Temperature dependence of positron diffusion in metals

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Data are presented for the positron diffusion coefficient D_+ in single crystals of Mo, Nb, Al, and Cd. The data clearly demonstrate that the temperature dependence of D_+ is much stronger than the $T^{-0.5}$ that is theoretically predicted, ranging from about $T^{-0.8}$ to a maximum of $T^{-2.6}$. In addition, our results show an anisotropy for the temperature dependences of D_+ in two principal directions of Cd ($T^{-1.0}$ along an a axis versus $T^{-2.6}$ along the c axis) which cannot be described by a simple diffusion model.

For more than a decade the widely adopted view has been that positron diffusion in metals is limited primarily by positron-acoustical phonon scattering (relaxation time $\equiv \tau_{ph}$). In this extreme, Bergersen et al.[1] show that the diffusion coefficient D_+ should vary with temperature as $T^{-1/2}$, with only minor deviation due to the much weaker contributions of conduction electron and impurity scattering (τ_{el} and τ_i, respectively). In this Rapid Communication we present evidence obtained with a variable-energy positron beam that the dependence of D_+ on temperature is in fact much stronger than $T^{-1/2}$ in all metals we have studied so far, which represent all three of the principal crystal structures. In addition we observe a strong asymmetry in the temperature dependence of D_+ for Cd. Finally, the data indicate that the temperature dependence of D_+ may not be universal as was predicted by the simple model of Ref. 1, although it is possible that the differences we observe are in part related to trapping or scattering from defects which remain even after careful annealing of the single crystals.

The positron diffusion coefficient D_+ can be written in terms of the relaxation time for scattering, τ,

$$1/\tau \equiv 1/\tau_i + 1/\tau_{el} + 1/\tau_{ph} \; ,$$

as

$$D_+ = \frac{k_B T \tau}{m^*} \; , \tag{1}$$

where m^* is the effective positron mass. The dominant contribution to the relaxation time is thought to be that due to positron-acoustical phonon scattering, which has been found to be[1]

$$\tau_{ph} = \frac{\pi \hbar^4 B}{\sqrt{3} E_d^2 (m^* k_B T)^{3/2}} \; , \tag{2}$$

where B is the bulk modulus and E_d is the deformation potential. E_d is expressed as the sum of contributions due to volume dependence of the positron's zero-point energy in the ionic lattice E_0, the electron-positron correlation E_{corr}, and the electron chemical potential μ, viz.,

$$E_d = \frac{r_s}{3} \frac{dE_0}{dr_s} + \frac{r_s}{3} \frac{dE_{corr}}{dr_s} + \Omega \frac{d\mu}{d\Omega} \; , \tag{3}$$

where r_s is the usual free-electron radius and Ω the volume. Contributions to the relaxation time due to conduction electron and impurity scattering are several orders of magnitude

weaker than those for phonons (except for relatively high impurity concentrations at temperatures below ≈ 10 K), so that the obvious result from (1) and (2) above is that D_+ is roughly proportional to $T^{-1/2}$.

The development of variable-energy positron beams over the last several years,[2] together with advances in data taking and handling techniques, now make it possible to measure the positron diffusion length L_+ in the near-surface (≈ 1 μm) region of single crystals. L_+ is related to D_+ by

$$L_+ = (D_+ \tau_{eff})^{1/2} \; , \tag{4}$$

where τ_{eff} (which is the effective lifetime of the positron in a freely diffusing state[3]) is typically only weakly dependent on temperature in metals, before the onset of thermally generated vacancies. For the purposes of data presentation in the present Rapid Communication we will assume τ_{eff} is independent of temperature. The measurement of D_+ is discussed in detail in several references,[2-5] so we present here only a brief description.

