Appl. Phys. 4, 343—347 (1974)

Applied Physics

Diffusion Constant and Surface States of Positrons in Metals*

Robert Paulin and Roger Ripon

Institut National des Sciences et Techniques Nucléaires Saclay, France

Werner Brandt

New York University, New York, N. Y. 10003, USA

Received 26 November 1973 / Accepted 22 April 1974

Abstract. Positron lifetime spectra and angular correlation curves for seven fine-grained powders of Fe, Co, Ni, and W are analyzed. From the lifetime data, the positron diffusion constant in metals at $T = 300\,^{\circ}\mathrm{K}$ was found to be $D_+ = (1.0 \pm 0.5) \times 10^{-2}\,\mathrm{cm}^2\,\mathrm{sec}^{-1}$. Evidence is presented that positrons are trapped in metal surface states.

Index Heading: Positron annihilation

If the motion of thermalized positrons in solids is diffusion limited, their rate of trapping at defects, κ_d, and their trapping or escape rate at surfaces, κ_s, are proportional to the positron diffusion constant D_+ in the bulk of the solid [1]. For point defects, κ_d depends on the effective positron-capture radius of the defect, r_d, and grows linearly with the defect concentration C_d. The surface trapping rate, κ_s depends essentially on the surface-to-volume ratio of the solid. For example, in a crystal of atomic cell volume Ω, defects can trap positrons at the rate $\kappa_d = 4\pi r_d D_+ C_d/\Omega$. If the crystal has the shape of a small sphere of radius R, the surface can trap positrons at the rate $\kappa_s = \pi^2 D_+/R^2$. This suggests that D_+ can be determined from the positron annihilation characteristics in small solids through the dependence of κ_s on their surface-to-volume ratio, and then used to make absolute determinations of defect concentrations in the crystal bulk through measurements of κ_d. In pursuing such a program, we measured the positron annihilation characteristics in small-grained powders of Fe, Co, Ni, W, and two FeNi alloys. They yield the value $D_+ = (1.0 \pm 0.5) \times 10^{-2}\,\mathrm{cm}^2\,\mathrm{sec}^{-1}$ for the positron diffusion constant in such metals at 300 °K. The powder grains were so small compared to the range of the positrons emitted from sources of ^{22}Na and ^{64}Cu that the positrons were uniformly deposited throughout each grain. After thermalization, positrons diffuse until they either annihilate in the crystal bulk, with lifetime τ_c, or reach the surface where they escape or are trapped to annihilate with lifetimes $\tau_s > \tau_c$. Positrons reaching the surface manifest themselves in the lifetime spectra through a long-lifetime component with intensity Φ_s given by [1],

$$\Phi_s = \mu \frac{\beta}{g_s} \frac{\mathrm{I}_{\mu/2}(g_s/\beta)}{\mathrm{I}_{(\mu/2)-1}(g_s/\beta)}, \tag{1}$$

where

$$\beta = (D_+ \tau_c)^{1/2}/R, \tag{2}$$

$$g_s = (1 - \tau_c/\tau_s)^{1/2}. \tag{3}$$

$\mathrm{I}_n(x)$ denotes the modified Bessel function of order n; μ is a geometrical factor with the values $\mu = 1$ for foils, $\mu = 2$ for fibers, and $\mu = 3$ for spheres. The fraction F_s of all positrons that annihilates at the

---

* Paper A31 presented at 3rd Internat'l Conf. Positron Annihilation, Otaniemi, Finland (August 1973).

