Rev. 185, 805 (1969); see also the review by M. W. Wortis, in *Phase Transitions*, edited by C. Domb and M. S. Green (Academic, London, in press).

[17]A. Bienenstock and J. Lewis, Phys. Rev. 160, 393 (1967); D. C. Rapaport and C. Domb, J. Phys. C: Proc. Phys. Soc., London 4, 2684 (1971).

[18]D. Gaunt and G. A. Baker, Jr., Phys. Rev. B 1, 1184 (1971); see also the very recent work of M. Ferer and M. Wortis, to be published, and references contained therein.

[19]G. Paul and H. E. Stanley, Phys. Lett. 37A, 427 (1971), and Phys. Rev. B 5, 2578 (1972); J. Oitmaa and I. G. Enting, Phys. Lett. 36A, 91 (1971), and J. Phys. C: Proc. Phys. Soc., London 5, 231 (1972).

[20]D. D. Betts, C. J. Elliott, and R. V. Ditzian, Can. J. Phys. 49, 1327 (1971); M. H. Lee and H. E. Stanley, Phys. Rev. B 4, 1613 (1971), and references contained therein. M. Wortis, unpublished.

[21]The exponent obtained approaching the tricritical point along an H/T = const path should be the same as that along an H = const path provided the phase boundary is not parallel to the T axis at T_t.

[22]Previous Ising-model high-temperature series have been for *nearest-neighbor* antiferromagnets in a finite field (Ref. 17) or for next-nearest-neighbor antiferromagnets in *zero* field [G. Paul and H. E. Stanley, Phys. Rev. B 5, 3715 (1972), and references contained therein].

[23]It should be noted that the Monte Carlo exponent is estimated along a constant magnetization path which need not ordinarily be expected to give the same exponent as obtained from a constant field path. We wish to thank Professor R. B. Griffiths for very helpful discussions concerning this point. See also Ref. 7.

Vacancy-Impurity Binding Energy in Aluminum–1.7 at .% Zinc Using Positron-Annihilation Lifetimes*

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Positron-annihilation lifetimes were measured in pure aluminum and in aluminum–1.7 at.% zinc at temperatures between 20 and 550°C. The data were analyzed using an extension of the trapping model to obtain the vacancy formation energy in aluminum (E_F = 0.62 ± 0.02 eV). Under certain restrictive assumptions the binding energy of vacancies to zinc atoms in aluminum was found to be E_B = 0.019 ± 0.004 eV. A relaxation of these assumptions yielded only an upper bound (E_B < 0.04 eV).

A complete understanding of defects in metals requires knowledge of the sign and magnitude of the interaction between vacancies and impurities. Until recently it has been generally assumed that vacancies and impurities are bound to each other, but the experimental values of the binding energy in a given alloy can vary from 0.0 to 0.5 eV. There has been a growing feeling that the larger values are incorrect because they were often obtained by quenching techniques where vacancy and impurity clustering effects could lead to higher apparent values for the binding energy. On the other hand, the only equilibrium measurements to date have been performed at high temperatures where vacancy clustering causes difficulties.[1,2]

Positron-annihilation methods eliminate the problems mentioned above because they are performed in equilibrium at temperatures where the vacancy concentration is much lower. Positrons have been shown to be quite sensitive to vacancy-type defects in metals,[3-6] and details of the annihilation process have been used recently to deduce the vacancy formation energy in aluminum (E_F = 0.66 ± 0.04 eV) using 2-γ angular-correlation methods.[7]

In this Letter we report the use of positron-annihilation lifetimes to measure the binding energy of vacancies to zinc atoms in aluminum. We show for the first time that it is possible to extend the trapping model to include the effects caused by the presence of vacancy-impurity complexes. As a consequence of this inclusion, the vacancy-impurity binding energy is extracted from the analysis. Because of the low concentration of vacancies at the temperatures employed, analysis of the data also has been extended to include the contribution to positron trapping that arises from dislocations.

