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Positron Lifetimes and Annihilation Lineshape in Cd and Au from 4.2 K to the Melting Points

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Abstract. By means of an integrated source-specimen technique the temperature dependence of positron lifetimes and annihilation lineshapes has been measured on the same specimens of gold and cadmium from 4.2 K to the melting points, and also in electron-irradiated and quenched gold. The anomalous temperature dependence of positron annihilation at intermediate temperatures (200 to 350 K in Cd, 270 to 750 K in Au) discovered by Lichtenberger, Schulte, and MacKenzie is confirmed.
The data are incompatible with the idea that the intermediate temperature dependence is due to thermal expansion. They are well explained by an extension of the trapping model which includes the formation of metastable self-trapped positrons.
From lineshape measurements after electron irradiation at 180 K and after quenching it is deduced that the trapping rate of positrons at vacancy-type defects in Au is temperature independent below room temperature.

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Recent measurements of the Doppler broadening of the positron annihilation line in Cd and several other metals down to 100 K by Lichtenberger et al. [1, 2] have revealed a temperature dependence intermediate between that observed at high temperatures, generally attributed to positron trapping by vacancies in thermal equilibrium, and the much weaker temperature variation at low temperatures. Lichtenberger et al. [1] pointed out that the low-temperature data indicated a rather small effect of ordinary thermal expansion on the shape of the positron annihilation line and suggested that the intermediate temperature dependence might be due to "phonon-assisted trapping of positrons". One of the present authors [3] showed that the formation of *metastable* self-trapped positrons (somewhat analogous to "small polarons" in ionic crystals) could explain the observed temperature dependence.

Triftshäuser and McGervey [4, 5] reported a rather strong temperature dependence of the peak counting rate in the "sub-vacancy" region of the angular correlation curve of Cu, Ag, and Au and attributed it to thermal expansion. Quite apart from the interesting question whether self-trapping of positrons in metals is possible or not, or whether the effects of thermal expansion on positron annihilation can be as large as supposed by Triftshäuser and McGervey [4, 5] and also by other authors [6, 7], the correct interpretation of the intermediate temperature dependence is very important for the analysis of positron

trapping by vancancies. This has led us to measure both lifetimes and Doppler broadening in cadmium and gold from the temperature of liquid He up to the melting points. The results confirm qualitatively the low-temperature behaviour reported by Lichtenberger and show clearly that the effects of thermal expansion on positron annihilation are too small to account for the observed intermediate temperature variation. The experimental results are analysed in terms of an extension of the trapping model which includes the effects of metastable self-trapping [3, 8]. It is shown that in the determination of the mono-vacancy formation energy of Au by positron annihilation divacancy and detrapping effects may be neglected but that it is important to include the temperature variation of the annihilation parameters of the *trapped* positrons in addition to the self-trapping effects.

1. Experiment

The experiments were carried out on well annealed samples of 99.9999% purity Cd and 99.999% purity Au. The technique of preparation of sealed specimens allowing measurements in thermal equilibrium up to temperatures close to the melting point and exhibiting extremely low source contributions is described elsewhere [9]. Positron sources of approximately 10 μCi ^{22}Na were used, which permitted to measure both lifetimes and annihilation lineshapes on the *same* samples.

Positron lifetimes were measured with a conventional fast-slow coincidence system as described by Crisp et al. [10]. The constant-fraction discriminators were adjusted such as to yield a symmetric spectrum, upon which worked a digital stabilizer in order to improve gain stability. The lifetime spectra were obtained by routing part of the events into another memory group of the multichannel analyser by means of 1.28 MeV–511 keV coincidences. Mean lifetimes were computed from the differences in the centroids of the symmetric and routed spectra after appropriate background subtraction. Time calibration was performed by measuring two prompt spectra from two ^{60}Co sources at a distance of 30 cm from each other. The fact that the use of ^{60}Co with energies 1.17 MeV and 1.33 MeV (instead of the correct energies 1.27 MeV and 0.511 MeV when measuring with ^{22}Na) did not yield an absolute time calibration was of minor importance since in the present work we were interested in relative changes of the lifetimes only. A better calibration may be obtained by using the annihilation quanta from a ^{68}Ge source.

