22] that the quantities τ_b, τ_v, F_b, and F_v have either no temperature dependence, or at most a small dependence presumably from thermal expansion, weak relative to the effects of the presence of vacancies. The simplest analysis procedure has been to extrapolate F (or $\bar{\tau}$) from the temperature regions where F (or $\bar{\tau}$) was essentially equal to F_b (or τ_b) into the temperature region where F and F_b (or $\bar{\tau}$ and τ_b) differ. Similarly, the temperature dependence of F_v (or τ_v) has been determined in the temperature region commonly referred to as the "saturation regon," in which the F (or $\bar{\tau}$) signal is dominated by F_v (or τ_v). However, the curvature shown in Fig. 4 is ~5 times larger than that to be expected from linear

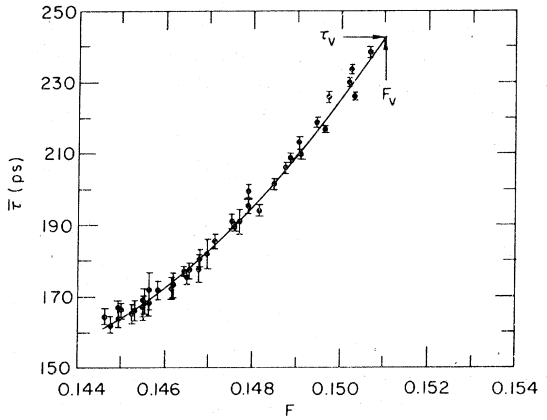

FIG. 4. Mean lifetime $\bar{\tau}$ vs the peak-count parameter F. The curve shown is a least-squares fit to the data. The values of τ_v and F_v used for E_v^F determinations are indicated.

temperature dependences of τ_v, τ_b, F_v, and F_b. Therefore, it should be expected that one or more of these quantities could vary quite strongly with temperature. This conclusion has, of course, been reached assuming that the positron thermalization time can be neglected in the trapping model. One can demonstrate by using Eq. (3) that no curvature will be contributed to Fig. 4 by any trap exhibiting temperature-independent τ_i, F_i and A_i (e.g., an overlooked source correction). More importantly it should be remembered that this observation of inconsistency with the assumptions of the simple analysis is independent of whether direct trapping or thermal detrapping are included or not.

It should be pointed out that the two-state trapping model might represent an oversimplification of the physical situation. A more refined treatment would take into account that the electrons are divided into two groups, valence and core electrons. If the balance between the annihilations with core and valence electrons is changed, the peak-count parameter and the mean lifetime may react quite differently, since they are sensitive in different ways to this balance. If this balance is temperature sensitive to any significant degree then it should be expected that the actual temperature dependence of F (apart from a scaling factor and a constant) could depend on how many center channels one uses to calculate F. However, in the present work the choice of F was made to coincide as closely as possible with angular-correlation peak counting, and this question was not investigated further.

Attention is now drawn to the experimental consideration of Eq. (5). For $\alpha = 0$, the right-hand side of Eq. (5) simply gives the reciprocal of the bulk lifetime τ_b. By inserting the quantities obtained from the lifetime data (I_1, I_2, Λ_1, Λ_2) and $\alpha = 0$ into Eq. (5), τ_b was determined using resolution function $R0$ and is plotted versus temperature T in Fig. 5. It should be pointed out that if in fact $\alpha \neq 0$, then the τ_b so calculated in the present work is not in reality the bulk lifetime. In order to demonstrate the resolution function dependence of τ_b two limiting curves are also shown in Fig. 5. These curves represent the best fits to the points obtained when using the limiting resolution functions $R2$ and $R4$ instead of $R0$. In the temperature region 20–300 °C the bulk lifetime $\tau_b(T)$ varies linearly with temperature with a slope of 5.2 ± 1.0 psec/200 K. The resolution function uncertainty is included in the stated error. This slope is somewhat greater than those previously reported [3.7 ± 0.3 psec/200 K (Ref. 23) and 4.4 ± 0.8 psec/200 K (Ref. 24)] for temperatures within the region ~78–300 K. However, this increasing slope of τ_b vs T in Al can be understood on the basis of a combination of the positron's response to lattice expansion[25] and the additional effect of positron-electron-phonon coupling.[26]

