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Positron-annihilation studies of voids in neutron-irradiated aluminum single crystals*

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We have measured the angular correlation of positron-annihilation radiation from single crystals of aluminum in which voids had been induced by neutron irradiation. The angular-correlation curve is narrower than that for aluminum containing vacancies. The data fit well a curve computed on the assumption that the positrons are annihilated at the void surfaces. After the sample was heated to 325 °C the angular-correlation curve became identical to that of normal Al.

I. INTRODUCTION

The creation of voids in neutron-irradiated materials, and their deleterious effects on mechanical properties, pose serious problems in reactor technology. In the case of irradiated aluminum it is puzzling that, even during annealing studies, no voids smaller than about 100-Å diameter are seen in the electron microscope. Hence, additional experimental techniques known to be sensitive to very small voids have been sought.[1,2] Recent investigations have demonstrated the sensitivity of positrons to the presence of vacancies in metals,[3-6] and to very small voids (20–30-Å diameter) in neutron-irradiated molybdenum.[7,8] Aluminum offers a much better possibility for studying the behavior of positrons in the presence of voids than molybdenum does, because portions of the angular-correlation curve are clearly separable into valence- and core-electron contributions. We have therefore begun a study of neutron-irradiated aluminum.

II. EXPERIMENTAL TECHNIQUE AND RESULTS

Single-crystal slabs of Al were grown in a graphite mold by a modified Bridgman technique from 69-Grade (99.9999+%-stated-purity) starting material.[9] Suitable samples for small-angle x-ray-scattering (SAXS) studies were cut and irradiated in the High Flux Isotope Reactor of Oak Ridge National Laboratory at 55 °C to fluences of up to 4.5×10^{21} n/cm^2 ($E > 0.1$ MeV).[1] After irradiation, the specimen surfaces were cleaned and electropolished to remove corrosion products resulting from contact with the reactor cooling water, and small pieces were spark cut for electron microscopy. The residual radioactivity of the specimens was analyzed with a Ge(Li) detector to ensure that there were no γ rays emanating from the samples in the energy range recorded in the positron-annihilation experiments.[10]

In agreement with previous transmission-electron-microscopy (TEM) studies in quenched[11] and neutron-irradiated[1,12] aluminum, the voids were found to be octahedra bounded by the eight $\{111\}$ planes, with some truncation on $\{100\}$ planes. The void diameters (distances between opposite bounding planes) were found to be between 125 and 495 Å. The number density of voids in these specimens was found to be consistent with previous work on polycrystalline material[1] ($N_v \approx 4\times10^{14}$ voids/cm^3). In addition to voids, TEM revealed the presence of dislocation tangles and small Si precipitates, the latter resulting from the transmutation of Al. No vacancy or interstitial loops were seen.

The angular-correlation data were recorded in an apparatus of the standard long-slit type having a total resolution of 0.3 mrad. The samples were cooled *in vacuo* to 100 °K in order to reduce the smearing due to the thermal motion of the positron. The positron source was a Cu^{64} disk of initial activity 800 mCi, placed 4.5 mm from the crystal and shielded from the γ-ray detectors. Each Cu^{64} source was used for 1 day; sources could be replaced without disturbing the sample, so that counts were accumulated for several days on each sample.

Figure 1 shows the results obtained from a sample that had been irradiated to a fluence of 2.0×10^{21} n/cm^2 ($E > 0.1$ MeV). The figure also shows, for comparison, curves obtained from normal Al and from Al containing vacancies, induced by heating normal Al to a temperature of 600 °C. The effect of vacancies "saturates" near this temperature, where nearly all of the positrons are trapped in vacancies,[3] but the effect of voids is clearly much greater. Curves obtained from two other samples, irradiated to 1.6×10^{21} n/cm^2 and 4.5×10^{21} n/cm^2, respectively, were almost identical to the one shown, except that the curve from the sample receiving the smallest dose was about 10% broader than the curves from the other two. After annealing at 325 °C, where the voids are known to anneal out,[1,12] the angular-correlation curve became identical to that of unirradiated Al.

