

Thermal Expansion Effects in Positron Lifetimes* **

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Received 2 January 1974

Abstract. The precision of relative positron lifetime measurements is now sufficient to observe directly changes due to lattice thermal expansion. This information is necessary for the determination of accurate vacancy formation energies from positron annihilation data obtained over a higher temperature range. Measurements have been made of the change in positron lifetime in the metals Au, Ag, Cu, and Al over the temperature range 100–300 K where there is no contribution from positron trapping at vacancies. The results are compared with theoretical calculations which take account of positron annihilations with both valence and core electrons.

Index Headings: Positron lifetime – Positron annihilations

There is now considerable interest in the study of the temperature dependence of the positron annihilation rate in metals as a practical tool in the determination of the energy of formation of vacancies. It is well known that a positron which is trapped in a vacancy has a characteristic lifetime which is typically about 60 psec (or 30–50%) longer than that of a free positron. Consequently, the observed annihilation rate, which is the weighted average of the contributions from free and trapped positrons, decreases with increasing concentration of vacancies; this introduces the temperature dependent factor $\exp[-E_v/kT]$, where E_v is the energy of formation of vacancies [1, 2]. This exponential temperature dependence is the principal interest in metallurgical studies and it is, fortunately, the dominant effect. However there is, in addition, a temperature dependence in the lifetime of free (not trapped) positrons which arises as a result of the reduction in the electron density due to thermal expansion. Thermal expansion corrections are small, accounting for changes in lifetimes of only a few pico-seconds over temperature ranges of several hundred degrees, but they must be taken into account if values for E_v are

to be obtained to better than about $\pm 5\%$. In this paper we present preliminary results of measurements of the change in lifetime due to thermal expansion effects alone for the noble metals and aluminum, and we compare the results with what can be expected from theory.

Experimental Method

Samples were prepared from materials specified in Table 1. Following a preliminary surface etch, they were annealed for 12 h at a temperature about 100 degrees below the melting point and then very slowly cooled to room temperature. The samples were etched once again and assembled into a "sandwich" configuration which consisted of two wafers of the specimen enclosing a thin nickel foil on which was deposited the positron source (Na^{22} in

Table 1

Sample	Nominal purity (%)	Supplier
Gold	99.99	Johnson and Matthey (Toronto)
Silver	99.95	A. D. McKay (New York)
Copper	99.999	A. D. McKay (New York)
Aluminum	99.999	Alfa Materials (Beverly, Mass.)

* Supported by the National Research Council of Canada.

** Paper B 2 presented at 3rd Internat. Conf. Positron Annihilation, Otaniemi, Finland (August 1973).

Table 2. Comparison of theoretical and experimental values of the expansion dependent lifetime coefficient γ

Sample	Free lifetime τ_1 [psec]	$\Delta\tau_1$ [psec] between 100–300 K	Experimental γ	Theoretical		Total γ (calculated) ^a			
				γ_c from [8]	γ_v from [7]	A_c from lifetime	γ	A_c^* from angular correlation	γ^*
Gold	140	2.2 ± 0.3	6.0 ± 1.0	6.8	1.1	0.56	4.3 ± 0.6	0.70	5.1 ± 0.8
Silver	150	1.6 ± 0.8	3.0 ± 1.5	6.1	1.1	0.52	3.7 ± 0.6	0.65	4.4 ± 0.7
Copper	134	1.3 ± 0.5	3.2 ± 1.2	5.6	1.4	0.51	3.6 ± 0.5	0.60	3.9 ± 0.6
Aluminum	172	3.0 ± 0.5	4.4 ± 0.8	5.8	2.1	0.11	2.5 ± 0.4	0.15	2.7 ± 0.4

^a The total γ was calculated twice using (5). One value was obtained using the core fraction A_c determined from lifetime data. The use of the core fraction A_c^* from angular correlation studies, leads to the second estimate γ^*

NaCl). They were mounted in a chamber which could be evacuated during the course of the run. We were able to do lifetime measurements within the temperature range 100–450 K, however, most measurements concentrated on the temperature range 100–300 K — i.e. sample temperatures were kept well below the range in which vacancy effects become important [3, 4]. Lifetime spectra for each temperature were fitted using standard maximum likelihood techniques to a two component decay function convoluted with the resolution of the apparatus. Listed in Table 2 are average values of the shorter lifetimes τ_1 at room temperature, together with the average change in lifetime, $\Delta\tau_1$, over the temperature range 100–300 K. The longer lifetimes τ_2 are believed to arise as a result of annihilations at surfaces and in the radioactive source and these are not listed individually. Typically, $\tau_2 \simeq 430$ –490 psec and had a relative intensity of about 4%.

