Vacancy-Formation Energies in Metals from Positron Annihilation*

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The trapping of positrons at vacancy sites in some metals provides a new and sensitive method for the equilibrium determination of vacancy-formation energies. Data are presented for Al, Cd, In, Pb, and Zn and fitted to a model allowing presentation in the form of Arrhenius plots. The vacancy concentration is not determined because it appears as a product with the positron trapping rate.

We have measured a certain characteristic of positrons annihilating in metals as a function of temperature. These data can be presented in the form of Arrhenius plots and a formation energy for vacancies can be determined. In the following we sketch the basis for the technique and present results for Al, Cd, In, Pb, and Zn.

In a metal a migrating positron is strongly repelled from the ion cores, and a vacancy in many cases appears as a trapping site.[1] If some positrons annihilate in this trapped state and the others while free, then any characteristic, F, of a positron-annihilation experiment will have the value of the weighted mean of this characteristic in the two different states, i.e.,

$$F = F_f P_f + F_v P_v, \tag{1}$$

where P_f and P_v represent the probabilities of annihilation in the free and trapped states, respectively ($P_f + P_v = 1$), and F_f and F_v are the values of F in these two states. Assuming that the positrons are initially free and are captured at a constant rate per vacancy μ,[2] the fraction of positrons which annihilate in the free state is given by

$$P_f = \int_0^\infty \lambda_f \exp[-(\lambda_f + \mu C_v)t]\,dt = \lambda_f/(\lambda_f + \mu C_v), \tag{2}$$

where λ_f is the annihilation rate in the free state, and C_v is the concentration of vacancies. From this we may obtain the fraction of positrons which annihilate when trapped in a vacancy to be

$$P_v = \mu C_v/(\lambda_f + \mu C_v). \tag{3}$$

The rate at which positrons are disappearing from the free population and being trapped at vacancies, μC_v, is given by

$$\mu C_v = A' e^{-E_v/kT} \tag{4}$$

in which A' is a constant and E_v is the energy of formation of a vacancy.[3] By substituting these expressions for the probability of annihilation in a free state and at a vacancy into the original Eq. (1) and using a new constant $A = A'/\lambda_f$, we can obtain the following:

$$(F - F_f)/(F_v - F) = \mu C_v/\lambda_f = A e^{-E_v/kT}. \tag{5}$$

In general, F can be a characteristic of the positron momentum or lifetime distribution, or of any other observable of the decay process. The essential feature is that F_f and F_v be different. In the model which Eq. (1) describes, we have assumed that changes in F due to effects other than vacancies (such as thermal expansion of the sample) are negligible or separable.

We shall now discuss which particular observable F we used, and describe the experiment very briefly. Positrons enter a metal, thermalize, and then annihilate with electrons of the conduction band as well as with electrons from the ionic cores. The momentum of the electron and positron pair at the instant of annihilation is reflected in the angle between the two photons from the annihilation.[4] This distribution of angles is different in the two cases when positrons annihilate with conduction electrons and when positrons annihilate with electrons of the ionic core. The ionic-core electron momentum distribution is that expected of any atomic-orbital system, being Gaussian-like. On the other hand, electrons in the conduction band have a momentum distribution with a comparatively sharp upper limit. The relative intensities of these two distributions depend upon the overlap of the positron wave functions with the conduction and with the core electrons. If positrons are captured in vacancies there will be a resultant diminution in the fraction which annihilate with core electrons, and this is the basis of the effect we have measured. The apparatus—the usual long-slit angular-correlation machine with resolution of 1 mrad[4]—was set at zero angle, that is, zero component of momentum in a certain direction. In this position, the coincidence counting rate was measured as a function of specimen temperature. The temperature was advanced in increments during the two days required to accumulate the data for each sample, and a vacuum or argon atmosphere was maintained. Samples had been spark cut to convenient shape (6 mm×6 mm×10 mm) from 99.999% purity stock, then chemically etched, annealed for a day in vacuum or in argon at a temperature close to the melting point, and reetched. The average grain size was about 3 mm. The reversibility of any temperature effect was verified by rerunning at room temperature after reaching the upper temperature limit of each sample. The counting rates in both end detectors were monitored and used to correct the coincidence counts for any effects of source-to-sample distance changes and source decay.