III. INTERPRETATION

Several features of Fig. 1 are noteworthy. (i) The effect of voids, like that of vacancies, is to reduce the number of annihilations in the high-

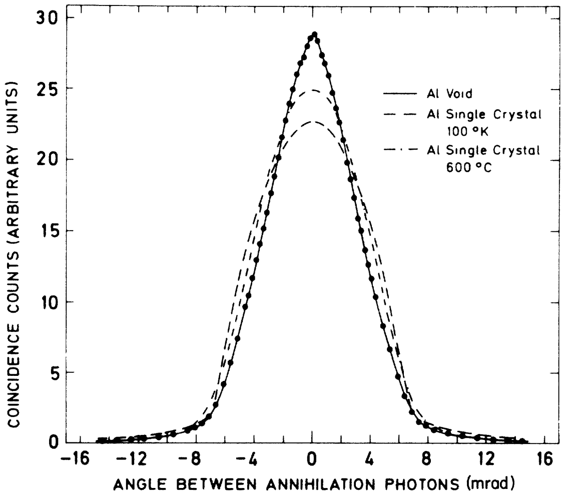

FIG. 1. Comparison of angular correlation of annihilation radiation from normal Al, from Al heated to 600°C so that positrons are trapped at vacancies, and from Al containing voids. Points are the experimental points for Al containing voids; the solid line is simply a smooth curve through these points.

momentum part ("tail") of the curve. (ii) All of the curves descend rapidly towards a "cutoff" near 6.7 mrad—the angle corresponding to the Fermi momentum in Al—but the cutoff is smeared significantly from that observed in normal Al. (iii) The void curve is much more sharply peaked than the other two, with a shape similar to that seen when positronium is formed in a solid—e.g., Teflon.[13] All of these features are consistent with the idea, proposed by Hodges and Stott,[14] that positrons are captured into surface states in a void. A positron in such a state would see fewer core electrons, hence the high-momentum part of the curve would be reduced (feature i). Such a positron would annihilate mostly with valence electrons whose maximum momentum p/mc is 6.7 mrad, but the momentum observed would include a significant contribution from the momentum of the confined positron, hence the loss of sharpness in the "cutoff" (feature ii).[15] Finally, the sharpness of the peak (feature iii) may be explained qualitatively from the surface-state model as follows: The momentum distribution of the γ rays, given by the square of the Fourier transform of the product of the electron and positron wave functions, reproduces the Fermi distribution inside the metal (i.e., *outside* the void), where the electron wave functions can be considered to be momentum eigenfunctions. But in the void the wave functions preserve the Fermi distribution only in the momentum components p_x and p_y, parallel to the wall of the void; the value of p_z acquired by the gamma rays is determined by the exponential decay of the electron wave function in the void. Electrons that penetrate farther into the void have a greater annihilation probability combined with a more narrow range of values of p_z; the resulting distribution of measured values of p_z is more strongly peaked than the Fermi distribution. Furthermore, it follows directly from the Schrödinger equation that, for a given energy, the electrons which penetrate farther into the void are these with smaller values of p_x and p_y. Thus the momentum distribution of the γ rays is enhanced at low momentum, and the angular-correlation curve becomes more sharply peaked near zero angle.

The result of a first-order calculation based on these ideas is compared with the experimental data in Fig. 2. In the calculation the annihilations are divided, for convenience, into two groups: "inside" annihilations, resulting from the portion of the wave-function product inside the metal, and "outside" annihilations, resulting from the portion of the wave-function product in the void. The "inside" annihilations are assumed to yield a distribution similar to that of normal aluminum, except that it is "smeared" as a result of the momentum resulting from the exponential tail of the positron wave function $\psi \propto e^{\alpha' z}$ in the metal. The decay con-

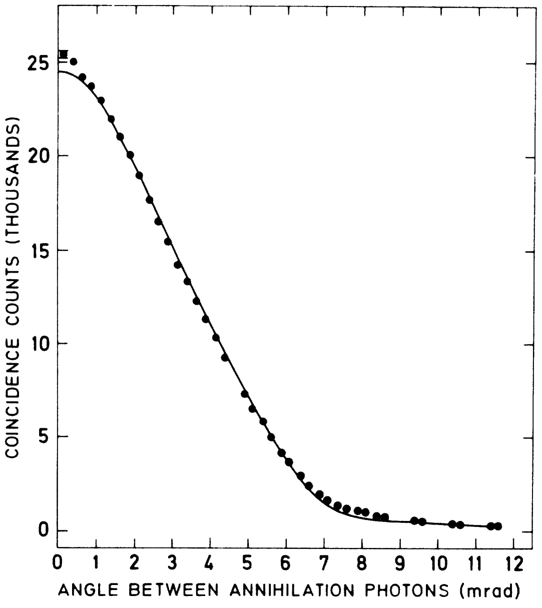

FIG. 2. Comparison of theory and experiment, plotted as a function of the absolute value of the angle. Solid line is the theory, computed as described in the text. Points are the same experimental points shown in Fig. 1, "folded" as follows: at angles less than 4.5 mrad, points for positive angles and corresponding negative angles are averaged and plotted as single points; at angles greater than 4.5 mrad, points obtained at positive angles alternate with points obtained at negative angles.