The shape of the annihilation line (*Doppler broadening*) was measured with a digitally stabilized high-resolution Ge(Li) detector. Additional improvement in stability was achieved by avoiding a biased amplifier by using a fast 8 k ADC (LABEN mod. 8215) and purely digital zero suppression. The resolution (FWHM) at 10000 counts per second was 1.24 keV at the 514 keV gamma line of ^{85}Sr. Simultaneously with the annihilation radiation, the 497 keV nuclear gamma ray of ^{103}Ru was measured in order to monitor the resolution of the system during the experiments. In the case of Cd, this line was used to deconvolute the measured spectra numerically and model independently with respect to energy resolution. For the computer program performing the deconvolution, van Cittert's [11] iterative method of unfolding was modified to improve convergence speed and avoid amplification of noise [12]. The lineshape is characterized by a "wing" parameter W defined as the ratio of the number of counts in the regions $|\Delta E_\gamma| > 0.5\, p_F \cdot c$ (ΔE_γ is the deviation of the energy of the annihilation quantum from 511 keV, p_F the Fermi momentum, and c the velocity of light) and of the total number of counts in the annihilation line. This parameter is particularly sensitive to changes in the probability P_c that the positron annihilates with *core electrons*. By fitting the sum of a Gaussian plus an inverted parabola to a deconvoluted spectrum and comparing W with the intensity I_G of the Gaussian component we estimated that our definition of W in the Cd experiments corresponds to $W \approx 0.2 I_G$. I_G was estimated as 0.59 at 100 K. In discussions of the physical significance of W, e.g. when comparing the temperature dependence of W at low temperatures with thermal expansion data (Subsect. 3.1a) it must be kept in mind that in Cd and Au annihilations with valence electrons (in addition to conduction electrons) contribute significantly to W.

2. Results

Figures 1 and 2 show the temperature dependence of the annihilation parameters of gold and cadmium. All curves clearly display a marked change in temperature dependence well below the onset of significant vacancy trapping. In Cd the effect is less pronounced than reported by Lichtenberger et al. [1], and a small temperature dependence persists down to ~100 K. This was also found in recent angular correlation measurements by Kim and Buyers [13]. Their *peak counting rates* measured from 100 K to 450 K agree

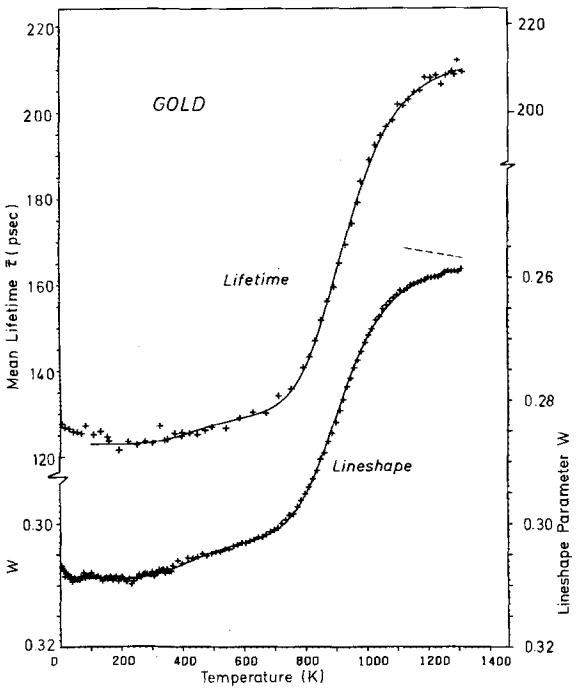

Fig. 1. Mean lifetimes and annihilation line shape parameters in 99.999% *gold* in thermal equilibrium measured in a sealed-source specimen [9]. Solid curves: trapping model including metastable self-trapping (300 K to 700 K). Effects of thermal expansion are negligible (50 K to 300 K). Dashed line: temperature dependence of the *W* parameter for positrons trapped at vacancies