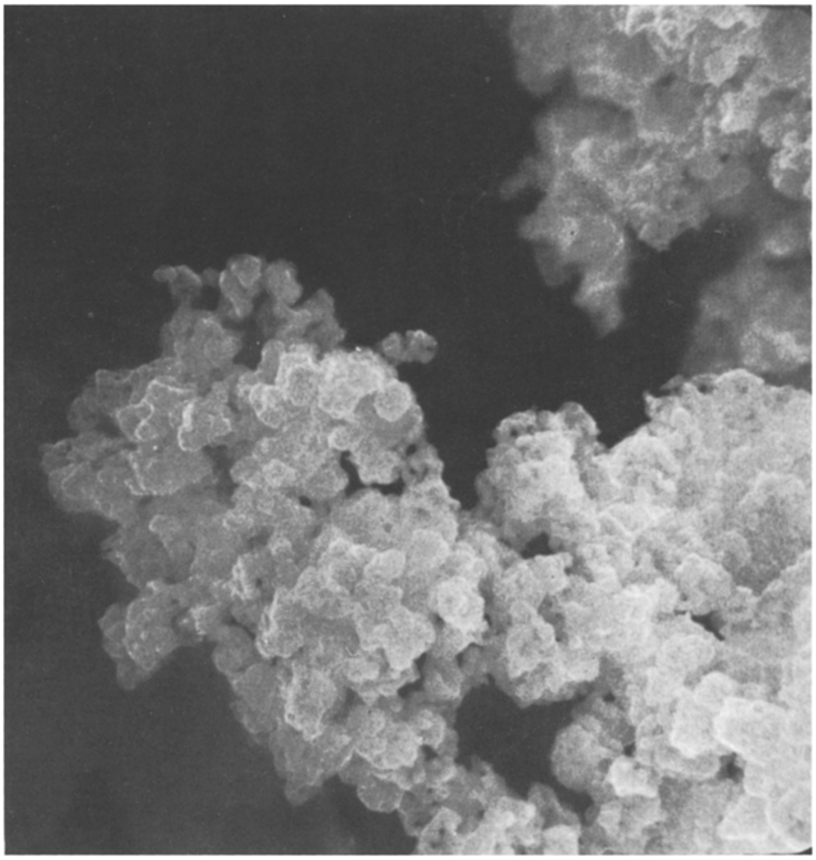

Fig. 1. $Fe_{0.9}Ni_{0.1}$ powder sample as seen in the electron microscope with 6850 magnification

surface is simply related to the function Φ_s by setting g_s equal to one,

$$F_s = \Phi_s(g_s = 1)\,. \tag{4}$$

Equation (1) applies to grains without defects and with shapes of well defined geometries. In real powders, the grains contain defects and have odd shapes, as illustrated in Fig. 1. These two difficulties can be overcome as follows. Irrespective of the particular geometry, (1) can be approximated for $\mu = 2$ and 3 within the experimentally attainable accuracy by

$$\Phi_s = 1 - e^{-1.1\,Sd(D_+\tau_c)^{1/2}/g_s}\,, \tag{5}$$

where S is the specific surface of the powder (in cm^2/g) and d the specific gravity (in g/cm^3) of the grain material. Figure 2 compares (5) with the exact (1). The powder constant S can be determined independently by a variety of methods. If a fraction of positrons is trapped by defects along their diffusion paths in the grains, one observes an effective diffusion constant D_+^{eff} for the arrival rate at the surface which is related to D_+ as

$$D_+^{\mathrm{eff}} = \frac{D_+}{1 + \kappa_d \tau_c / g_s^2} \equiv f D_+\,. \tag{6}$$

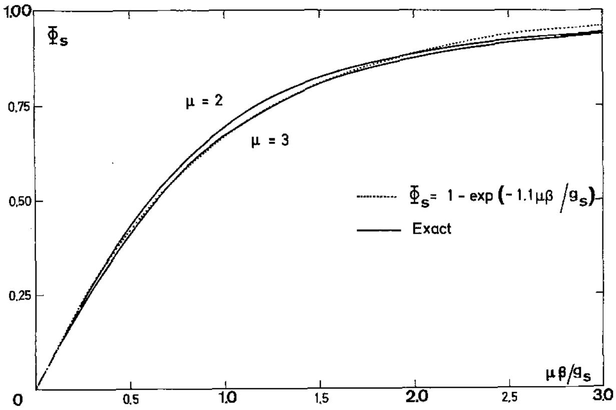

Fig. 2. Exact solutions of Φ_s from (1) for $\mu = 2$, 3 compared to the approximate expression of Φ_s given by (5)

Table 1. Positron lifetime and angular correlation data in metal powders. The uncertainties in the lifetimes are ±5%, in the intensities ±10%, and in the changes of zero-angle count rates (last column) ±5%