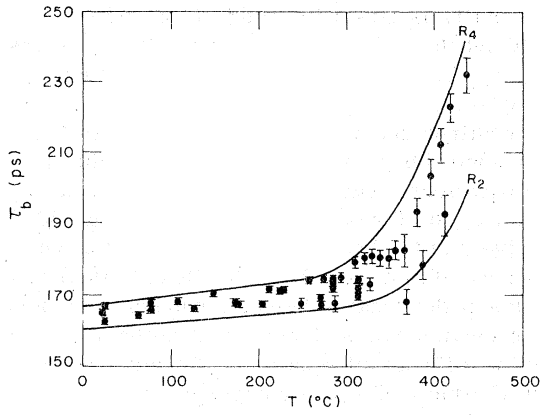

FIG. 5. Bulk lifetime τ_b plotted vs temperature T (°C). The points and their error bars were obtained using $R0$, while the curves drawn are best fits to the limiting cases using $R2$ and $R4$.

For temperatures greater than 370 °C τ_b rapidly increases toward that value characteristic of positron annihilation in a vacancy-trap state (244 psec). Since the lifetime is effectively inversely proportional to the electron density at the positron, this behavior, if real and simply not just a manifestation of the analysis model, may indicate an unexplained and dramatic decrease of the electron density at the positron while in the bulk state.

Conversely, if α is not zero, then even within the trapping model Fig. 5 does not describe the actual behavior of the bulk lifetime, and it might be assumed that the "real" bulk lifetime exhibits a simple straight-line temperature dependence due to lattice expansion. Nevertheless, the preceding discussion regarding the plot of $\bar{\tau}$ vs F (Fig. 4) has already shown that, based upon the simple trapping model, a strong temperature dependence is likely to exist in at least one of the quantities τ_b, F_b, τ_v, or F_v, regardless of the assumptions made concerning the direct-trapping fraction α. Thus, inclusion of a nonzero α in this model will not alleviate the problem of strongly temperature-dependent decay rates. It is logical to proceed from this point with only one new complexity, temperature-dependent decay rates, and to leave arguments concerning direct trapping to the future.

It has been previously observed that the bulk-lifetime in Al behaves in an unexpected way. Jamieson *et al.*[24] found that in the low-temperature region (well before any vacancy signal is detected) the lifetime changed ~60% faster with temperature

than their theory predicted. For temperatures >230 °C the tabulated data of McKee *et al.*[8] was used by us to extract the bulk lifetime (with $\alpha = 0$) as a function of temperature. This bulk-lifetime temperature dependence was found to be in qualitative agreement with that found in the present work.

Some discussion is required about the possibility of artifacts in the analysis of the experimental data. The uncertainty coming from the limited knowledge of the resolution function has already been accounted for in Fig. 5. Moreover, the effects of using different resolution functions (e.g., $R2$ and $R4$) in Fig. 4 would not have been significant. The influence of the source correction was studied as well. As expected according to Eq. (3) the results in Fig. 4 were not changed, nor were the trends shown in Fig. 5 altered, even when using a second source correction term in the 100-psec range to simulate an unresolved component from the source envelope.

For the remaining discussion it is assumed that no thermal detrapping takes place,[14] since theoretical estimates[27,28] of the positron-vacancy binding energy in Al are in the electron volt range. The two assumptions $\delta = 0$ and $\alpha = 0$ mean that the first-order differential equations in $n_b(t)$ and $n_v(t)$ can be easily solved and yield the following relationships:

$$I_1 = 1 - I_2 ,$$

$$I_2 = \kappa(\lambda_b + \kappa - \lambda_v)^{-1} ,$$

$$\Lambda_1 = \lambda_b + \kappa ,$$

$$\Lambda_2 = \lambda_v ,$$

$$A_v = \kappa(\lambda_b + \kappa)^{-1} .$$

In Fig. 6 the positron lifetime in a vacancy τ_v $= 1/\lambda_v$ is shown as a function of temperature. As in Fig. 5, the points shown were obtained using resolution function $R0$, while the two curves shown were obtained using the limiting resolution functions $R2$ and $R4$. For temperatures greater than 350 °C the lifetime is essentially independent of the resolution function uncertainty, while below 350 °C it depends strongly on the resolution function. There is, however, a strong correlation between the data in Figs. 5 and 6. If, for example, one chooses to consider one of the more unlikely resolution functions, then one obtains a perhaps more acceptable temperature dependence of $\tau_b(T)$, but at the expense of a drastically varying $\tau_v(T)$. The most probable resolution function ($R0$) yielded results which are consistent with the assumption that τ_v is essentially temperature independent. While this weak or negligible temperature dependence of τ_v may at first seem somewhat surprising, similar results have also been reported[29] for Au over a wide temperature range. In addition, a weak temperature dependence for τ_v in Al due to thermal expansion has also been recently predicted theoretically.[25]

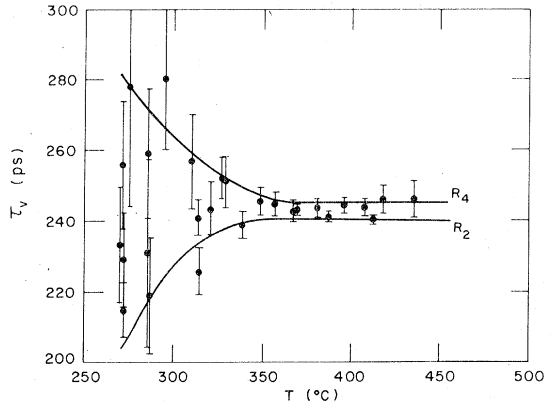

FIG. 6. Positron lifetime in a vacancy τ_v plotted vs temperature T (°C). The points and their error-bars were obtained using $R0$, while the curves drawn are best fits to the limiting cases using $R2$ and $R4$.

In summary, it has been established, within the framework of the two-state trapping model assuming negligibly short positron thermalization times, that the present aluminum data indicate a strong temperature dependence in τ_b. The effects of this strong temperature dependence will now be considered in terms of the application of PAS to the measurement of the vacancy formation enthalpy.

V. VACANCY FORMATION ENTHALPY IN ALUMINUM

The application of PAS to the extraction of vacancy formation enthalpies has been based upon the assumptions that the simple two-state trapping model provides a valid description of the positron's decay in a metal and also that the positron trapping rate $\kappa = \mu_v C_v$, where C_v is the total equilibrium vacancy concentration and μ_v is a specific trapping rate averaged over the vacancy ensemble present.[30] For an ensemble consisting of only monovacancies, the dominant situation in PAS vacancy formation enthalpy measurements, $\mu_v = \mu_{1v}$. Usually, μ_{1v} is considered to be temperature independent, but this is not easily justified. Different theoretical approaches have predicted different temperature dependences of $\mu_{1v}(T)$. Hodges,[31] McMullen and Hede[32] and Bergersen and Taylor[33] each concluded that the temperature dependence of $\mu_{1v}(T)$ would be very weak ($\sim T^0$), while Seeger,[34-36] using a classical diffusion picture, obtained a $T^{-1/2}$ dependence. At the present time the experimental evidence for the temperature dependence of $\mu_{1v}(T)$, which has been observed to range between about

T^0 and T, is both scarce and contradictory.[29,37] Fortunately, the theoretically suggested temperature dependences of $\mu_{1v}(T)$, all rather weak compared to the exponential temperature dependence of C_v, affect the formation enthalpies reported in the present work by $\lesssim 3\%$ and have been neglected here.

The possible implications of the observed strong temperature dependence of τ_b in Al, as deduced using the simple trapping model, upon μ_v could potentially be more significant. Since the large and rapid increase of the bulk lifetime above ~370 °C, if indeed real, might indicate an increasing localization of the positron in the lattice and hence a change in the propagation mechanism of the positron through the lattice leading to a decrease in $\mu_v(T)$ with temperature, it was decided to disregard data points above 372 °C when determining the formation enthalpy. Below 372 °C the observed changes in $\tau_b(T)$ are more gradual and hence $\mu_v(T)$ could be considered to be temperature independent. As previously discussed, neither direct trapping nor thermal detrapping was assumed to be present.