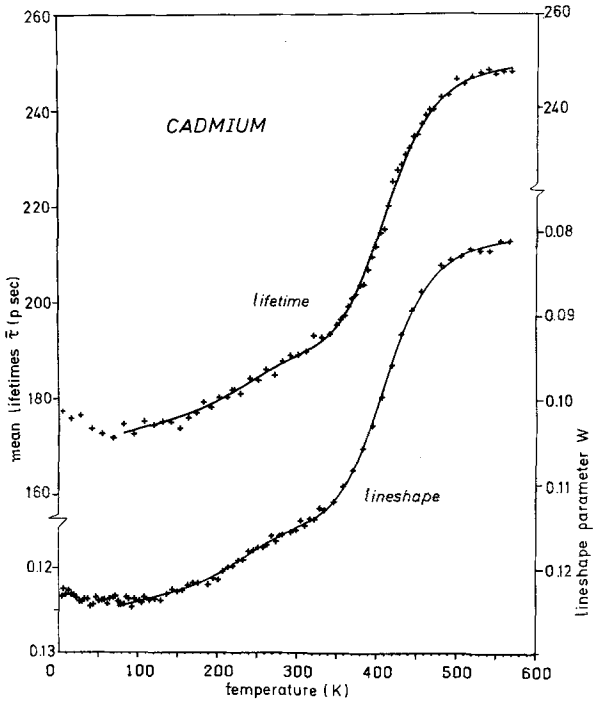

Fig. 2. Mean lifetimes and annihilation line shape parameters from deconvoluted spectra in 99.9999% *cadmium* in thermal equilibrium measured on a sealed-source specimen [9]. Solid curves: trapping model including thermal expansion effects visible in the region 100 K to 200 K and metastable self-trapping (200 K to 350 K). The sharp increase of the curves at 350 K is attributed to vacancy trapping

perfectly with a *lineshape parameter* derived from our data by summing over the *low momentum* region of the deconvoluted annihilation line. The difference between our lineshape measurements and those of Lichtenberger et al. [1] may partly result from deconvolution and partly be due to the comparatively small number of data points between 100 K and 250 K in the earlier measurements [1]. We also find good agreement between *lifetimes* and lineshape parameters derived from deconvoluted Ge(Li) spectra, in contrast to previously reported discrepancies between lifetimes [14] and Doppler-broadening [1] or angular correlation data [4, 5, 7].

At temperatures below about 50 K a small but significant change in the annihilation parameters is observed (narrowing of the photon line, increase in lifetime). This low-temperature effect is also present in quenched gold but not in electron-irradiated gold, as may be seen from Fig. 3. Here the temperature dependence of the *W*-parameter of gold is shown for three runs: after electron irradiation[1] with a dose of 2×10^{17} electrons/cm^2 (2.8 MeV) at 180 K, after quenching from 1010 K, and after a faster quench from 1120 K. On the basis of the experimental evidence available at present we suggest that during the slowing-down process positrons travelling in crystallographic directions [15] can preferentially leave the sample (which, after annealing, consisted of large grains) and annihilate in the He gas surrounding the sample, on the walls of the cyrostat, or on the specimen surface. The absence of the low-temperature effect after electron irradiation is explained by the blocking of the crystallographic channels by interstitial atoms. The preceding explanation would work irrespectively whether the positrons may be described as "classical" particles channeled in wells of low potential energy or whether the description of the positron motion in terms of two Bloch waves (one with nodes at the atomic sites, transmitted anomalously in a crystal without interstitial atoms, and the other one with maximum intensity at the atomic sites and scattered anomalously)[2].

[1] Performed at the DYNAMITRON of the "Institut für Strahlenphysik der Universität Stuttgart".

[2] For a review of the literature on the subject see [15].

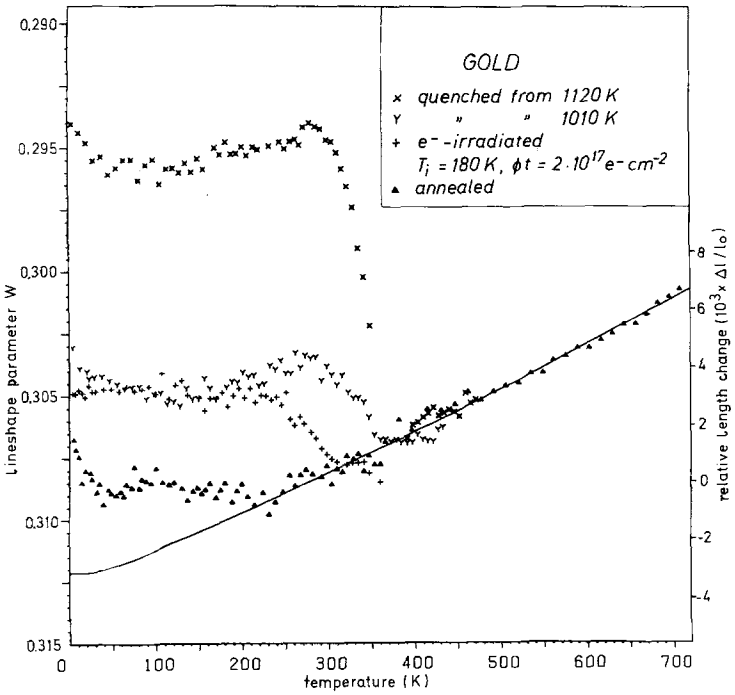

Fig. 3. Temperature dependence of the W parameter in *gold* after irradiation at 180 K with 2.8 MeV electrons to a dose of 2×10^{17} electrons/cm^2 and after quenching from 1010 K and 1120 K. All measurements were performed on the same sample. Solid line: relative length change of gold [16] on a scale to coincide with W in the temperature range 270 K to 700 K (see Subsec. 3.1)