Material	r_s [a.u.]	S^e [$10^4\,\mathrm{cm}^2/g$]	Sd [$10^6\,\mathrm{cm}^{-1}$]	τ_1 [nsec]	τ_2 [nsec]	$I_2 = 1 - I_1$[f]	$\Delta I_0/I_{0c}$
Fe[a]	2.1	4.0	0.32	0.21	0.45	0.23	0.105
Fe[b]	2.1	0.48	0.04	0.19	0.45	0.04	0.04
Co[c]	2.1	4.35	0.39	0.20	0.37	0.29	0.15
Ni[a]	2.1	3.45	0.31	0.16	0.31	0.48	0.21
W[d]	1.6	0.70	0.135	0.21	0.45	0.09	—
$Fe_{0.9}Ni_{0.1}$[a]	2.1	12.8	1.02	0.21	0.40	0.42	0.19
$Fe_{0.45}Ni_{0.55}$[a]	2.1	7.3	0.61	0.20	0.35	0.38	0.15

[a] Powders kindly supplied by Dr. P. Dugleux, Ecole des Mines, Paris; the method of preparation is described in J. L. Doremieux, P. Dugleux, and G. Ciseron, Silicates Industriels **37**, 125 (1972).

[b] Manufactured by O.N.I.A., Toulouse, France.

[c] Manufactured by Ugine-Carbone, Grenoble, France.

[d] Purchased from Koch-Light, Colnbrook Bucks, England (Catalogue N° 8768 w).

[e] [4], S values are reproductible to ±2%.

[f] All but the Fe ($Sd = 0.04$) and W powders show third components of relative intensities $I_3 = (2-8)\,10^{-3}$ and lifetimes $\tau_3 \gtrsim 13$ nsec.

The factor f can be obtained from lifetime measurements. The positrons trapped in defects annihilate with lifetimes $\tau_d > \tau_c$. Normally they cannot be resolved as a separate component from those annihilating in the bulk with lifetime τ_c. Rather, a mean lifetime $\bar{\tau}$ intermediate between τ_c and τ_d is observed, which is related to κ_d as

$$\kappa_d \tau_c = \frac{\bar{\tau} - \tau_c}{\tau_d - \bar{\tau}} . \tag{7}$$

The factor f in (6) becomes

$$f(\bar{\tau}, g_s) = \left[1 + \frac{\bar{\tau} - \tau_c}{g_s^2 (\tau_d - \bar{\tau})} \right]^{-1} . \tag{8}$$

Thus, even though powders are usually composed of imperfect and irregularly shaped grains, the intensity of the lifetime component Φ_s attributable to positrons annihilating in the surface with lifetime τ_s can be expressed accurately in closed form as

$$\Phi_s = 1 - \exp\{-1.1\, Sd [D_+ \tau_c f(g_s, \bar{\tau})]^{1/2} / g_s\} . \tag{9}$$

Accordingly, Φ_s depends on positron lifetime data through $\bar{\tau}$, τ_c, τ_d, and τ_s, and on the grain surface-to-volume ratio through the powder constant Sd. This leaves D_+ to be determined from measurements of Φ_s.

Positron lifetime spectra were measured on the seven powders listed in Table 1. Two components were resolved of relative intensities I_1 and $I_2 = 1 - I_1$, and lifetimes τ_1 and τ_2, respectively.

We identify τ_1 with $\bar{\tau}$, I_2 with Φ_s, and τ_2 with τ_s. Independent measurements on well annealed iron and nickel slabs yielded only one lifetime, 0.16 nsec, which we take to be equal to τ_c. For τ_d we chose the value 0.22 nsec as a suitable upper limit for $\bar{\tau}$ based on our measurements on all powders. On rearranging (9), we show in Fig. 3 the quantity $Y = g_s/[1.1\, f(g_s, \bar{\tau})^{1/2} \ln(1 - I_2)^{-1}]$, based only on lifetime data,

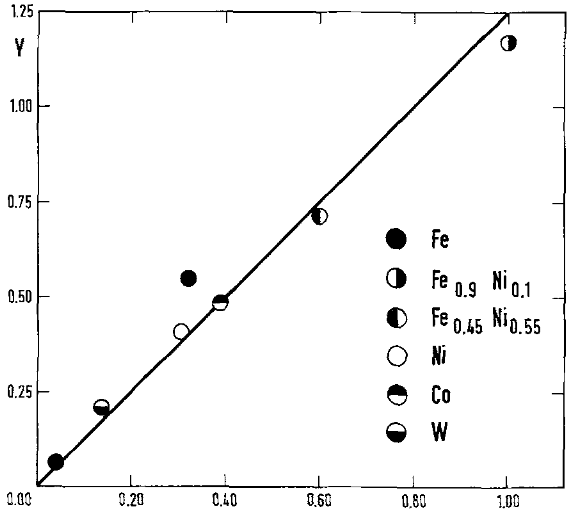

Fig. 3. The function Y discussed in the text versus Sd. The slope of the best straight line through the experimental points has the value $(D_+ \tau_c)^{1/2} = 1.25 \times 10^{-6}$ cm

