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POSITRON ANNIHILATION MEASUREMENT OF THE VACANCY FORMATION ENTHALPY IN COPPER

by

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Positron Annihilation Measurement of the Vacancy Formation Enthalpy in Copper*

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Doppler-broadening and lifetime data obtained for Cu in the temperature region ∿25 to 1040°C are presented. The experiment utilized a new source-implantation technique. The value of the deduced vacancy formation enthalpy is 1.31 ± 0.05 eV. Since the Doppler-broadening data were the primary source for the determination of the vacancy formation enthalpy, the analysis of these data are discussed. The suitability of introducing divacancies into the analysis is also considered. It is concluded that the measured formation enthalpy is that for monovacancies.

The present work on Cu [1,2] highlights three important aspects of the interpretation of Doppler-broadening data as they are generally applied to the thermal equilibrium determination of the vacancy formation enthalpy in metals. First, the vacancy formation enthalpy for Cu is determined using the two-state trapping model (TSTM). Second, a quantitative evaluation is made of the unequal contributions of information from the different temperature regions of the data to the determination of the vacancy formation enthalpy. Third, the question of the suitability of including the presence of divacancies in the TSTM analysis of the data for Cu is considered.

A new technique, that of ion-implantation of Na^{22} [3,4], was used to fabricate an annealed [5] sample-source package of Cu (99.999 wt.% nominal purity) which exhibited a "source component" of ∿1% intensity and ∿470 ps lifetime. The Cu sample package was annealed in situ, prior to the start of the experiment, for $\sim 6 \times 10^3$ s at 1035°C in a vacuum of 10^{-7} to 10^{-6} Torr. The sample was held in a loose fitting 99.999 wt.% nominal purity Cu jacket, which served as a sacrificial source of copper to protect the sample weld. The temperature was measured to a precision of ∿1%.

The model expression for the TSTM monovacancy analysis of the Doppler-broadening data is $F = [1/(1+Q)]F_b(T) + [Q/(1+Q)]F_v(T)$, where the subscripts b and v refer to the bulk and vacancy-trapped states of the positron, respectively. In this expression, $Q = Q_0(1 + \gamma T)\exp(-H^F_{1v}/kT)$, where $Q_0 = (\mu_{1v}\ \tau_b)_{T=0}\ \exp(S^F_{1v}/k)$. The temperature coefficient γ of the bulk lifetime, τ_b, has been taken as $\gamma = 7.6 \times 10^{-5}\ K^{-1}$ [6]. The quantities S^F_{1v}, H^F_{1v}, and μ_{1v} are the monovacancy formation entropy, monovacancy formation enthalpy, and the specific trapping rate for a positron at a monovacancy, respectively. The functions $F_b(T)$ and $F_v(T)$ were assumed to be linear in temperature, $F_b(T) = F_{b0}(1 + \alpha T)$ and $F_v(T) = F_{v0}(1 + \beta T)$, where F_{b0}, α, F_{v0}, and β are determined from the least-squares fitting procedure of the data along with Q_0 and H^F_{1v}.

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Figure 1 shows the Doppler-broadening lineshape-parameter F as a function of temperature for Cu. the curve shown in Fig. 1 for F(T) is the six-parameter model least-squares fit ($\chi^2 = 1.1$ for 90 degrees of freedom) to the data, while the dashed lines are the simultaneously determined values for $F_b(T)$ and $F_v(T)$. Figure 2 shows the corresponding Arrhenius plot. The values of $\ln\{[F(T)-F_b(T)]/[[F_v(T)-F(T)](1+\gamma T)]\}$ shown in Fig. 2 are derived from the experimental data F(T), as well as the fitted model parameters α, β, F_{b0}, and F_{v0}. It should therefore be emphasized that the values of the points shown in Fig. 2 depend upon these fitted parameters and, hence, the model used to obtain them. The solid line is the best model fit to the data of Fig. 1 and is given by the expression $\ln [Q_0 \exp(-H^F_{1v}/kT)]$. The vacancy formation enthalpy determined in this way, ignoring any possible divacancy contribution, is 1.31 $\pm$ 0.05 eV.

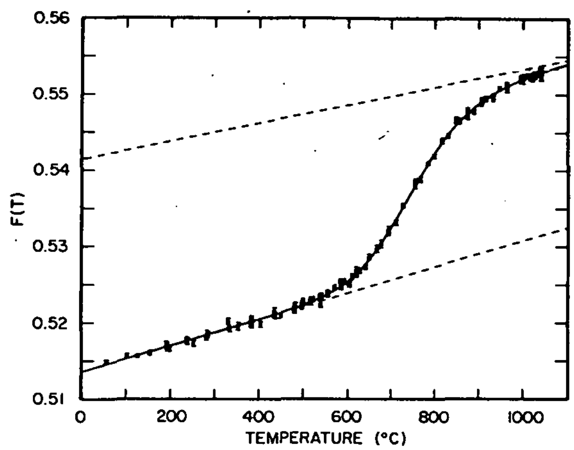

Fig. 1. The experimental Doppler-broadening lineshape parameter F(T) vs. T and the TSTM fit to the data.