Standard delayed-coincidence lifetime measurements were made using $\frac{3}{4}$-in. cylinders of KL-236 plastic scintillator,[8] RCA 8575 photomultipliers, and integrated-circuit constant-fraction discriminators.[9] Instrumental resolution was typically 0.240 nsec full width at half-maximum for a Co^{60} source with energy windows set at

0.85–1.28 and 0.34–0.51 MeV. Aluminum of 99.9999% purity from Cominco, Inc. and aluminum–1.7 at.% zinc produced by the Materials Research Corporation were the specimen materials. The samples were made by electron-beam welding two pieces of specimen material, with $Na^{22}Cl$ sandwiched between them. After a 600°C anneal in vacuum for 12 h, the data for the temperature range 20–550°C were accumulated. The samples were not handled after the anneal.

The vacancy-formation and binding energies were determined from least-squares analysis of the positron-lifetime data. Initially the conventional method of positron-lifetime analysis described below was used, but in order to fit the data more precisely a number of modifications, which will be discussed, were necessary.

The trapping model[3-5,10] relates the behavior of positrons to vacancy-type defects in the metal by first assuming that positrons become trapped at a rate κ which is proportional to the concentration of defects, and further that a positron in a trap annihilates at a rate λ_1, while a positron in the lattice annihilates at a rate λ_2. Using these assumptions we can write a set of simple rate equations for $n_1(t)$ and $n_2(t)$, the number of trapped and free positrons, respectively.

$$dn_1/dt = -\lambda_1 n_1 + \kappa n_2, \quad dn_2/dt = -\lambda_2 n_2 - \kappa n_2.$$

These two differential equations can be solved for the time distribution of the annihilations,

$$P(t) = -\frac{d(n_1+n_2)}{dt} = \frac{N_0}{\lambda_2-\lambda_1+\kappa}\{\lambda_1\kappa\exp(-\lambda_1 t) + (\lambda_2-\lambda_1)(\lambda_2+\kappa)\exp[-(\lambda_2+\kappa)t]\}, \tag{1}$$

where the solution has been normalized so that N_0 is the total number of observed events.[4]

The conventional method of extracting information from positron-annihilation lifetime data is as follows. If the defects are assumed to be thermally induced vacancies only, then the trapping rate is given by

$$\kappa = \mu c = \mu c_1 \exp(-E_F/kT), \tag{2}$$

where c is the atomic fraction of vacancies, μ and c_1 are constants, and E_F is the energy required to form a single vacancy. The annihilation rate in the perfect lattice, λ_2, is obtained by assuming that at low temperatures $P(t)$ is a single exponential with rate λ_2. The annihilation rate in a vacancy trap, λ_1, is obtained by assuming that at high temperatures $P(t)$ is again a sin-

TABLE I. Results of data analysis.

Parameter	Pure Aluminum			Aluminum–1.7 at.% Zinc
	Conventional Method	Modified Resolution Function Included	Temperature-Independent Defects Included	Impurity Effects Included
χ^2/ν	2.50	2.00	1.02	1.10
$1/\lambda_2$ (nsec)	0.160-0.170	0.164±0.003[a]	0.160±0.002	0.160±0.001
$1/\lambda_1$ (nsec)	0.240-0.250	0.242±0.004	0.243±0.002	0.243±0.001
I_s (%)	4-8	5-7	4.7±0.3	5.2±0.2
$1/\lambda_s$ (nsec)	0.450-0.550	0.450-0.550	0.560±0.010	0.585±0.007
$W_{\frac{1}{2}}$ (nsec)	0.240-0.250	0.190-0.210	0.190-0.210	0.190-0.205
E_F (eV)	0.50-0.70	0.50-0.70	0.62±0.02	0.62 fixed
E_B (eV)	-	-	-	0.019±0.004
μc_1 ($nsec^{-1}$)	-	-	4.31×10^5	4.31×10^5 fixed
μc_0 ($nsec^{-1}$)	-	-	0.42±0.07	0.25±0.05
ρ_d (cm^{-2})	-	-	10×10^8	5×10^8

[a]± uncertainties are 1 standard deviation.

gle exponential with rate λ_1. At intermediate temperatures κ is adjusted by least squares while λ_1 and λ_2 are held fixed. In order to be of the same form as real data, $P(t)$ is folded with an instrumental resolution function $G(t)$, which is assumed to be a Gaussian,

$$G(t') = (4\ln 2/\pi)^{1/2} W_{1/2}^{-1} \times \exp[-4\ln 2(t'-t_0)^2 W_{1/2}^{-2}]. \quad (3)$$

The full width at half-maximum, $W_{1/2}$, and the centroid t_0 are adjusted in the analysis process. The component due to positron annihilations in the source is of the form

$$S(t) = I_s \lambda_s \exp(-\lambda_s t). \quad (4)$$

and is determined from the low-temperature data and subtracted out of all higher-temperature data. The formation energy E_F is determined from the slope of the graph of $\ln\kappa$ versus $1/kT$.