stant α' of the positron wave function is chosen to be 0.8 $Å^{-1}$, in agreement with the potential of Hodges and Stott for positrons near the surface of aluminum. The smearing of the final angular-correlation curve is calculated by assuming a random spatial orientation of the various void walls.[16]

The distribution resulting from the "outside" annihilations is computed as follows. We define $\vec{p}_r$ as the resultant of p_x and p_y, and we construct a cylinder in momentum space, the locus of constant $|\vec{p}_r|$, through the Fermi sphere. The probability of annihilation in a state lying between p_r and $p_r + dp_r$ is $P(p_r)dp_r$, given by the integral over all p_z of the product of a volume element and the probability of annihilation for that volume element.[17]

We approximate the potential energy for the electron at the void surface by a square potential step of height $W + E_F$, where W is the work function[18] and E_F the Fermi energy; then the z dependence of the electron wave function is $e^{-\alpha z}$, where $\alpha^2 = (2mW + 2mE_F - p_z^2)/\hbar^2$, and z is measured from the void wall. If we neglect the small variation in the positron wave function over the region where $e^{-\alpha z}$ is large, we find the annihilation probability to be proportional to $1/\alpha^2$. Thus,

$$P(p_r) \propto \int_0^{(p_F{}^2 - p_r{}^2)^{1/2}} \frac{2\pi p_r}{2m(W + E_F) - p_z{}^2}\, dp_z\,,$$

where $p_F{}^2 = 2mE_F/\hbar^2$. The integration yields

$$P(p_r) \propto p_r \ln\left(\frac{[2m(E_F + W)]^{1/2} + (p_F{}^2 - p_r{}^2)^{1/2}}{[2m(E_F + W)]^{1/2} - (p_F{}^2 - p_r{}^2)^{1/2}}\right),$$

$$p_r \leq p_F\,.$$

To translate this probability into a predicted angular correlation, we again assume that the void walls are oriented randomly, so that $\vec{p}_r$ may point in any direction. The probability that the tip of $\vec{p}_r$ lies in a given volume element $d\vec{p}$ is then proportional to

$$[P(\vec{p})/4\pi p^2]\, d\vec{p}\,.$$

The probability of observing a coincidence at a given angle is then found by integrating this expression over a plane in p space. If $p_\perp = \theta mc$ is the component of $\vec{p}$ perpendicular to this plane, and $p_\parallel$ is the component of $\vec{p}$ parallel to this plane, the integral is

$$\int_0^{(p_F{}^2 - p_\perp^2)^{1/2}} \ln\left(\frac{[2m(E_F + W)]^{1/2} + [p_F{}^2 - (p_\parallel^2 + p_\perp^2)]^{1/2}}{[2m(E_F + W)]^{1/2} - [p_F{}^2 - (p_\parallel^2 + p_\perp^2)]^{1/2}}\right) \times \frac{2\pi p_\parallel}{\sqrt{p_\parallel^2 + p_\perp^2}}\, dp_\parallel\,.$$

After numerical integration of this expression, the resulting function of $p_\perp$, or θ, is convoluted with a Gaussian function of standard deviation 1.4 mrad, describing the momentum of the positron. This value, which gives the best fit to the data, is smaller than the momentum of the positron in the surface state computed by Hodges and Stott,[14] but their larger momentum results from the simplifying assumption that the positron potential is a step function at the wall of the void; a more gradually varying potential would lead to a much lower positron momentum in the region where the electron is likely to be found.

The over-all "theoretical" distribution of Fig. 2 is found by adding together the "outside" and "inside" distributions, with the relative weights of the two determined primarily by fitting to the tail of the curve (beyond 10 mrad) on the assumption that all of the positrons are trapped in voids. The best fit is found by taking 65% "outside" and 35% "inside" annihilations.