The data, after small corrections for thermal expansion of the samples, are shown in Fig. 1. We believe that the uncertainties in the corrections are less than the statistical standard deviations which are indicated in the figure. These data reflect the gradual change in the fraction of core annihilations to conduction-electron annihilations as more and more positrons are trapped and annihilate near vacancy sites. At low temperatures (room temperature in most cases) there are very few thermally activated vacancies; thus the low-temperature limit of the measured parameter F determines F_f, the value corresponding to free positrons. At high temperatures, when there are many vacancies, most positrons will be captured. A further increase in temperature and the resultant increase in the number of vacancies will have no observable effect after the probability of finding a positron in a vacancy site is already nearly 100%. Thus, the high-temperature limit determines F_v, the value of the parameter F when a positron annihilates at a vacancy site. The high-temperature saturation can be seen in several of the cases illustrated in Fig. 1.

The data were fitted by Eq. (1) [with P_f and P_v as defined in Eqs. (2), (3), and (4)] by a maximum-likelihood technique using as parameters the four variables F_f, F_v, A, and E_v. The fitted functions are the lines in Fig. 1. A more revealing presentation can be obtained by plotting the logarithm of the ratio $(F-F_f)/(F_v-F)$ vs $1/T$, which yields an Arrhenius plot [Eq. (5)]. Such a presentation is shown in Fig. 2, where the data in this form and the corresponding fitted functions are displayed. The slope corresponds to the formation energy E_v. The intercept at $1/T=0$ is the parameter A, which is the product of an entropy factor $\exp(S_v/k)$ (where S_v is the vacancy-formation entropy) and μ/λ_f. The annihilation rate for free positrons λ_f can be measured separately, but we cannot separate the product of the entropy factor and the trapping rate μ to determine an absolute vacancy concentration.

Values obtained for E_v and for the product $\mu\exp(S_v/k)$ are listed in Table I. In the case of aluminum, if we take the entropy factor to be 2,[5] our value for μ is of the order calculated by

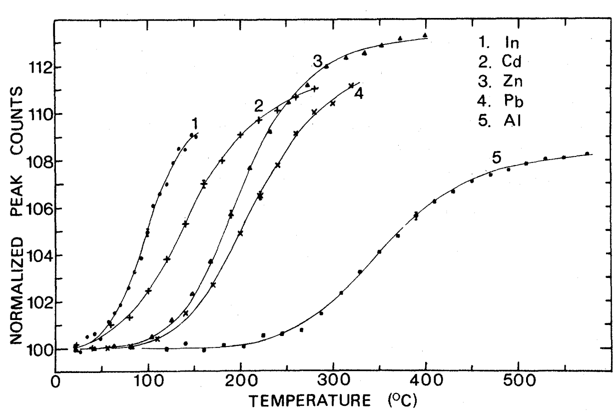

FIG. 1. Counting rate at the peak ($\theta=0$) of angular correlation curve versus temperature for In, Cd, Zn, Pb, and Al. The statistical standard deviations are indicated for a few points. The lines represent the best fit of the model described in the text to the data. Normalization assigns the low-temperature limit as equal to 100.

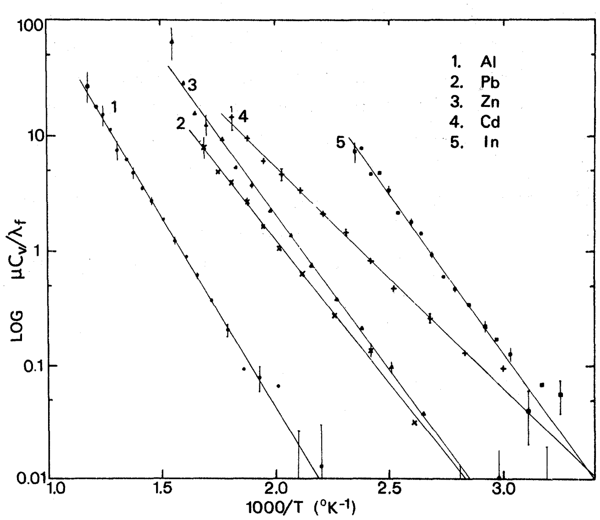

FIG. 2. Arrhenius plots for positron trapping by vacancies. These points (with standard deviations) and lines are derived from the data and fitted lines of Fig. 1. The slope of a line corresponds to the vacancy-formation energy.