We assume that $\Delta\tau_1$ is a function solely of the change in the linear dimension of the sample, Δl . Both changes being small, it is further assumed that

$$\frac{\Delta\tau_1}{\tau_1} = \frac{-\Delta\lambda_1}{\lambda_1} \propto \frac{\Delta l}{l}, \quad (1)$$

where $\lambda_1 (= 1/\tau_1)$ is the annihilation rate. In order to make a comparison of the results for the different samples which is independent of their coefficients of thermal expansion, we define a dimensionless positive parameter

$$\gamma \equiv \frac{-\Delta\lambda_1}{\lambda_1} \bigg/ \frac{\Delta l}{l}. \quad (2)$$

We note as an intuitive guide, that for a free electron gas in the absence of enhancement effects $\lambda_1 \propto l^{-3}$ and therefore $\gamma = 3$. Thermal expansion data from

various sources [5, 6] were used in calculating the values of γ which are listed in Table 2.

Comparison with Theory

To simplify the analysis, it is convenient to divide γ into two parts, i.e.

$$\gamma_v \equiv \frac{-\Delta\lambda_v}{\lambda_v} \bigg/ \frac{\Delta l}{l}, \quad (3)$$

where λ_v is the annihilation rate with valence electrons, and γ_v is a measure of the change in that rate; and a similar relation for core electrons

$$\gamma_c \equiv \frac{-\Delta\lambda_c}{\lambda_c} \bigg/ \frac{\Delta l}{l}. \quad (4)$$

The fraction of positrons annihilating with core electrons and with valence electrons are, respectively, $A_c = \lambda_c/\lambda_1$ and $A_v = \lambda_v/\lambda_1$, λ_1 being the measured annihilation rate. It readily follows that

$$\gamma = A_v\gamma_v + A_c\gamma_c. \quad (5)$$

We have determined some of these parameters from the theoretical work of Bhattacharyya and Singwi [7] which describes the annihilation rate of a positron in an electron gas taking into account enhancement effects. Their results are partially reproduced in Fig. 1. Our procedure is to plot the measured rate λ_1 as shown for example in the figure; this point lies above the theoretical curve by an amount equal to the core annihilation rate λ_c . From λ_c and λ_v we thus obtain both A_c and A_v . The figure also yields γ_v from

$$\gamma_v = \frac{-\partial\lambda_v}{\partial r_s} \cdot \frac{r_s}{\lambda_v} \quad (6)$$

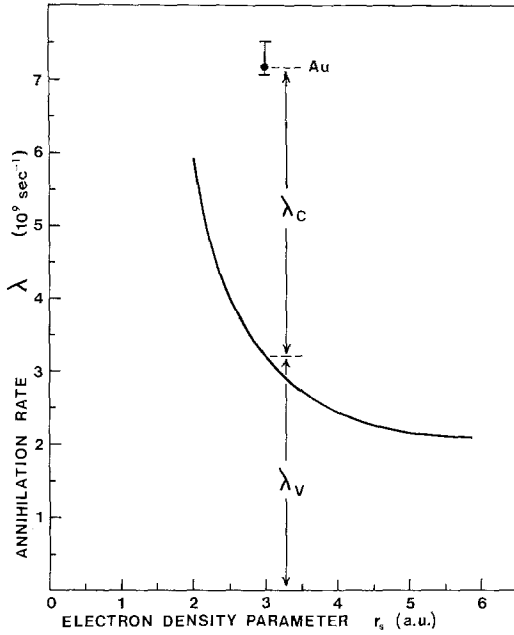


Fig. 1. The curve shows the theoretical positron annihilation rate for an electron gas, λ_v , as a function of the electron density parameter r_s (from Bhattacharyya and Singwi [7]). The method used to assign the core rate λ_c and the valence rate λ_v is illustrated for the case of gold

which is equivalent to (3). We previously noted that $\gamma_v = 3$ for the case of a non-interacting positron. However, an interacting positron is surrounded by a polarization cloud which is less sensitive to the electron density in the metal, resulting in values of γ_v ranging from 2.1 for aluminum to 1.1 for gold, as shown in Table 2.