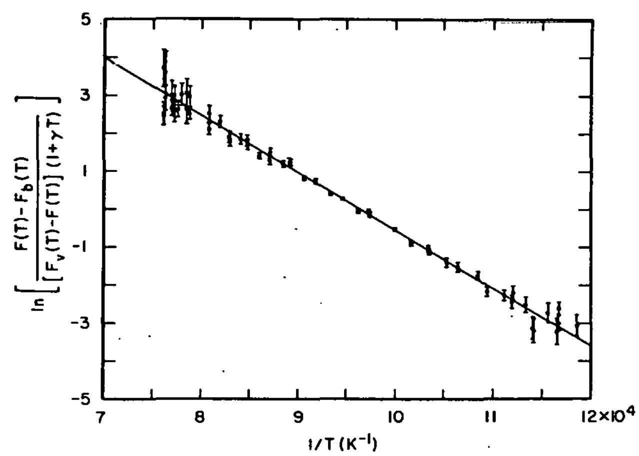

Fig. 2. The Arrhenius plot of the data and fit shown in Fig. 1.

We now turn to a quantitative consideration of how the different temperature regions of the sigmodial curve shown in Fig. 1 contribute to the determination of H^F_{1v}. Displacing one of the data points (i) of Fig. 1 by one standard deviation from its position would change H^F_{1v} by a small amount δH_i. The relative sensitivity, $(\delta H_i)^2/\Sigma_i(\delta H_i)^2$, of H^F_{1v} to such a displacement is shown in Fig. 3 for the actual temperatures of the data set, which is represented by the superimposed fitted values (arbitrarily normalized) of F(T). The four maxima and two end-point extrema represent the determination of three, effectively straight-line regions, which approximate the sigmoidal curve. Since the two central peaks constitute ~50% of the area under the relative sensitivity function, it can be concluded that the major part of the information about H^F_{1v} in this determination is derived from the temperature region 630 to 800°C.

If divacancies contribute significantly to the temperature dependence of F(T), then the previously determined value of 1.31 eV is an apparent vacancy formation enthalpy, H^F_v, rather than the monovacancy formation enthalpy H^F_{1v} [7]. A monovacancy-divacancy trapping model requires the introduction of the additional parameters μ_{2v}, S^B_{2v}, H^B_{2v} and $F_{2v}(T)$, which are the specific trapping rate of the positron at a divacancy, the divacancy binding entropy,

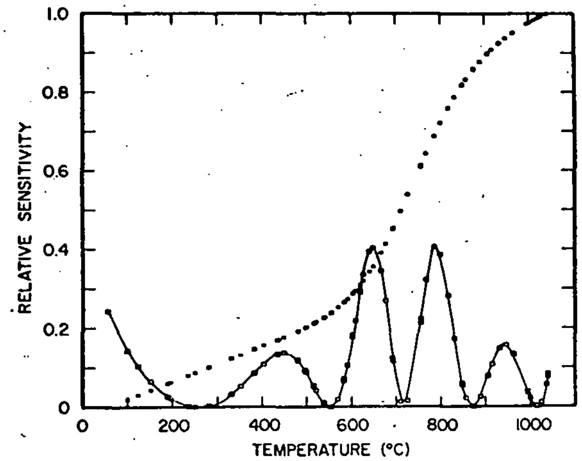

Fig. 3. The relative sensitivity (see text) of the deduced value of H^F_{1v} to the individual data points. The arbitrarily-normalized fitted values of F(T) are superimposed for comparison.

the divacancy binding enthalpy and the positron annihilation lineshape parameter for a divacancy, respectively. This increases substantially the number of parameters to be fitted. The situation is simplified by considering only one lineshape parameter, $F_v(T)$, for the trapped states, where $F_v(T)$ is thus a suitably weighted average of the actual lineshape parameters for the monovacancy and divacancy [7]. The previous model expression for the TSTM can now be used when Q is redefined as

$$Q_1 = Q_0(1+\gamma T)\exp(-H^F_{1v}/kT)$$
$$\times\{1+6\exp(S_o)\exp[(-H^F_{1v} + H^B_{2v})/kT]\},$$

