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A Study of Mono and Divacancies in Cu and Au by Positron Annihilation

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Abstract. The peak counting rate of the angular correlation curve was measured for Cu and Au in the temperature range between $-196°$ C and 1200° C. The experimental data were analysed by means of the trapping model under consideration of positron trapping by mono- and divacancies and detrapping of positrons from monovacancies. Such an analysis leads to acceptable results for both monovacancy and divacancy parameters.

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Positron annihilation is a very suitable method for investigating the properties of thermally generated vacancies in metals because of the high statistical accuracy of the experimental data [1, 2]. In [3] we have shown for Al and Cu that near the melting point the positrons are trapped not only by monovacancies but also by divacancies. For high melting metals, such as the noble metals, the detrapping of positrons from monovacancies must be considered [3]. For further confirmation of this conclusion we present in this paper a study of the behaviour of the angular correlation peak counting rate for Cu and Au. For these metals different divacancy fractions are expected on the basis of the known total vacancy concentration at the melting point [1, 4, 5].

Experiment

The experimental arrangement was the same as described in [3]. The positron source was prepared in an in-situ-technique. The samples (Cu of 99.999% and Au of 99.99% purity) were cylinders of 0.3 cm diameter and 2 cm length having a bore of 0.1 cm diameter. Into this specimen 20 mCi Co^{58} (in the form of cobaltchlorite) of very high specific activity (3 Ci/mg) was filled, and the bore was closed by a screw of the sample material. The sample-source unit was put into a molybdenum container which was evacuated and closed. The whole system was placed into a water cooled chamber in a vacuum of 5×10^{-6} Torr and was radiation-heated by a tungston wire. This in-situ-technique prevents errors which can be introduced by a temperature dependence of the source-sample distance in the conventional arrangement and allows also measurements in the liquid state. The data, measured before and after melting, were reproducible with the exception of a small hight-difference which can be explained by the change of the shape of the sample during melting and a small part of annihilation events in the container material, which was estimated to be roughly 2% of the total number of annihilation events (compare also [12]). Peak counting rates F of various temperatures (below melting point) were normalized to the peak counting rates from the sample in the original state at the same temperature. No difference in the shape of the curve was found. The curve of the original state was used in this way for quantitative analysis. After the first melting the step of the F-parameter at the melting point was reproducable. An alloying of the sample with the container material was not expected [6] and even not observed after 48 h remaining in the molten state.

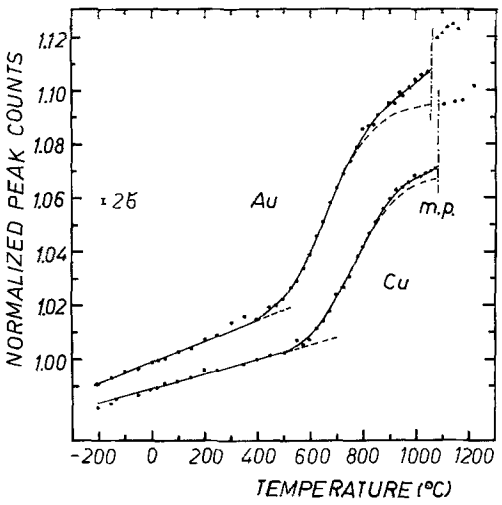

Fig. 1. Normalized coincidence counting rate at the peak ($\theta=0$) of the angular correlation curve as a function of the temperature for Cu and Au. The full line illustrates calculation using the parameters which were estimated from the procedure explained in the text. It shows that the calculation hardly differ from the experimental data within the error limit. The dotted line near the melting point corresponds to the course of F if only positron trapping by monovacancies would happen [e.g. $\nu_{1V}=0$, $C_{2V}=0$ in (1)]. For clarity the curve for Cu was shifted by one unit of the vertical scale to the lower side

The temperature was measured using two Pt-PtRh thermocouples, their calibration was controlled under the conditions of the experiment. The temperature stability was better than $\pm 2°$ C. The measurements were done with the help of a common angular correlation device. The angular resolution was 8 mrad $\times$ 115 mrad which guaranteed a rapid data accumulation. The measured peak counting rate (2×10^6 counts per experimental point) was corrected with respect to the source decay, γ-absorption and background and was normalized to the value at room temperature.