The good fit to the data over the entire range of angles is impressive, in view of the fact that so few adjustable parameters were used in the calculation. The adjustable positron momentum affects only the fit near 0 and near 7 mrad, and the value of the electronic work function has little effect.[18]

The slight bump observed at the peak of the experimental distribution could be an indication that a small percentage (0.5%) of the positrons annihilate as singlet positronium (P_s). Obviously the evidence for this is not very strong, but in all the samples studied there is a distinct "break" on both sides of the curve near 1 mrad. This is illustrated in Fig. 3, where we show the slope of the observed data. To test this hypothesis, we are measuring the angular correlation from one sample in the presence of a magnetic field of 9 kG. The magnetic field causes a mixing of the $m = 0$ states of triplet and singlet positronium. This should result in an increased intensity at zero angle.[19]

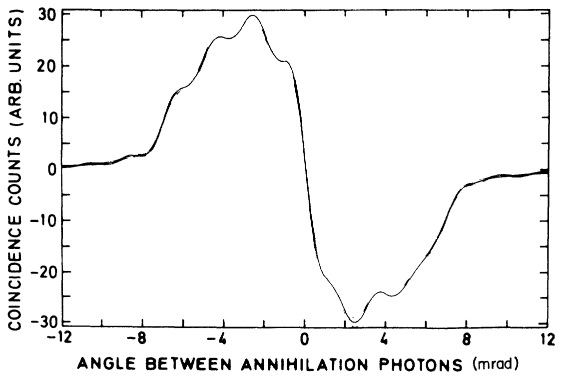

FIG. 3. Slope of the curve for irradiated Al shown in Fig. 1. The data have been fitted to a smooth curve by means of spline functions. Note the distinct peak at 0.92 mrad on *both* sides of zero angle. Indicated is an "error band" which results from the fitting procedure and is due to the statistical uncertainties of the experimental points.

Finally, we note that Petersen *et al.*[20] have performed lifetime measurements on another Al single crystal from the same irradiation experiments. Their results suggest that over 90% of the positrons are trapped in the voids prior to annihilation.

In our calculation we have assumed that 100% of the positrons were trapped in the voids; however, the assumption of 90% trapping would not seriously affect the fit to our data but would simply change the relative percentage of "inside" and "outside" annihilations of trapped positrons.

With the information reported here on the behavior of positrons in large voids, we are now in a better position to study the effects of varying void sizes by annealing treatments below 325 °C. Such experiments are now in progress.

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[1] J. E. Epperson, R. W. Hendricks, and K. Farrell (unpublished).

[2] R. W. Hendricks, J. Schelten, and W. Schmatz (unpublished).

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

[4] J. D. McGervey and W. Triftshäuser, Phys. Lett. A 44, 53 (1973).

[5] I. K. MacKenzie, Phys. Lett. A 30, 115 (1969).

[6] A. Seeger, J. Phys. F 3, 248 (1973).

[7] O. Mogensen, K. Petersen, R. M. J. Cotterill, and B. Hudson, Nature 239, 98 (1972).

[8] R. M. J. Cotterill, I. K. MacKenzie, L. Smedskjaer, G. Trumpy, and J. Träff, Nature 239, 99 (1972).

[9] Obtained from Cominco Inc., Spokane, Wash.

[10] Traces of Sc^{46}, Zn^{65}, and Co^{60} were found; the estimated purity of the crystals after growth, irradiation, and cleaning was $\approx 99.99\%$.

[11] M. Kiritani, Y. Shimomura, and S. Yoshida, J. Phys. Soc. Jap. 19, 1624 (1964).

[12] N. H. Packan, Oak Ridge National Laboratory Report No. ORNL-TM-3109, 1971 (unpublished).

[13] T. M. Patterson and A. T. Stewart, in *Positron Annihilation*, edited by A. T. Stewart and L. O. Roelling (Academic, New York, 1967).

[14] C. H. Hodges and M. J. Stott, Solid State Commun. 12, 1153 (1973).

[15] This observation implies a high positron momentum, in contrast to the suggestions of (7) that in their Mo samples the positrons can be described by wave functions corresponding to the zero-point energy in the entire void volume. At this point, it is not clear whether this is a result of the significant differences in void sizes between the Al and Mo specimens.

[16] Of course the void walls are not actually randomly oriented, since they are $\{111\}$ planes in a single crystal. But this approximation seems to give reasonable agreement with our results.

[17] Note that the p_z here is the p_z which characterizes the state in momentum space, and is not the observed p_z, which depends on the tail of the wave function.

[18] A work function of 1.5 eV gives the best fit, but the normal work function of 4.1 eV gives a curve only 0.1 mrad broader. One should expect the presence of the positron to reduce the electronic work function.

[19] M. Heinberg and L. Page, Phys. Rev. 107, 1589 (1957).

[20] K. Petersen, N. Thrane, G. Trumpy, and R. W. Hendricks (unpublished).