We hope to clarify the nature of the low-temperature variation of the annihilation parameters by further experiments.

3. Data Analysis and Discussion

3.1. Annealed Specimens

The data obtained from measurements in thermal equilibrium are shown in Figs. 1 and 2. The curves may be separated into a *low-temperature part, the intermediate-slope regime* (in Au between 270 K and about 750 K, in Cd between 200 K and about 350 K), and the *high-temperature "S"*, which is attributed to positron trapping by vacancies in thermal equilibrium We shall discuss these three temperature regimes in turn.

a) Low Temperatures. The transition between the low-temperature regime and the intermediate temperature regime is marked by the sharp change in the annihilation parameters occurring at about 270 K (Au) or 200 K (Cd). Neither in Au nor in Cd may this change be attributed to thermal expansion, since the observed transition temperatures lie well above $\theta_D/4$ (θ_D:Debye temperature). Above $\theta_D/4$ the thermal expansion of both metals changes only very gradually with temperature [16–18].

In Au the line-shape measurements below about 270 K do not show any temperature variation that could be associated with thermal expansion, whereas in Cd a small residual temperature dependence remains below 200 K. The different behaviour of Cd and Au has presumably to do with the strong anisotropy of the thermal expansion of Cd. In Au the lattice parameter is essentially determined by the Born-Mayer repulsion of the ion cores, whose thermal movement is mainly responsible for thermal expansion. In thermally expanded crystals conduction and core electrons fill the unit cell in much the same way as at 4 K (apart from a general dilation), so that no significant effect on the shape of the annihilation line may be expected[3]. The situation is clearly different in the case of Cd. At absolute zero the c/a-ratio is 14% larger than the ideal value 1.633 associated with hexagonal close packing of spheres, so that the c lattice parameter cannot be mainly controlled by core-core repulsions but must be determined by the band structure of the conduction electrons. Therefore, the further increase of the c/a-ratio with temperature up to 530 K [17, 18]

[3] In the temperature range in question the de-Broglie wavelength of thermalized positrons is large compared with the dominant wavelength of the lattice vibrations, so that in spite of their small mass, non-localized positrons are unable to follow the fluctuations in the positions of the individual ion cores.

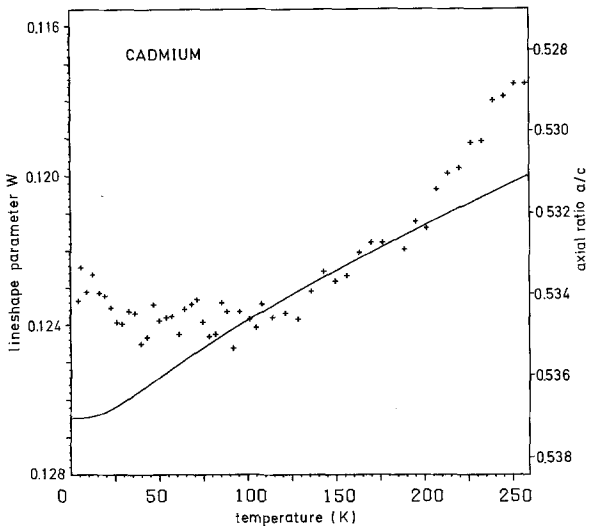

Fig. 4. Comparison of the temperature variation of the W parameter in cadmium with the relative change in a/c (solid line) at low temperatures

(Fig. 4) indicates a *gradual* change in the electronic structure which may well be accompanied by a change in the positron annihilation parameters. We emphasize, however, that no abrupt change occurs near 200 K, so that associating the temperature variation of the W-parameter below 200 K with the temperature variation of the c/a-ratio excludes the same explanation for the "intermediate temperature effect".