Experimental Results

The experimental data were analysed by means of the trapping model [2] assuming positron trapping by mono- and divacancies and detrapping of positrons from monovacancies. Then, the peak counting rate F is given by

$$F=\frac{\lambda_f F_f+\frac{\lambda_{1V}}{\lambda_{1V}+\nu_{1V}}\sigma_{1V}C_{1V}F_{1V}+\sigma_{2V}C_{2V}F_{2V}}{\lambda_f+\frac{\lambda_{1V}}{\lambda_{1V}+\lambda_{1V}}\sigma_{1V}C_{1V}+\sigma_{2V}C_{2V}}. \quad (1)$$

λ_f and λ_{1V} denote the annihilation rate of positrons which are free or trapped at monovacancies, respectively. We used $\lambda_f=7.35\times10^9\ s^{-1}$ for Cu [7],

$\lambda_f=8.25\times10^9\ s^{-1}$

for Au [7] and $\lambda_{1V}=0.57\,\lambda_f$ [8]. F_f, F_{1V} and F_{2V} represent the characteristic peak counting rates for free positrons and positrons trapped by monovacancies and divacancies, respectively. σ_{1V} and σ_{2V} are the trapping rates per unit defect concentration of mono- and divacancies. The detrapping rate of positrons from monovacancies, ν_{1V}, is given by

$$\nu_{1V}=\frac{kT}{h}\exp(-\Delta\varepsilon_{1V}/kT), \quad (2)$$

where $\Delta\varepsilon_{1V}$ denotes the binding energy of a positron at a monovacancy [2]; k being the Boltzmann's constant, h is the Planck's constant and T represents the absolute temperature.

The vacancy concentrations in thermal equilibrium are given by

$$C_{1V}=\exp(S^F_{1V}/k)\exp(-H^F_{1V}/kT) \quad (3)$$

and

$$C_{2V}=6\exp(S^F_{2V}/k)\exp(-H^F_{2V}/kT). \quad (4)$$

S^F_{1V} is the entropy and H^F_{1V} the enthalpy of the formation of a monovacancy. S^F_{2V} and H^F_{2V} denote the corresponding values for divacancies [1]. The values F_{1V}, F_{2V}, λ_f, λ_{1V}, σ_{1V}, σ_{2V}, S^F_{1V}, S^F_{2V}, H^F_{1V} and H^F_{2V} were taken as temperature independent [1, 2, 7, 8].

The results of our study are shown in Fig. 1. Differences compared to the results of other authors, for instance, Triftshäuser and McGervey [11] exist only in the magnitude of the change of peak counting rate, which can be explained due to the different experimental conditions. The curve through the experimental points was obtained by a computer fit of the expression (1) to the experimental data. This was done in three steps. Firstly, in the low temperature region where positron trapping by vacancies is not expected, $F_f(T)$ was determined. Because of the good linearity in the lower half of the whole temperature region, $F_f(T)$ was linearly extrapolated up to the melting point. In [9] it was found that such a procedure gives a better fit than the supposition of $F_f=$constant. A behaviour of the peak counting rate which could be attributed to the positron self-trapping [10] was not observed for Cu and Au[1].

[1] The Fourth International Conference on Positronannihilation has shown that, the problem of self-trapping is still under discussion.

(For Ni we found a strong nonlinear dependence of F between $-196°$ C and 900° C.) In the temperature region below 850° C for Cu and 750° C for Au the monovacancy parameters were determined by the fit assuming $\nu_{1V}=0$ and $C_{2V}=0$. This was done by using the derivative dF/dT. In this way, the number of free parameters is reduced by one. F_{1V} disappeares because of the assumptions $F_{1V}=$constant. Thus we obtain the monovacancy parameters H^F_{1V} [(1.16 ± 0.02) eV for Cu, (0.96 ± 0.02) eV for Au] and $\sigma_{1V}\exp(S^F_{1V}/k)$ [$(1.5\pm0.4)\times10^{15}\,s^{-1}$ for Cu, $(0.55\pm0.15)\times10^{15}\,s^{-1}$ for Au]. The value of F_{1V} can be determined from (1) for temperatures lower than 850° C and 750° C, respectively, using the experimental peak counting rates and the monovacancy parameters mentioned.