The core annihilation rate γ_c was computed using the pseudo-potential method of Stott and Kubica [8]. The technique is, essentially, to calculate the positron wave functions of proper symmetry for each metal, at room temperature. The important parameters are the crystal structure (f.c.c.), the lattice parameter a and the core electron distribution (Herman and Skillman [9]). The positron-core electron overlap integral I was calculated leading, in principle, to the core annihilation rate [10]

$$\lambda_c = 5.0 \times 10^{10} \varepsilon_c I \text{ sec}^{-1} \quad (7)$$

where ε_c is the core enhancement rate. This procedure was repeated using a lattice parameter, $a - \Delta a$, appropriate for 100 K leading to a new overlap integral $I + \Delta I$. It follows that the core contribu-

tion to γ is given by

$$\gamma_c = \frac{\Delta I}{I} \frac{\Delta a}{a}. \quad (8)$$

It is assumed in the above that the core electron distribution is not a function of the lattice spacing — i.e. thermal expansion simply increases the separation between neighbouring core distributions. It follows in this approximation that the core enhancement factor does not change and that γ_c is not a function of ε_c . Calculated values of γ_c are listed in Table 2. In view of the wide variation in A_c , the small variation in values of γ_c for the metals which we have studied is perhaps surprising. This effect can be understood once it is realized that the radial dependence of the positron wave function near the nuclei is almost the same for all the metals; it is only the amplitude that shows strong variations.

Theoretical and experimental values for γ are listed for comparison in Table 2. We believe that our theoretical values may be subject to some systematic error because of the method used to determine A_c . It can be argued that the total measured annihilation rates are likely to be low because of unresolved components with longer lifetimes, and this will lead to values of A_c which are low. On the other hand, core fractions estimated from angular correlation studies are likely to be high since higher momentum components of valence electrons will contribute to the wings of the observed distribution. We have also listed in Table 2 provisional values for the core fraction A_c^* as estimated from our angular correlation studies, and we derive from that a revised theoretical value for γ (labelled γ^* in Table 2).

Discussion

Table 2 shows that for the noble metals there is adequate agreement between observed and calculated values of γ . On the other hand, for aluminum the agreement is poor. The contrast in these results is surprising.

In the case of the noble metals, it is the core annihilation rate which is dominant. Our description of this effect makes use of a core of rigid atomic d -electrons. This is possibly valid for copper, but is certainly less realistic for gold. The most obvious refinements in the core model may very well lead to poorer agreement with experiment.

In the case of aluminum, where the major expansion effect is determined by the valence electrons, our calculations rely primarily on the theory of Bhattacharyya and Singwi [7] which has been shown to be reliable in determining the absolute annihilation rates. The value of 2.1 for γ_v was determined using the slope of the $\lambda(r_s)$ function, which introduces a possible source of error. It was argued earlier, however, that γ_v cannot be greater than 3.0 and even then the total theoretical γ would be only about 3.4, which is still somewhat lower than the experimental value, 4.4 ± 0.8 .

In conclusion, we have obtained approximate agreement between calculated and observed effects of lattice expansion on the positron annihilation rate. Detailed agreement has not been achieved and further work is required. It should be noted that in order to obtain precise values of vacancy formation energies, it will also be necessary to understand how lattice expansion affects the annihilation rate of a positron trapped in a vacancy. For a trapped posi-

tron, γ can be expected to be relatively more dependent on valence electron contributions.

Acknowledgement. It is a pleasure to acknowledge assistance and helpful discussions with P. Kubica and M. J. Stott.

References

1. M. Doyama, R. R. Hasiguti: *Crystal Latt. Defects* **4**, 139 (1973)
2. A. Seeger: *J. Phys. F.* **3**, 248 (1973)
3. J. D. McGervey, W. Trifthäuser: *Phys. Letters* **44 A**, 53 (1973)
4. B. T. A. McKee, H. C. Jamieson, A. T. Stewart: *Phys. Rev. Letters* **31**, 634 (1973)
5. D. B. Fraser, A. C. Hollis Hallett: (a) *Canad. J. Phys.* **43**, 193 (1965); (b) *Proc. 7th Intern. Conf. Low Temp. Physics*, Toronto, Ont. (University of Toronto Press), p. 689
6. *Handbook of Tables for applied engineering science*. (The Chemical Rubber Co. 1970), p. 201
7. P. Bhattacharyya, K. S. Singwi: *Phys. Rev. Letters* **29**, 22 (1972)
8. M. J. Stott, P. Kubica: To be published
9. F. Herman, S. Skillman: *Atomic Structure Calculations*. (Prentice-Hall Inc. New York 1963)
10. R. A. Ferrell: *Rev. Mod. Phys.* **28**, 308 (1956)