TABLE I. Values of the product of trapping rate and entropy factor, and values of the vacancy formation energy measured for five metals.

Metal	$\mu \exp(S_v/k)$ (sec^{-1})	E_v (eV)	Previous E_v (eV)	Ref.
Al	1.2×10^{15}	0.66 ± 0.04	0.65	5
Cd	1.9×10^{14}	0.39 ± 0.04	0.44	7
Pb	6.2×10^{14}	0.50 ± 0.03	0.49	8
In	1.5×10^{17}	0.55 ± 0.02	...	...
Zn	3.6×10^{15}	0.54 ± 0.02	0.44	7

Hodges.[6] The next column of Table I lists our values of E_v for the metals aluminum, cadmium, indium, lead, and zinc. The uncertainties indicated are standard deviations based on the statistical uncertainty of the data. Uncertainties in the end-limit parameters provide the largest contribution to these standard deviations. The second-last column of Table I lists values of E_v obtained by other methods as discussed in recent reviews.[5,7,8] No value has been found in the literature for E_v in indium. The case of aluminum has been extensively investigated by various techniques, and the agreement of our value of $E_v = 0.66 \pm 0.04$ eV with the value of 0.65 eV obtained by a recent analysis of Seeger and Mehrer[5] is very interesting.

In conclusion, we have shown the utility of a positron-annihilation technique in the determination of E_v in some metals. The technique has the advantage of being sensitive to low concentrations of vacancies ($\sim 10^{-6}$), and hence is not susceptible to complications from divacancy formation. It also has the advantage of being an equilibrium technique. It has the disadvantage of not being useful for all metals—e.g., we observed no large effects of vacancies in the alkali metals, or in tin or bismuth. Probably vacancies in these metals do not trap positrons or have a low trapping rate. For metals such as those listed in the table, this technique provides a relatively simple and apparently accurate measurement of vacancy-formation energies. The confidence in these results depends, of course, on the validity of the simple model which we have assumed as a basis of the analysis. Further measurements and understanding should indicate what refinements to this model are necessary.

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[1] I. K. MacKenzie, T. L. Khoo, A. B. McDonald, and B. T. A. McKee, Phys. Rev. Lett. 19, 946 (1967); B. Bergersen and M. J. Stott, Solid State Commun. 7, 1203 (1969).

[2] We assume that the trapping rate is temperature independent. However, introducing a factor such as $T^{1/2}$ would not much affect the fitted value obtained for E_v—e.g., in the case of aluminum the fitted value of E_v would be reduced 4%.

[3] We neglect any temperature dependence of the vacancy-formation entropy and energy.

[4] A. T. Stewart, in *Positron Annihilation*, edited by A. T. Stewart and L. O. Roellig (Academic, New York, 1967), p. 17.

[5] A. Seeger and H. Mehrer, in *Vacancies and Interstitials in Metals, Proceedings of an International Conference, Jülich, Germany, 1968*, edited by A. Seeger *et al.* (North-Holland, Amsterdam, 1970), p. 1.

[6] C. H. Hodges, Phys. Rev. Lett. 25, 284 (1970).

[7] D. Schumacher, in *Vacancies and Interstitials in Metals, Proceedings of an International Conference, Jülich, Germany, 1968*, edited by A. Seeger *et al.* (North-Holland, Amsterdam, 1970), p. 889.

[8] J. S. Koehler, in *Vacancies and Interstitials in Metals, Proceedings of an International Conference, Jülich, Germany, 1968*, edited by A. Seeger *et al.* (North-Holland, Amsterdam, 1970), p. 169.