Figure 4 shows that in the temperature interval 100 K to 200 K the temperature variation of the W parameter of Cd is proportional to c/a, i.e.

$$d \ln W/dT \cong 4.5 d \ln (a/c)/dT. \tag{1}$$

The proportionality factor of 4.5 appears too high to be compatible with the idea that the Gaussian component of the line-shape is entirely due to annihilations with core electrons. Equation (1) is in qualitative agreement, however, with the idea that high-momentum components of the valence electrons contribute to the wings of the Gaussian (comp. Sec. 1).

b) Intermediate Temperatures. An analysis analogous to the Cd analysis of Subsec. a) is not possible for the Au low-temperature data, since there is no detectable variation of W at temperatures at which thermal expansion is already quite pronounced. In order to demonstrate how strongly the thermal expansion of Au deviates from the temperature dependence of the W-parameter in the temperature range 50 K to 700 K we have included in Fig. 3 the thermal expansion data of Nix and McNair [16] on such a scale that the two curves approximately coincide between 270 K and 700 K. From what has been said above it should be clear that this coincidence is without physical significance since it does not hold below 270 K, and that thermal expansion effects cannot be detected in our Au data.

Having shown that a thermal-expansion explanation of the intermediate slope is not possible, we attribute it to metastable positron self-trapping [3]. This interpretation is supported by recent angular correlation measurements on Cd of Kim and Buyers [13] who found that the temperature variation of the angular correlation curve shows the smearing near the Fermi momentum that is expected if positron localization takes place in the "sub-vacancy region".

In the presence of metastable self-trapped positrons (subscript st) the trapping model has to be generalized by replacing "free positrons" (subscript f) by "non-trapped" positrons (subscript nt). For any parameter F depending linearly on the positron annihilation rates we have

$$F_{nt} = \frac{\tau_{st} f_f F_f + \tau_f f_{st} F_{st}}{\tau_{st} f_f + \tau_f f_{st}}, \tag{2}$$

where τ_f and τ_{st} denote the positron lifetimes in the free and self-trapped states, respectively, and

$$f_f = 1 - f_{st} = [1 + A T^{-3/2} \exp(-\varepsilon_0/k_B T)]^{-1} \tag{3a}$$

the fraction of free positrons [3]. In (3a) we have used the abbreviation

$$A = \frac{1}{V_a} \prod_j \frac{\nu_j}{\nu_j} \left(\frac{2\pi\hbar^2}{m_+ k_B}\right)^{3/2}, \tag{3b}$$

where ν_j, ν_j' are the vibrational frequencies of the crystal with free or self-trapped positrons. ε_0 denotes the energy of the self-trapped state, measured from the lowest state of the quasi-continuum of positron Bloch states, m_+ the effective mass of the positrons, V_A the atomic volume, and k_B Boltzmann's constant.

Allowance for metastable self-trapping introduces at least three parameters, namely ε_0, A, and F_{st}. We found that attempts to obtain all the parameters describing self-trapping, vacancy trapping and possibly thermal expansion simultaneously by least-square fits to the experimental data lead to numerical instabilities. We therefore adopted the approximate procedure of first fitting the intermediate temperature regime to (2), and of using the result so obtained for deducing vacancy parameters (see Subsec. c). If desired, one may

repeat this procedure in order to improve the fit by iteration.

The parameters describing the self-trapped state are listed in Table 1. Estimates of the quantity $\Pi(v_j/v_j')$ from (3) with $m_+ = m_0$ give 3×10^{-2} to 4×10^{-2} for Au and 10^{-1} to 2×10^{-1} for Cd. These results are in qualitative agreement with the expectation that the localization of the positron leads to an increase of the lattice vibration frequencies.

c) High Temperature. When attempting to fit the trapping model to the high temperature S-curve, we have first to decide whether it suffices to consider one type of trap or whether two or more types of traps should be included (in physical terms: whether we should consider divacancies in addition to monovacancies). Numerous trials showed that by including a second trap with $|F_{2V}-F_f|>|F_{1V}-F_f|$ a significant improvement of the fit cannot be achieved. We shall therefore restrict ourselves to one type of trap and use the trapping model in the form

$$\frac{dn_{nt}}{dt} = -\sigma C n_{nt} + v_t n_t - \frac{n_{nt}}{\tau_{nt}} \tag{4a}$$

$$\frac{dn_t}{dt} = \sigma C n_{nt} - \left(v_t + \frac{1}{\tau_t}\right) n_t . \tag{4b}$$