Three methods are commonly employed to extract vacancy-formation enthalpies from positron lifetime data. First, in the I_2/I_1 method the ratio $I_2/I_1 = \kappa(\lambda_b - \lambda_v)^{-1}$ is plotted versus $1/T$ in an Arrhenius plot. This method relies on the assumption that $(\lambda_b - \lambda_v)$ is only weakly temperature dependent. This assumption is clearly unjustified for the data already presented here. Second, the mean-lifetime or $\bar{\tau}$ method is based on Eq. (1b). At low temperatures, where the equilibrium concentration of vacancies is sufficiently low that the positrons are insensitive to them, the mean lifetime and the bulk lifetime are identical. In the intermediate temperature region, in which $\bar{\tau}$ has a significant contribution from the positrons annihilating in vacancy traps, τ_b is determined by linear extrapolation of the low temperature data, while τ_v is considered to be temperature independent and is determined from the highest temperature data. This procedure in principle allows the determination of A_v and thereby $\kappa = (1/\tau_b)(\bar{\tau} - \tau_b)/(\tau_v - \bar{\tau})$. However, this depends upon the validity of the required extrapolations. The $\bar{\tau}$ method is predominantly used when the resolution function is too broad to resolve the individual lifetime components. In the present work, as well as previously,[15] the lifetime spectra have been resolved into two components, thus giving rise to the third (and most correct) method, the κ method. Using this method it is unnecessary to make any assumptions about $\tau_b(T)$ or $\tau_v(T)$, since κ can be calculated directly as $\kappa = I_2(\Lambda_1 - \Lambda_2)$, where I_2, Λ_1, and Λ_2 are the experimentally measured intensity and decay rates.

The use of Doppler-broadening data in extracting the vacancy formation enthalpy (DB method) is based upon the use of Eq. (2) and therefore is almost identical to the $\bar{\tau}$ method. In the DB method it is possible to observe only the product $\kappa\tau_b = (F - F_b)/(F_v - F)$. Hence, this technique also involves the assumption that τ_b is either temperature independent, or only weakly so, in addition to the assumptions made about the F_b and F_v temperature dependences. It is expected that only minor differences will be apparent when comparing the correct κ method to the $\bar{\tau}$ or DB methods. For most of the temperature region over which the positrons are sensitive to vacancy concentration changes the linear extrapolation of $\tau_b(T)$ appears to be justified for Al (see Fig. 5). Furthermore, at high temperatures the uncertainties in κ or $\kappa\tau_b$ become large due to the proximity of $\bar{\tau}$ to τ_v or F to F_v.

It was previously shown that lifetime analysis results depend upon the choice of resolution function. Hence, it is necessary to assess the effect of the resolution function uncertainty on the determination of the formation enthalpy. Likewise, it is important to compare the values of the vacancy formation enthalpy E_v^F deduced from the various analysis methods just discussed. Values of E_v^F obtained with different resolution functions, with and without any constraint on τ_v, are presented in Table I. When τ_v was not constrained it was observed that the deduced formation enthalpy depended strongly on the resolution function, which is understandable in view of the resolution function dependence of τ_v (Fig. 6). It was already demonstrated that the assumption of a temperature independent τ_v is consistent with the present data. From Table I it is clear that this assumption is important, since it made the deduced formation enthalpy independent of the choice of resolution function. When τ_v was assumed temperature inde-

TABLE I. Vacancy-formation enthalpy in Al for temperatures $250 < T < 372$ °C. The resolution function ($R2$, $R0$, $R4$) dependence is shown. $R2$ and $R4$ differ by two standard deviations from the most probable resolution function $R0$. The effect of assuming τ_v = constant is shown, as is the effect of using the incorrect I_2/I_1 method as opposed to the more correct κ method. The uncertainties presented were derived from counting statistics.