The function of F, which is computed from (1) using the known parameter $F_f(T)$, F_{1V}, H^F_{1V} and $\sigma_{1V}\exp(S^F_{1V}/k)$ together with $\nu_{1V}=0$ and $C_{2V}=0$, is shown in Fig. 1. It deviates from the measured data near the melting point (dashed line).

We attribute this deviation to the presence of divacancies. Their properties can be estimated with the help of a plot of the quantity Z versus T^{-1}. Z is given by

$$Z=\ln\left[\lambda_f\left(\frac{F-F_f}{F_{2V}-F}\right)+\frac{\lambda_{1V}}{\lambda_{1V}+\nu_{1V}}\sigma_{1V}C_{1V}\left(\frac{F-F_{1V}}{F_{2V}-F}\right)\right]$$
$$=-\frac{H^F_{2V}}{kT}+\ln\left[6\sigma_{2V}\exp(S^F_{2V}/k)\right]. \qquad (5)$$

For F_{2V} we used the peak counting rate in the liquid phase at the melting point which should be the upper limit for F_{2V}. If detrapping is not considered in the analysis [we set $\nu_{1V}=0$ in (5)], Z shows a positive curvature, as can be seen in Fig. 2. This is caused by detrapping of positrons from monovacancies which enhances positron trapping by divacancies. (Taking a lower value for F_{2V} as used here will lead to a stronger curvature of Z.) The consideration of a non-vanishing detrapping rate corrects the preference of divacancies. We have chosen ν_{1V} in such a manner that Z shows an optimum linearity (cf. Fig. 2). This provides a binding energy of

$$\Delta\varepsilon_{1V}=(1.1\pm0.4)\text{ eV}$$

for Cu and

$$\Delta\varepsilon_{1V}=(1.1\pm0.2)\text{ eV}$$

for Au. From the slope and from the intersection of Z with the ordinate at $T^{-1}=0$ we obtain the divacancy parameters H^F_{2V} [(2.0 ± 0.1) eV for Cu, (1.69 ± 0.05) eV for Au] and $\sigma_{2V}\exp(S^F_{2V}/k)$ [$(3.3\pm^{4.8}_{2.0})\times10^{16}\,s^{-1}$ for Cu, $(1.2\pm^{0.7}_{0.5})\times10^{16}\,s^{-1}$ for Au].

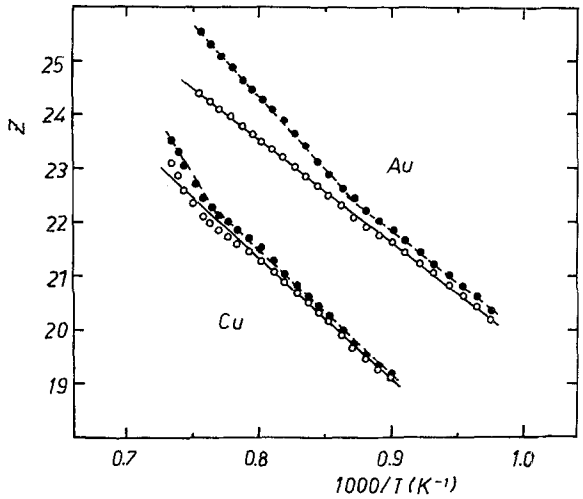

Fig. 2. Plot of Z given by (5) versus the reciprocal absolute temperature for an estimation of the divacancy parameters. The circles are taken from a smoothed curve through the experimental points. Closed circles: assuming $\nu_{1V}=0$ in (5); open circles: assuming a non-vanishing ν_{1V} with $\Delta\varepsilon_{1V}=1.1$ eV