plotted versus the independently determined powder variable Sd [4]. The locus of the points forms a straight line with the slope $(D_+\tau_c)^{1/2} = 1.25 \times 10^{-6}$ cm, corresponding to a positron diffusion constant $D_+ = (1.0 \pm 0.5) \times 10^{-2}\,\mathrm{cm}^2\ \mathrm{sec}^{-1}$ at $T = 300\,°\mathrm{K}$. This result agrees with the value $D_+ = 1.3 \times 10^{-2}\,\mathrm{cm}^2\,\mathrm{sec}^{-1}$ calculated from a theory based on positron-electron scattering [5, 6]. It opens the way to absolute determinations of defect concentrations in metals from positron annihilation measurements.

Our analysis attributes the long lifetime component to positron states in the metal surface. To support this assertion we measured the angular correlation curves for these powders with 1 mrad resolution and compared them with those obtained for well-annealed poly crystalline Fe and Ni slabs. The angular correlation in the powders is always narrower than in the annealed large slabs. The narrowing can be expressed in terms of the change of the count rates I_0 at zero angle, normalized to the total number of counts over all angles, relative to that in the annealed slabs, I_{0c}. They are listed as $\Delta I_0/I_{0c} \equiv (I_0 - I_{0c})/I_{0c}$ in the last column of Table 1. For a first orientation, we attribute most of the narrowing to positrons annihilating in surface states, and neglect the narrowing contributed from positrons annihilating in defects inside the grains. The change in I_0 is given by

$$\frac{\Delta I_0}{I_{0c}} = F_s\left(\frac{I_{0s}}{I_{0c}} - 1\right), \tag{10}$$

where I_{0s} is the saturation value which would be obtained if all positrons were to annihilate in surface states. Figure 4 exhibits the experimental values of I_0/I_{0s} versus F_s as calculated with (4) and (9) from the lifetime data and the D_+ value given above. The slope of the straight line yields the value $I_{0s}/I_{0c} = 1.5$.

For a tentative discussion of the surface states, we assume that the electron density near the metal surface, located at $x = 0$, can be approximated by

$$\varrho(x) = 3/4\pi r_s^3(x) = (\varrho_0/2)\{1 - \mathrm{sgn}\,x[1 - \exp(-|x|/a_s)]\}, \tag{11}$$

where $\varrho_0 = 3/4\pi r_s^3$ is the conduction-electron density in the bulk at $x \ll 0$, r_s the interelectronic distance in units of $a_0 = 0.53$, and $a_s \simeq r_s^{1/2}$ the surface screening length. The r_s values of the metals under consideration are listed in Table 1.

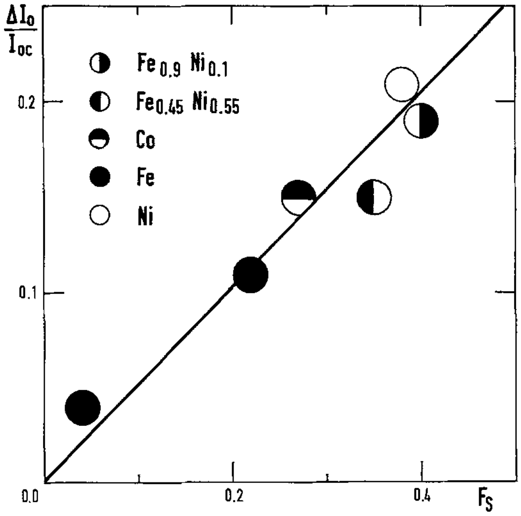

Fig. 4. The narrowing of the angular distribution, as measured through the relative variation of count rates at zero angle, versus the fraction of positrons trapped on the surface, cf. (10)

In the statistical approximation, the lifetime of positrons located at x can be estimated from the relation [7]

$$\tau_s(x) = [r_s^3(x)/12]\,\{1 + [r_s^3(x) + 10]/6\}^{-1}\ \mathrm{nsec}. \tag{12}$$