Our results for pure aluminum using the conventional method are given in the first column of Table I. Dashes are given where values were found to vary. Note the value of 2.50 for χ^2/ν (χ^2 per degree of freedom), which is much larger than 1.00 indicating poor agreement between the theory and the data.

Our first modification of the conventional method was intended to lower χ^2/ν and to increase the precision of the fitted parameters. A Gaussian was folded with a double-sided exponential to give the instrumental resolution function

$$R(t'') = \int_{-\infty}^{0} G(t'-t'') \exp(t'/\tau_L)\, dt' + \int G(t'-t'') \exp(-t'/\tau_R)\, dt', \quad (5)$$

where τ_L and τ_R characterize the left and right sides of the resolution function. The results for pure aluminum using this modification are given in the second column of Table I. Note the improvement in the precision of λ_1 and λ_2 and the slight reduction of χ^2/ν. (τ_L and τ_R were found to be of the order of 0.040 nsec, as expected from measurements of the instrumental resolution using Co^{60}.)

Our second modification to the conventional method resulted from difficulties in determining a unique value for E_F. Figure 1 shows a plot of $\ln\kappa$ versus $1/kT$ for pure aluminum using the conventional method. (The results with the modified resolution function are similar.) Because of the curvature, E_F varies from 0.50 to 0.70 eV depending upon which region is used for a straight-line fit. The flattening off at low temperatures suggests the presence of temperature-independent defects such as dislocations. To include this in our model we modify Eq. (2) by adding a constant term to obtain

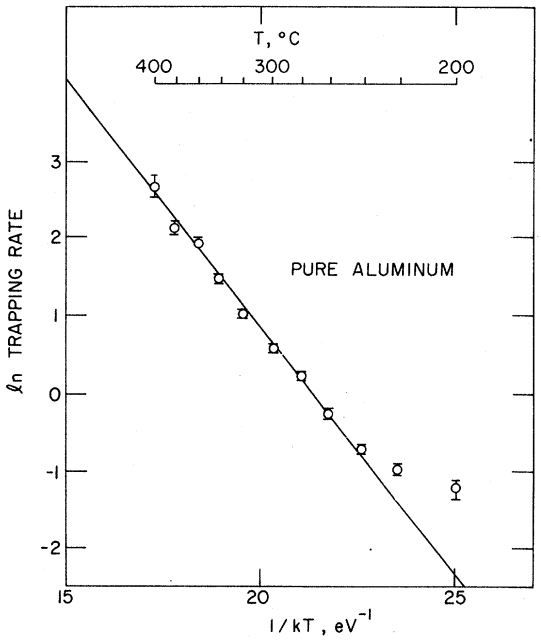

FIG. 1. Results using the conventional method of analysis. Note the flattening off at low temperatures. The straight line is a least-squares fit over the range 20–400°C and yields $E_F = 0.64$ eV.

$$\kappa = \mu c = \mu[c_1 \exp(-E_F/kT) + c_0]. \quad (6)$$

It then becomes impossible to determine λ_2 as before since at low temperatures there are still two components to $P(t)$. In order to overcome this difficulty, the lifetime data for all temperatures were analyzed simultaneously using Eqs. (1), (4), (5), and (6) as the fitting function. The results of this analysis for pure aluminum are given in the third column of Table I. Note that the fit is significantly improved as indicated by $\chi^2/\nu = 1.02$. Our data yield a formation energy for single vacancies in pure aluminum of 0.62 ± 0.02 eV. Previous values deduced from non-equilibrium and high-temperature equilibrium experiments yielded values between 0.71 and 0.86 eV.[11,12] However, a recent reexamination of these experiments on aluminum led to a value of 0.65 eV when effects of clustering were reconsidered.[13] More recently, the positron-annihilation results of McKee *et al.* gave 0.66 ± 0.04 eV.[7] These results along with the ones reported here lend support to the significantly lower value for E_F.