Constraints:	None	τ_v = constant	
Data treatment method:	κ	κ	I_2/I_1
Resolution function No.	E_v^F (eV)	E_v^F (eV)	E_v^F (eV)
$R2$	0.43 ± 0.04	0.66 ± 0.01	0.67 ± 0.01
$R0$	0.66 ± 0.05	0.66 ± 0.01	0.74 ± 0.01
$R4$	0.89 ± 0.06	0.66 ± 0.02	0.80 ± 0.01

pendent, a value of $E_v^F = 0.66 \pm 0.02$ eV was obtained using the κ method. If this assumption had not been made, the uncertainty in E_v^F would have been considerably larger. The uncertainty suggested by comparing the E_v^F values in the first column of Table I is, however, too large, since it was pointed out previously that $R2$ and $R4$ overestimate the actual possible resolution function uncertainties by at least a factor of 2. Taking this factor into account, a value of $E_v^F = 0.66 \pm 0.09$ eV is obtained without any assumptions whatsoever regarding τ_b and τ_v. Our analyses further suggest that the uncertainty could be reduced to ~0.05 eV by use of a computer program which permitted fitting of the resolution function simultaneously with the lifetime parameters. Finally, the effect of using the incorrect I_2/I_1 method is also shown in Table I. It can be seen that this method yields results which are systematically greater than the results obtained using the κ method with τ_v = constant.

The results shown in Table I were obtained using the data from the limited temperature range 250–372 °C, because of the large change observed in $\tau_b(T)$ at higher temperatures. The inclusion of the data from the high-temperature region in the analysis, still requiring a simple Arrhenius behavior, would have decreased the deduced formation enthalpy to 0.64 eV. The reason for this decrease is clearly evident in Fig. 7 in which $\ln\kappa$ is plotted versus T^{-1} using resolution function $R0$. It can be seen that κ deviates significantly from the normally expected Arrhenius behavior with increasing temperature above ~370 °C. The resolution functions $R2$ and $R4$ yielded negligible or greater deviations, respectively, but each produced strongly temperature dependent behavior in τ_v (Fig. 6).

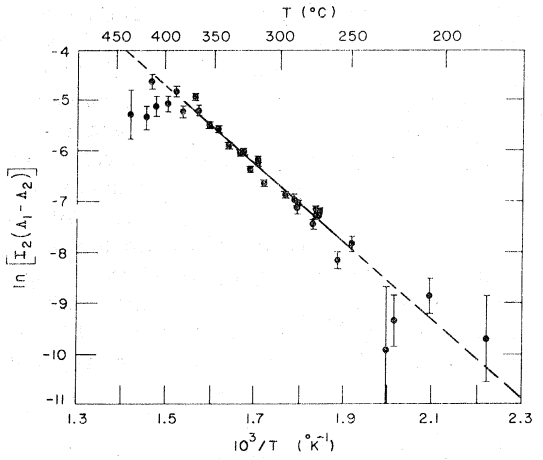

FIG. 7. Trapping rate $\kappa = I_2(\Lambda_1 - \Lambda_2)$, derived from the lifetime data using $R0$, vs $1/T$ (K^{-1}). The solid line indicates the region used in obtaining the vacancy formation enthalpy.

Since the total equilibrium vacancy concentration C_v rises exponentially, or faster due to the presence of divacancies, with increasing temperature, such $\kappa(T)$ behavior would have to be due to the temperature dependence of $\mu_v(T)$, since positron detrapping from vacancies can be neglected[14] in Al. As stated previously, however, such a temperature dependence of $\mu_v(T)$ would be physically consistent with the observed temperature dependence of $\tau_b(T)$, but both could also be a result of the model used in analyzing the data.

The Doppler-broadening data were analyzed independently of the lifetime data. As pointed out above, assumptions had to be made about $F_b(T)$ and $F_v(T)$ in the vacancy region. The present Doppler-broadening data were analyzed assuming that dF_b/dT was constant and equal to the low-temperature slope of F. For the present analysis it was furthermore assumed that F_v was temperature independent. Using these assumptions a formation-enthalpy value of 0.63 ± 0.02 eV was obtained from the temperature region 20–435 °C. This value should most appropriately be compared with the 0.64 eV obtained from the lifetime data analyzed for the entire temperature region, and less so to $E_v^F = 0.66 \pm 0.02$ eV, the result obtained using only data below the strongly temperature-dependent region of the bulk lifetime.