For the "clean" surfaces of Ni grains one finds that $\tau_s(x) = \tau_2$ when $x \simeq a_s$. Recently Smith *et al.* [8] reported an Hartree-Fock calculation of the interaction of a proton with a W surface which has an energy minimum of ~ 1 eV just at $x \sim a_s$. Hodges and Stott [9] reach similar conclusion for positrons. The larger values of τ_2 in Fe and FeNi alloys presumably result from the fact that their surfaces are affected by oxide formation during their passivation treatment, which should reduced the enhancement of the electron density available for annihilation in positron surface states. In this model, positrons trapped at the surface at x experience, on the average, the electron density $\varrho(x) = 3/4\pi r_s^3(x)$, enhanced by an enhancement factor $\approx 1 + (r_s^3 + 10)/6$, cf. (12). In the statistical approximation the electron gas at x has a Fermi momentum

$$p_F(x) = (9\pi/4)^{1/3}/r_s(x). \tag{13}$$

The normalized angular distribution of γ-ray pairs resulting from positron-electron annihilations at x would then have a zero angle count rate

$$I_{0s} = 3/4\,p_F(x) = (3/16\pi)^{1/3}\,r_s(x). \tag{14}$$

In the bulk, annihilations with the valence electrons are characterized by the count rate $I_{0c}^{v}=3/4\,p_F$ and with core electrons by I_{0c}^{c}, such that

$$I_{0c}=(I_{0c}^{v}+C\,I_{0c}^{c})/(1+C)\,, \qquad (15)$$

where C is the ratio of core-to-valence annihilation probabilities. Combining (14) and (15), one obtains

$$\frac{I_{0s}}{I_{0c}}=M\frac{1+C}{1+DC}\,, \qquad (16)$$

with the abbreviations

$$M\equiv\frac{I_{0s}}{I_{0c}^{v}}=\frac{p_F}{p_F(a_s)} \quad \text{and} \quad D\equiv\frac{I_{0c}^{c}}{I_{0c}^{v}}\,.$$

The core contribution to the angular correlation curve for the metals considered here are large, and clear separations into core and valence contribution are problematic. Assuming gaussian core contributions, we estimate from measurements of the angular correlations of annealed Ni and Fe crystals that $C\simeq 2$ and $D\simeq 0.4$, so that $(1+C)/(1+DC)\simeq 1.7$. From the lifetimes it follows, if the statistical approximation (13) applies, that $M\simeq p_F/p_F(x\simeq a_s)=(2e)^{1/3}=1.8$, yielding by this route $I_{0s}/I_{0c}\simeq 3$. This value is to be compared with the empirical value 1.5 from Fig. 4.

We conclude that the angular correlation data and lifetime data on fine metal powders qualitatively show the same trends and are consistent with the idea of positron diffusion to and trapping by surface states. The quantitative agreement is poor if the discussion is based on the interrelation between momentum and density implied by the statistical approximation (13). Apparently, the positrons in surface states of Fe and Ni encounter sufficiently many electrons carrying high momenta from the metal *d* shells and presumably also from the surface oxygen layers to reduce I_{0s}/I_{0c} by a factor two relative to what one would have expected on the basis of the statistical conduction electron gas model of a metal surface.

References

1. W. Brandt, R. Paulin: Phys. Rev. B**5**, 2430 (1972)
2. R. Paulin, G. Ambrosino: J. Phys. (Paris) **29**, 263 (1968)
3. I. K. MacKenzie, T. L. Khoo, A. B. MacDonald, B. T. A. MacKee: Phys. Rev. Letters **19**, 946 (1967)
4. B. Rasneur (C.E.N. Saclay, France): Kindly measured the *S* values by the B.E.T. method with argon
5. W. Brandt: Appl. Phys. **5** (October 1974)
6. R. Paulin, R. Ripon, W. Brandt: Phys. Rev. Letters **31**, 1214 (1973)
7. W. Brandt, J. Reinheimer: Phys. Letters **35**A, 109 (1971)
8. J. R. Smith, S. C. Ying, W. Kohn: Phys. Rev. Letters **30**, 610 (1973)
9. C. H. Hodges, M. J. Stott: Sol. State Commun. **12**, 1153 (1973)