Here n_{nt} and n_t denote the numbers of non-trapped or trapped positrons in an ensemble. The trap concentration is denoted by C, the trapping rate per unit concentration by σ. Following Frank and Seeger [19] we have included the possibility of detrapping, characterized by the escape frequency v_t. The annihilation rate of non-trapped positrons is, according to (2), given by

$$\frac{1}{\tau_{nt}} = \frac{f_f}{\tau_f} + \frac{f_{st}}{\tau_{st}} . \tag{5}$$

Table 1. Self-trapping parameters deduced from the intermediate temperature regimes in Au and Cd

	Gold		Cadmium[a]	
	Lifetimes	W parameter	Lifetimes	W parameter
ε_0 [eV]	0.22	0.22	0.17	0.17
A [K$^{3/2}$]	3.7×10^6	6.9×10^6	1.2×10^6	1.6×10^6
$\frac{F_{st}-F_f}{F_t-F_f}$[b]	0.13	0.19	0.31	0.30

[a] The analysis of the Cd data allows for the small temperature dependence of τ_f and W_f due to the anisotropic thermal expansion discussed in Subsec. 3.1a (see Fig. 4).

[b] F_f at 4.2 K, F_t at the melting point.

The trapping rate is written as [19, 20]

$$\sigma(t) \approx \sigma^\infty = \frac{4\pi r_0}{V_A}\left(\frac{1}{D_{nt}} + \frac{1}{k r_0 \Delta r_0}\right)^{-1} , \tag{6}$$

where r_0 denotes the capture radius, and $kr_0\Delta r_0$ the capture rate of the traps. For the effective diffusion coefficient of the non-trapped positrons we write [8]

$$D_{nt} = D_f f_f + D_{st} f_{st} . \tag{7}$$

The temperature dependences of D_f and D_{st} will be discussed later.

The solution of (4) may either be obtained directly or as a special case of the general solutions derived earlier [20]. The average value of a parameter F depending linearly on the positron annihilation rates is given by

$$F = \frac{\int_0^\infty \left[\frac{F_{nt}}{\tau_{nt}} n_{nt}(t) + \frac{F_t}{\tau_t} n_t(t)\right] dt}{n_{nt}(0) + n_t(0)} \tag{8}$$

or, in the notations of [20]

$$F = \frac{\frac{F_{nt}}{\tau_{nt}}\left(\frac{A_0^0}{\lambda^{(0)}} + \frac{A_0^1}{\lambda^{(1)}}\right) + \frac{F_t}{\tau_t}\left(\frac{A_1^0}{\lambda^{(0)}} + \frac{A_1^1}{\lambda^{(1)}}\right)}{n_{nt}(0) + n_t(0)} . \tag{9}$$

Here the following abbreviations have been used

$$\lambda^{(0,1)} = \tau_0^{-1} - \kappa \pm (\kappa^2 + v_t\sigma C)^{1/2}$$

$$A_0^{(0,1)} = \frac{n_f(0)\,[\kappa \pm (\kappa^2 + v_t\sigma C)^{1/2}] + v_t n_t(0)}{\kappa \pm (\kappa^2 + v_t\sigma C)^{1/2} + \frac{v_t\sigma C}{\kappa \pm (\kappa^2 + v_t\sigma C)^{1/2}}}$$

$$A_1^{(0,1)} = -\frac{\sigma C_1}{\kappa \pm (\kappa^2 + v_t\sigma C_1)^{1/2}} A_0^{(0,1)}$$

$$\tau_0^{-1} = \tau_{nt}^{-1} + \sigma C$$

$$\kappa = \tfrac{1}{2}(\tau_0^{-1} - \tau_t^{-1} - v_t) = \tfrac{1}{2}(\tau_{nt}^{-1} - \tau_t^{-1} + \sigma C - v_t) .$$

When initial trapping of positrons is negligible, i.e. $n_t(0)=0$ (9) reduces to

$$F = \frac{\lambda_{nt} F_{nt} + \sigma C F_t/(1+v_t\tau_t)}{\lambda_{nt} + \sigma C/(1+v_t\tau_t)} , \tag{10}$$

where $\lambda_{nt} \equiv 1/\tau_{nt}$ denotes the annihilation rate of non-trapped positrons given by (5). Equation (10) is a generalization of the expression for the mean lifetime reported earlier by Goland and Hall [21].