VI. COMPARISON WITH OTHER DATA

The observation of a rapid change of the bulk lifetime in Al above 370 °C is not yet understood, nor has it been established whether or not this might be a general phenomenon in metals. Nevertheless, it is clear that this effect is too large to be explainable by a simple thermal expansion model. In recent papers the possibilities of a more complex temperature-dependent behavior of the positron in the lattice have been considered.[38-40] The possibility of positron self-trapping in the lattice, leading to an increased lifetime, recently put forward by Seeger[38] has been further investigated by Leung *et al.*,[39] who concluded that self-trapping was unlikely to take place. Hodges and Trinkaus[40] reached essentially the same conclusion as Leung *et al.*[39] except for the cases of Pb, Tl, and Al. It is interesting to note in relation to these theoretical investigations that the recent experimental results for Pb obtained by Sharma *et al.*[15] also indicate a temperature dependence of the bulk lifetime similar to that observed in the present work for Al; however, new data[41] from the same group has apparently resulted in reducing the effect or increasing the uncertainty regarding the magnitude of the effect reported earlier. It should be kept in mind that the observed $\tau_b(T)$ be-

TABLE II Tabulation of vacancy formation enthalpies for Al obtained by different investigators using positron annihilation. The experimental method (AC: angular correlation; DB: Doppler broadening; LT: lifetime) as well as the data treatment method are indicated. Assumptions made to obtain the results are also shown. The parameters listed under Assumptions were assumed either weakly temperature dependent or constant.

Experimental method	Data treatment	Assumptions	E_v^F (eV)	$\mu_v \exp(S_v^F/k)$ (10^{14} sec^{-1})	τ_b (20 °C) (psec)	τ_v (psec)	Reference
AC	DB	F_b, F_v, τ_b	0.66 ± 0.04	12	···	···	McKee *et al.* (1972)[a]
AC	DB	F_b, F_v, τ_b	0.66 ± 0.01	6 ± 3	···	···	Triftshäuser (1975)[b]
AC	DB	F_b, F_v, τ_b	0.67 ± 0.03	13 ± 7	···	···	Kim *et al.* (1974)[c]
LT	I_2/I_1	τ_b, τ_v	0.71	20	176	240	McKee *et al.* (1972)[d]
LT	$\bar{\tau}$	τ_b, τ_v	$\begin{matrix}0.68\\0.66\end{matrix} \pm 0.03$[g]	···	···	···	McKee[e]
LT	κ	τ_b, τ_v	0.62 ± 0.02	5 ± 2	161	243	Hall *et al.* (1974)[f]
LT (DB)	κ	τ_v	0.66 ± 0.02	8 ± 2	166	244	Present work
LT (DB)	κ	None	0.66 ± 0.09	···	166	244	Present work

[a] Reference 6.
[b] Reference 5.
[c] Reference 7.
[d] Reference 8.
[e] Reference 10.
[f] Reference 9.
[g] 0.66 eV was obtained assuming τ_v constant, while 0.68 eV was obtained assuming that τ_v and τ_b have the same temperature dependence.

havior, and its implications with respect to $\mu_v(T)$, may simply be a manifestation of the simple trapping model and the assumption of rapid positron thermalization in metals.