The relative fraction of incident positrons on a crystal which diffuse back to the crystal surface can be determined by measuring the amount of orthopositronium, Ps, which decays in the vacuum, since Ps does not form in a metal. This fraction can be determined on the basis of the measured-annihilation gamma-ray energy spectrum and is given by

$$f = \left[1 + \frac{P_1}{P_0} \left(\frac{R_1 - R}{R - R_0} \right) \right]^{-1} \; . \tag{5}$$

In the above, $R = (T - P)/P$, where T and P refer to the total and peak counts, respectively, in the annihilation gamma-ray energy spectrum, and the subscripts 0 and 1 refer to the situations where 0% and 100% of the incident positrons form Ps. By assuming that the stopping or implantation profile of the incident positrons is exponential, the dependence of f on incident-positron energy E is[4]

$$f = f_0 [1 + (E/E_0)^n]^{-1} \; , \tag{6}$$

where f_0 is the relative probability that a thermalized positron after arriving at the surface will be emitted into the vacuum as Ps, E_0 is the energy at which half of the incident positrons diffuse back to the surface, and n is an exponent related to the mean depth of the implantation profile, which has been experimentally determined to be ≈ 1.6.[4,6] We

have fixed n at 1.6 for the present analysis for reasons we will discuss later in the text. The so-called half-energy E_0, which is simply extracted from a fit of Eq. (6) to the data for f vs E, is related to D_+ through a proportionality constant A:

$$L_+^2 = (AE_0^n)^2 = \tau_{\text{eff}}D_+ \quad , \tag{7}$$

where

$$A = (3.3 \times 10^{-6} \text{ g/cm}^2)/(\text{density} - \text{keV}^n)$$

was found empirically by Mills and Wilson.[6]

The data for L_+^2 ($\propto D_+$) versus temperature are shown in Fig. 1 for the four different metals we have measured so far: Mo, Nb, Al, and Cd, representing all three of the principal (metallic) crystal lattices (bcc, fcc, and hcp, respectively). Data were generally taken as a function of increasing temperature for experimental convenience, although those data shown for Cd represent both decreasing ($\bullet$) and increasing ($\times$ and $\triangle$) temperature cycles. In all cases the temperature dependence observed for D_+ is much stronger than the $T^{-1/2}$, which would be predicted from Eqs. (1)–(4) above. The actual dependences, which were deduced from a simple linear regression, are shown on the figure beside the appropriate data and listed in Table I. Temperatures above or below which the data were excluded from the fits (indicated by dashed lines on the figure) were chosen for two reasons:

(1) High-temperature limits are the so-called threshold temperatures, at which positron trapping by thermally generated vacancies becomes observable in bulk-positron annihilation experiments.

(2) Low-temperature limits (for Al and Cd) were chosen somewhat arbitrarily, where the departure from linearity becomes obvious.

It is interesting to note that both the Cd and Al data at low temperatures show signs that the diffusion length is reduced beyond what would be expected from the power law deduced at higher temperatures. This may be due to positron localizing at defects or impurities which have a small
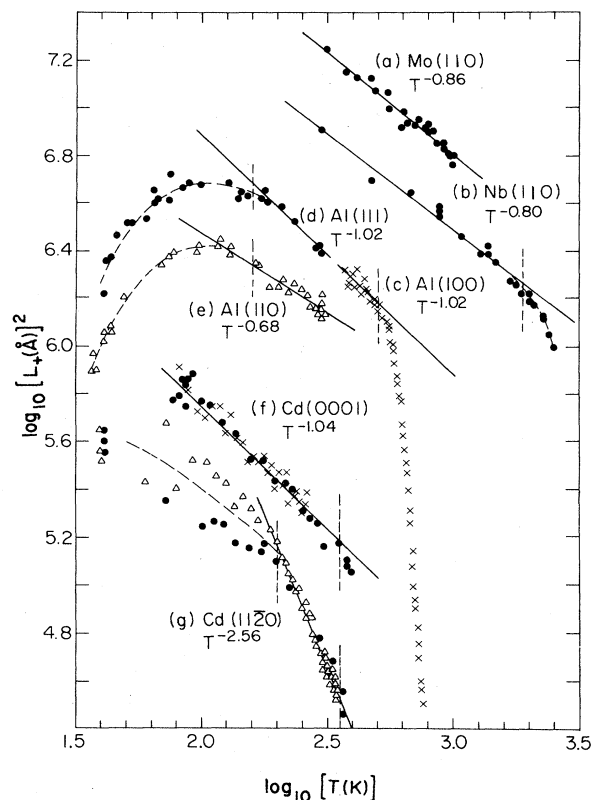