Let us next discuss the temperature dependence of the trapping rate σ^∞ in the presence of metastable self-trapping. We expect the diffusion of the free positrons to be limited by the scattering by accoustic phonons [8], i.e.

$$D_f = D_{ph} = \frac{(2\pi)^{1/2}\hbar^4 Y}{m_+^{5/2}\varepsilon_d^{5/2}} \cdot \frac{1-\mu}{(1-2\mu)(1+\mu)} \cdot (k_B T)^{-1/2} . \tag{11}$$

Here Y denotes Young's modulus, μ Poisson's ratio, and ε_d the positron deformation potential constant. For self-trapped positrons quantum diffusion has to be considered. According to Flynn and Stoneham [22] we may expect

$$D_{st} = \text{const.}\, T^{-1/2} \cdot \exp(-H_{st}^M/k_B T), \tag{12}$$

where H_{st}^M is the energy barrier for the hopping of the self-trapped positron from one interstitial site to an adjacent one. In order to reduce the number of parameters for the fitting we consider only two limiting cases:

(i) Fast Diffusion. In this case we have $D_+ \gg k_0 r_0 \Delta r_0$. The trapping rate is entirely controlled by the quantum mechanical capture process and therefore essentially temperature independent

$$\sigma^\infty = \frac{4\pi k r_0^2 \Delta r_0}{V_A}. \tag{13}$$

(ii) Fast Capture ($D_f \ll k_0 r_0 \Delta r_0$). Now the trapping rate is limited by the diffusion of non-trapped positrons

$$\sigma^\infty = \frac{4\pi r_0}{V_A} D_{nt} = \frac{4\pi r_0}{V_A}(f_f D_f + f_{st} D_{st}). \tag{14a}$$

In (14a) we may further neglect the term $f_{st} D_{st}$ since the diffusion of a free positron is believed to be much faster than the hopping of a self-trapped one. In the high temperature regime ("S"-curve) f_f varies very slowly with temperature, so we may approximate (14a) by

$$\sigma \cong \text{const} \cdot T^{-1/2}. \tag{14b}$$

We have based our analysis of the Au data in terms of (10) on the two limiting cases discussed above. The concentration of traps was written in the form

$$C = C_{1V}^{eq} = \exp(S_{1V}^F/k_B) \exp(-H_{1V}^F/k_B T) \tag{15}$$

with temperature independent enthalpy H_{1V}^F and entropy S_{1V}^F of monovacancy formation.

When varying the energy barrier for detrapping, the best fit was found for $\nu_t \equiv 0$. This appears to indicate that in Au detrapping is negligible, in agreement with the preliminary conclusions of Goland and Hall [21]. By contrast, the introduction of a temperature variation of W_t led to a significant improvement of the quality of the least-squares fit. When a linear temperature dependence of W_t was admitted, the best fit resulted from the choice

$$\frac{1}{W_t(1336\ \text{K})} \cdot \frac{dW_t}{dT} = 4 \times 10^{-5}\ \text{K}^{-1} \tag{16}$$

(dashed line in Fig. 1).

Table 2. Vacancy formation parameters in Au deduced for the two limiting cases for the temperature dependence of the trapping rate

Parameter	Doppler broadening	
	$\sigma = \text{const}$	$\sigma \sim T^{-1/2}$
H_{1V}^F [eV]	0.88	0.92
$\sigma\tau_f \exp(S_{1V}^F/k_B)$	10×10^4	7×10^{4a}

[a] at the melting point.

The goodness of the final fit did not depend on whether σ was chosen as temperature independent or proportional to $T^{-1/2}$. The results obtained from the Doppler broadening measurements of Au are listed in Table 2.

The sign of (16) indicates that with increasing temperature the neighbouring ion cores penetrate into a vacancy the more the higher the temperature, at least compared with the interatomic distance at the same temperature. This is in fact what one would expect on physical grounds, since the anharmonicity of the potential felt by the neighbours of a vacant lattice site is such that with increasing temperature their average position will move towards the centre of the vacancy, resulting in a stronger overlap of the core wave-functions with the wave-function of positrons trapped at vacancies.

Inspite of the high statistical accuracy of the Doppler broadening data on Au the choice between the two enthalpies of monovacancy formation can at present not be made on the basis of positron annihilation data alone. Because of the occurrence of metastable self-trapping the results on the temperature dependence of σ to be obtained in Subsec. 3.2 cannot be extrapolated to high temperatures. The comparison with other experimental results (both quenching and high-temperature equilibrium measurements) [23] indicates that $H_{1V}^F = 0.92$ eV is the better value of the two. If a small divacancy contribution to the total vacancy contribution near the melting point is allowed for [23], it leads to $S_{1V}^F/k = 0.6$. By contrast, a monovacancy formation energy $H_{1V}^F = 0.88$ eV would have to be associated with a formation entropy that may be too small to be acceptable.