In order to get a physical feeling for the con-

stant term in Eq. (6), we make the following order-of-magnitude calculations. Using the value of $c = 6\times10^{-5}$ at 450°C from simultaneous length-change–lattice-parameter experiments,[12] we obtain $c_0 = 10\times10^{-7}$. If we assume a dislocation to be a string of single vacancies, we can obtain an equivalent dislocation density

$$\rho_d = c_0 \times (\text{number of atoms cm}^{-2}) \approx 10\times10^8 \text{ cm}^{-2}.$$

Another way of interpreting the constant term comes from data on deformed aluminum,[10] which indicate that $\mu c_0 = 0.42$ nsec^{-1} corresponds to 0.2% deformation.

We now have a method for analyzing pure-aluminum data which gives a good fit and a unique value for E_F, and are therefore in a position to analyze data from identical measurements on aluminum–1.7 at.% zinc.

To include the effects of impurities so as to deduce E_B, the binding energy between a vacancy and an impurity atom, we modify Eq. (6) to

$$\kappa = \mu c = \mu\left(c_1\{(1-12i_0)\exp(-E_F/kT) + 12i_0\exp[-(E_F-E_B)/kT]\} + c_0\right), \tag{7}$$

where we have replaced the Boltzmann factor by the term in braces, i_0 being the impurity concentration.[14] Several assumptions are inherent in Eq. (7): (a) μ is temperature independent and the same for isolated vacancies, impurity-vacancy pairs, and dislocations, and (b) all impurities are isolated and do not interact with one another (the Zn concentration is within the solubility limit over the temperature range employed). Using Eqs. (1), (4), (5), and (7) as our functional form and holding μc_1 and E_F fixed at the values obtained from pure aluminum, we obtain the results given in the fourth column of Table I, in particular $E_B = 0.019 \pm 0.004$ eV. Under the less restrictive assumption that μc_1 is not held fixed the value of E_B is only bounded from above and negative values are not excluded (i.e., $E_B < 0.04$ eV). The results of recent tracer-diffusion measurements by Peterson and Rothman[2] led them to conclude that the binding energies of vacancies to non-transition-metal impurities in aluminum are effectively zero. They suggested that the nonzero values derived from quenching and ageing experiments were affected by clustering. We are led to similar conclusions by our results.

In summary, we have found that the vacancy-formation energy in aluminum is 0.62 ± 0.02 eV and that there is essentially no binding between vacancies and zinc atoms in aluminum. In addition, by including temperature-independent defects in our model we can improve the fit to the data significantly. We have shown that positron annihilation is a useful tool which overcomes many difficulties of other methods and allows a precise measurement of binding energies.

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[1]N. H. March and J. S. Rousseau, Cryst. Lattice Defects 2, 1 (1971).

[2]N. L. Peterson and S. J. Rothman, Phys. Rev. B 1, 1 (1970).

[3]W. Brandt, in *Proceedings of the International Conference on Positron Annihilation, Detroit, Michigan, 1965,* edited by A. T. Stewart and L. O. Roellig (Academic, New York, 1967), p. 180.

[4]B. Bergersen and M. J. Stott, Solid State Commun. 7, 1302 (1969).

[5]D. C. Connors and R. N. West, Phys. Lett. 30A, 24 (1969).

[6]C. L. Snead, Jr., A. N. Goland, J. H. Kusmiss, H. C. Huang, and R. Meade, Phys. Rev. B 3, 275 (1971).

[7]B. T. A. McKee, W. Triftshäuser, and A. T. Stewart, Phys. Rev. Lett. 28, 358 (1972).

[8]Similar to Naton 136.

[9]M. R. Maier and P. Sperr, Nucl. Instrum. Methods 87, 13 (1970). (It was necessary to adjust the delay lengths to achieve <0.020 nsec walk over the desired range of pulse heights.)

[10]P. Hautojärvi, A. Tamminen, and P. Jauho, Phys. Rev. Lett. 24, 459 (1970).

[11]J. Bass, Phil. Mag. 15, 717 (1967).

[12]R. O. Simmons and R. W. Balluffi, Phys. Rev. 117, 52 (1960).

[13]A. Seeger and H. Mehrer, in *Vacancies and Interstitials in Metals,* edited by A. Seeger, D. Schumacher, W. Schilling, and J. Diehl (North-Holland, Amsterdam, 1970), p. 41.

[14]A. C. Damask and G. J. Dienes, *Point Defects in Metals* (Gordon and Breach, New York, 1963), p. 22.