where $S_o = (S^F_{1v} - S^B_{2v})/k + \ln(\mu_{2v}/\mu_{1v})$. Rather than introduce an eight-parameter least-squares analysis, a grid search in (H^B_{2v}, H^F_{1v}) space was performed where the six parameters F_{b0}, F_{v0}, α, β, Q_0, and S_o were least-squares fitted at each node. The nodes were located at H^B_{2v} = 0.1, 0.3, 0.5, and 0.7 eV and H^F_{1v} = 1.30, 1.27, 1.20, 1.10, 1.00, and 0.90 eV. Values of H^F_{1v} = 1.31, 1.33 and 1.35 eV were also examined. For H^F_{1v} > 1.31 eV a significant increase in the χ^2 sum was observed, while for $H^F_{1v} \geq 1.31$ eV the fitted value for the divacancy term in the expression for Q became zero. Figure 4 shows three of these fits in the form of Arrhenius plots for the nodal points denoted by H^B_{2v} = 0.3 eV and H^F_{1v} = 1.27, 1.10, and 0.90 eV, corresponding to curves b, c, and d, respectively. As stated with regard to Fig. 2, the values of the points on this plot, if they were shown, are model dependent and thus vary with the monovacancy-divacancy parameters. The actual model-dependent values of the points have been eliminated from the figure to avoid confusion and only the smooth fits to the data are shown. The χ^2 sums of these fits were all indistinguishable from the monovacancy fit (the straight line "a") in Fig. 4. From Fig. 4 it can be seen that the various monovacancy-divacancy (b, c, and d) model fits and the monovacancy model (a) fit result in the same effective slope in the temperature region of maximum sensitivity, 630 to 800°C. One can therefore conclude that the present data determine an apparent formation enthalpy, H^F_v = 1.31 eV, over the region of maximum sensitivity, which is independent of whether a monovacancy-divacancy or simple monovacancy TSTM is applied to the analysis. Attention should be drawn to the large differences seen at high temperatures in the monovacancy-divacancy model fits (b, c, and d) of Fig. 4. Remembering that all of these fits are of equivalent statistical significance with respect to the present data, the statement can be made that with data of the present type alone it is not possible to deduce any unique, model-independent information about divacancies in Cu. This can be more fully appreciated by examining Fig. 5.

The sigmoidal curves shown in Fig. 5 correspond to the cases a, b, c, and d in Fig. 4, which cannot be resolved on this plot, thereby reflecting the statistical indistinguishability of the cases. The least-squares fitted temperature dependence of the $F_b(T)$ lines are also indistinguishable. The differences in a, b, c, and d manifest themselves in the least-squares fits

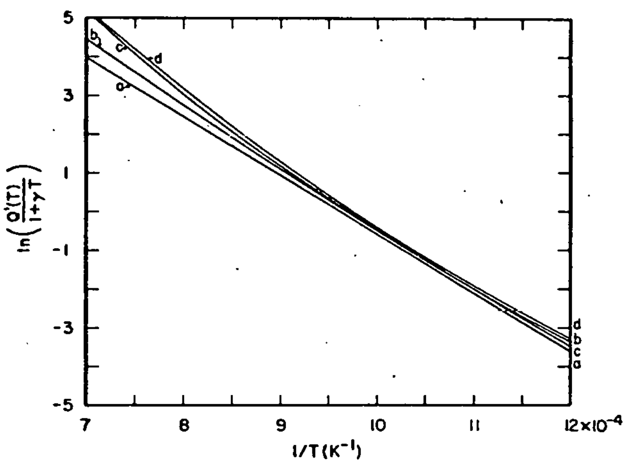

Fig. 4. Arrhenius plots of the monovacancy (a) and monovacancy-divacancy (b, c, and d) model analysis of the Cu data (see text).

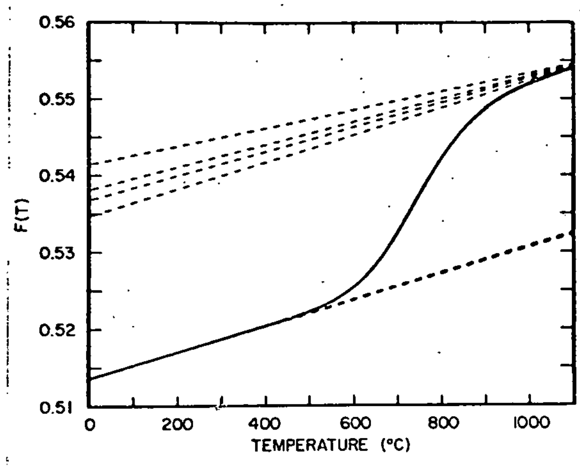

Fig. 5. Sigmoidal plots of the monovacancy and monovacancy-divacancy model analyses for the Cu data.

of the $F_v(T)$ lines, although even at high temperatures they too converge. From Fig. 5, one can conclude that the ability to obtain information about divacancies from this type of experiment depends on the knowledge one possesses about the monovacancy-(F_{1v}) and the divacancy-(F_{2v}) trapped states of the positron. Conversely, any divacancy parameter (e.g., H^B_{2v}, S^B_{2v}) obtained from such data alone will depend strongly on the assumptions made about $F_{1v}(T)$ and $F_{2v}(T)$.

The apparent vacancy formation enthalpy, $H^F_v = 1.31 \pm 0.05$ eV, determined in the temperature range 630 to 800°C, is in excellent agreement with the monovacancy formation enthalpy measured in the loss-free quenching experiments of Berger et al. [8] for the temperature region 525 to 650°C in which a value of $H^F_{1v} = 1.30 \pm 0.05$ eV was reported. Together, these two experiments establish a single-exponential Arrhenius plot of vacancy concentration against inverse temperature for Cu over a combined temperature range of 525 to 800°C. A comparison of the present results with other PAS experiments on vacancy formation in Cu is presented elsewhere [2].

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