The main interest of the present work on Cd lay in the measurements at low and intermediate temperatures in order to study the effects of self-trapping and anisotropic thermal expansion. The vacancy "S" was

measured with much poorer statistical accuracy. We refrain, therefore, for the time being, from quoting numerical values for H^F_{1V} on Cd.

From our work it is clear that both a very high statistical precision of the data and a careful analysis allowing for the possibilities of positron self-trapping and of a temperature dependence of F_t in the direction discussed above (which is opposite to that of earlier attempts in the literature) are undispensable prerequisites for obtaining reliable vacancy formation enthalpies by positron annihilation techniques. On the basis of our own experience we have serious doubts whether the narrow error limits given in recent papers can be justified.

3.2. *Quenched and Irradiated Gold*

The observed decrease of the W-parameter, i.e., the increase of the ratio of positron annihilation with conduction electrons to that with core electrons, is attributed, as usual, to trapping of positrons by vacancy-type defects introduced by quenching or irradiation. Apart from the decrease of W below 50 K discussed in Sec. 2, the lineshape is nearly temperature independent up to about room temperature where recovery sets in. The concentrations of vacant sites involved are far from saturation. The absence of thermal expansion effects on the lineshape associated with freely annihilating positrons ($F_f = \text{const}$) suggests strongly that over the temperature range 50 K to 270 K we may also take F_t as temperature independent. Since τ_F has also be shown to be temperature independent in this temperature regime, we may conclude from (2) that over the temperature range 50 K to 300 K the trapping rate per unit concentration σ is temperature independent within experimental errors. We have analyzed our data in terms of

$$\sigma(T) = \frac{1}{\tau_f C} \cdot \frac{W_{i,q}(T) - W_{eq}(T)}{W_t - W_{i,q}(T)}, \tag{17}$$

where $W_{i,q,eq}$ denote the W parameters measured after electron irradiation, quenching, or in thermal equilibrium, respectively, and τ_f, C, and W_t are constants. The relative change of σ in the temperature range 50 K to 270 K was found to be $-(4\pm6)\%$ after electron irradiation and $+(14\pm4)\%$ after quenching. For comparison with recent experiments of other authors [14, 24] we also analysed the data in terms of a temperature dependence $\sigma \sim T^n$ and found $n = -0.03 \pm 0.04$ after electron irradiation and $n = 0.09 \pm 0.02$ after quenching. This is in agreement with the lifetime experiments of McKee et al. [14] who found $n = 0.01 \pm 0.1$ between 100 K and 273 K after quenching from 923 K, whereas Hall et al. [24] reportet $n = 0.5 \pm 0.3$ down to 115 K for a specimen quenched from 1073 K. The positive temperature dependence of the trapping rate in quenched specimens might be due to vacancy clusters formed during the quench [25]. Since D_+ is unlikely to be temperature independent [8] we conclude that in (4) the term $kr_0 \Delta r_0$ is rate-determining and temperature independent. This is in agreement with the view of Hodges [26], according to whom the quantum-mechanical capture of positrons at vacancies leads to a temperature-independent trapping rate. Unfortunately we do not know the concentration of vacancies in our specimens, so we cannot give an absolute value of σ. The irreversible processes apparent in Fig. 3 (recovery effects) will be treated in another context.

Conclusions

We have shown that positron lifetimes and annihilation line shapes in Cd and Au can consistently be described over a very wide temperature range from approximately one fourth of the Debye temperature to the melting point by the trapping model if metastable self-trapping is included and if the temperature dependence of the annihilation characteristics of trapped positrons is allowed for. However, the complexity of the model introduces considerable uncertainty in the determination of monovacancy formation energies. It is fairly clear that positron annihilation experiments can yield reliable vacancy formation energies only if the diffusion and capture mechanisms of positrons in metals become known in more detail. Information about these mechanisms may be obtained from non-equilibrium measurements in the temperature range below significant vacancy trapping or by very precise equilibrium experiments, looking for deviations of $\tau_f \sigma C$ from a simple exponential. Since at present precision is not limited by counting statistics but by the stability of the electronic equipment, further improvement in this direction is necessary.

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