A summary of the vacancy formation enthalpies E_v^F obtained for Al by means of positron measurements are shown in Table II. For each value of E_v^F the respective experimental method, data treatment, and assumptions are indicated. In addition, the product of the specific trapping rate μ_v and the preexponential vacancy formation entropy factor $\exp(S_v^F/k)$ are tabulated along with deduced values of τ_b and τ_v. The high value of $E_v^F = 0.71$ eV obtained by McKee *et al.*[8] was probably due to the use of the I_2/I_1 method, and in fact Table I indicates that this treatment could lead to a systematic error of around +0.08 eV. Hall *et al.*[9] obtained a value of 0.62 eV by constraining both τ_b and τ_v to be temperature independent. Furthermore, an additional temperature-independent trapping rate was introduced to account for curvature in their Arrhenius plot. This latter assumption, however, apparently did not affect the value of their extracted formation enthalpy. The other values reported for E_v^F, obtained using the similar DB or $\bar{\tau}$ methods, appear to be in good agreement with the present results.

It is concluded from the data in Table II and the foregoing discussion that the most probable value for the vacancy formation enthalpy in Al as deduced from positron annihilation spectroscopy is $E_v^F = 0.66 \pm 0.02$ eV. This value, determined under equilibrium conditions, is in excellent agreement with the value of the monovacancy formation enthalpy, $E_{1v}^F = 0.66 \pm 0.01$ eV,[42] in Al obtained from quenching experiments from temperatures ≤ 400 °C, and is also consistent with equilibrium total vacancy concentration measurements at higher temperatures.[30,43] It can therefore be concluded that the value of E_v^F measured in the present work corresponds to the monovacancy formation enthalpy E_{1v}^F in Al.

In addition, one can obtain a value for the specific trapping rate of a positron at a monovacancy, $\mu_{1v} = (4 \pm 1) \times 10^{14}$ sec^{-1}, in Al below 372 °C by combining the value obtained for the product $\mu_v \exp(S_v^F/k) = (8 \pm 2) \times 10^{14}$ sec^{-1}, presented in Table II, with the value of the monovacancy formation entropy, $S_{1v}^F = 0.7k$, deduced[30] from equilibrium vacancy concentration and quenching data. This value for μ_{1v} is larger than the value of μ_v previously reported by Cotterill *et al.*[44] for Al ($\mu_v = 2.3 \times 10^{14}$ sec^{-1}), but their estimate of this parameter was based upon an assumption of $E_{1v}^F = 0.76$ eV, which in retrospect was incorrect. The present value for μ_{1v} in Al is similar in magnitude to that found[29] under high-temperature equilibrium conditions for Au.

VII. CONCLUSIONS

The present investigation of the temperature dependence of positron annihilation in aluminum, utilizing the two-state trapping model with the

assumption of negligibly short positron thermalization times, has led to the conclusion that a large and unexpected temperature dependence was present in one or more of the bulk and vacancy-trap positron annihilation parameters (τ_b, F_b, τ_v, F_v) irrespective of whether direct trapping or thermal detrapping of the positrons occurred. By assuming that no direct trapping took place, the temperature-dependent positron bulk lifetime $\tau_b(T)$ was extracted from the data. The $\tau_b(T)$ determined in this manner was found to increase rapidly toward the positron lifetime in a vacancy for temperatures greater than 370 °C. The present data do not indicate whether a saturationlike behavior of $\tau_b(T)$ can be expected for high temperatures, an important point that would help in the understanding of this effect. It should be pointed out, however, that it is not clear at this time whether the strong temperature dependence deduced for $\tau_b(T)$ and its ramifications with respect to $\mu_v(T)$ are in fact physically realistic, or whether the simple two-state trapping model and analysis with the assumption of rapid positron thermalization is simply an inadequate description of the physical situation. Further work is clearly needed to settle this question. While a similar effect has also been reported[15] for Pb using the same analytical model as that used here, it is important to the understanding of the behavior of positrons in metals to investigate whether or not this effect is found in other metals and how dependent the effect is upon the model used for the analysis of the PAS data. Measurements in Cu and Au are therefore in progress.

The monovacancy formation enthalpy in aluminum, $E_{1v}^F = 0.66 \pm 0.02$ eV, has been measured in the temperature range 250–372 °C by positron annihilation spectroscopy by incorporating the detailed temperature dependences of the positron annihilation parameters from lifetime data. It is concluded for the case of aluminum that neglecting the observed strong temperature dependence of τ_b in the commonly used positron analysis methods has only a minor effect upon the determination of the vacancy formation enthalpy.

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