For a separation of the specific trapping rate from the entropy term we assume $\sigma_{2V}\approx2\sigma_{1V}$ and use the total vacancy concentration at the melting point $C_V(T_m)$ (assuming $C_V=C_{1V}+2C_{2V}$). This is known from the thermal expansion method with a sufficient accuracy and amounts to $(2.0\pm0.5)\times10^{-4}$ for Cu [4] and $(7.2\pm0.6)\times10^{-4}$ for Au [5]. The final results are shown in the Table 1 together with positron annihilation data from the literature, which we analysed in the same way, and results given by the thermal expansion method. H^B_{2V} denotes the divacancy binding enthalpy, $G^B_{2V}(T_m)$ represents the Gibbs free energy of divacancy binding at the melting point [1]. The statistical error amounts to 0.1 eV for H^F_{1V} given by the thermal expansion method, 0.01–0.03 eV for H^F_{1V} and 0.05–0.1 eV for H^F_{2V} given by positron annihilation.

As can be seen in Table 1, the consideration of divacancies in the data analysis lowers the estimated monovacancy parameters H^F_{1V} and S^F_{1V}. The values of positron annihilation given by Trifthäuser and McGervey [11] are too large compared with the results of the thermal expansion method, especially for Cu. The consideration of divacancies, as was done by Sueoka [12], leads to lower values for H^F_{1V} and S^F_{1V}, but the divacancy parameters are till unacceptable. A further consideration of detrapping, as was done by us provides acceptable results for H^F_{1V} and S^F_{1V} as well

Table 1. Comparison of vacancy parameters for Cu and Au obtained by thermal expansion and positron annihilation technique applying different methods of data analysis

Vacancy parameters	Cu					Au			
	Thermal expansion		Positron annihilation			Thermal expansion		Positron annihilation	
	a	b	c	d	e	f	g	h	i
H^F_{1V} [eV]	1.17	1.06	1.29	1.20	1.16	0.94	0.92	0.97	0.96
S^F_{1V}/k	1.5	0.6	2.53	0.43	1.3	1.0	0.6	1.20	0.9
H^F_{2V} [eV]				2.20	2.00				1.69
S^F_{2V}/k				7.54	3.7				3.3
H^B_{2V} [eV]				0.20	0.32				0.23
$G^B_{2V}(T_m)$ [eV]		0.3		0.98	0.45		0.33		0.40
σ_{1V} [10^{15} s^{-1}]			1.03	3.79	0.56			0.37	0.30

a and f original data of Simmons and Balluffi [4, 5], analysed under consideration of only monovacancies; b and g reanalysis of the data of [4, 5] under consideration of mono- and divacancies, given by Seeger [1]; c and h Triftshäuser and McGervey [11], only monovacancies were considered; d Sueoka [12], mono- and divacancies were considered; e and i this work, data analysis under consideration of positron trapping by mono- and divacancies and detrapping from monovacancies.

as for H^F_{2V} and S^F_{2V}, which are not so far from those given by Seeger [1]. On the basis of our results we obtain a divacancy fraction $2C_{2V}/C_{1V}$ at the melting point of 10% for Cu and 23% for Au. The different divacancy concentrations are clearly indicated in the different behaviour of the peak counting rate around the melting point for Cu and Au (cf. Fig. 1). The sharp step at the melting point is caused by a rapid increase of the total vacancy concentration from 10^{-3} to 10^{-4} in the solid phase to 10^{-1} vacancies per atom in the liquid phase [13]. The vacancies coagolate and form the holes in the liquid structure.

Conclusion

The differences remaining between our results and those given by Seeger [1] can be caused by both methods. On the one hand, an improvement in accuracy of the thermal expansion measurements seems to be necessary. On the other hand, in the analysis of positron annihilation data, the temperature dependence of F_f [9, 10] should be better known as well as the temperature dependence of σ_{1V} [2, 8] and λ_f [7] should be taken into account. However, apart from this, we believe that the analysis of data, undertaken in this paper, and their results help us for a better understanding of positron annihilation at vacancies in thermal equilibrium.

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