FIG. 1. Data are shown for the $\log_{10}$ of the positron diffusion length squared L_+^2, vs $\log_{10}$ of temperature for the four metals studied so far ($L_+^2 = \tau_{\text{eff}}D_+$). The slopes represented by the lines drawn through the data points are much stronger than the theoretically predicted[1] $T^{-1/2}$, which would be expected from positron-acoustical phonon scattering. Any temperature dependence associated with the effective lifetime τ_{eff} would be insignificant by comparison with the slopes observed. The vertical dashed lines indicate the limits of the fit which are listed in Table I together with the statistical and estimated systematic uncertainties.

TABLE I. The temperature dependences of the positron diffusion coefficient (D_+) are listed for the data shown in Fig. 1. To obtain these, a weak temperature dependence normally observed for the effective lifetime τ_{eff} in Eq. (4) was neglected. The temperature limits for the least-squares fit were chosen according to the prescription described in the text. Statistical uncertainty was determined by the maximum range of slopes which could conceivably fit the data. The systematic errors were determined to be less than the statistical errors by refitting the data with different parameters in Eqs. (5) and (6). In the case of Al(110), where it is suspected that the annealing was insufficient to remove enough of the defects caused by sputter cleaning, the error is thought to be somewhat larger. Note also that the orientations for the Cd crystals were starting orientations ($\pm 2°$), and recrystallization during part of the heat treatment changed these by as much as $10°$.

Figure curve	Sample	Date data taken	Plot offset	Fit limits		x_T (D_+)	Statistical uncertainty
				Low T	High T		
(a)	Mo(110)	84/12	0.900	$\cdots$	$\cdots$	-0.86	$+30\%/-30\%$
(b)	Nb(110)	84/05	0.600	$\cdots$	1750	-0.80	$+23\%/-10\%$
(c)	Al(100)	83/05	0.337	$\cdots$	500	-1.02	$+62\%/-20\%$
(d)	Al(111)	82/12	0.250	160	$\cdots$	-1.02	$+33\%/-18\%$
(e)	Al(110)	82/11	0.150	160	$\cdots$	-0.68	$+60\%/-29\%$
(f)	Cd(0001)	81/07	0.100($\bullet$) 0.050($\times$)	$\cdots$	375	-1.04	$+17\%/-17\%$
(g)	Cd(11$\bar{2}$0)	82/01	none	170	375	-2.56	$+18\%/-11\%$

positron-binding energy, as proposed earlier.[3] During the course of the present study we found that it was nearly impossible to remove this effect by any amount of annealing,[7] even though the samples used were high-purity single crystals. If this effect is indeed caused by positron trapping, the positron's environment in the trap must be similar to that in the unperturbed lattice, since low-temperature bulk Doppler-broadening measurements[8] in the same Al(110) crystal represented by curve (e), Fig. 1, revealed no peak narrowing down to 85 mK, such as would be observed for defect trapping.

It is generally true of all our low-temperature data that early measurements produced a flat, or even in some cases positive, dependence of D_+ on T, and that successive heat treatments were required to produce the negative slopes thought to be representative of "free" positron motion. The data shown in Fig. 1 represent the *most negative* slopes obtained in this way, although we have no evidence that defect trapping is not still playing a role. Because of this uncertainty we do not believe that the differences between temperature dependences quoted for the three orientations of Al are significant; however, we feel that those for the two orientations of Cd (which received the same heat treatments) are clearly separated. The two Cd crystals were oriented along the c and a axes when received; however, it has subsequently been discovered that at some point during the *in situ* heat treatment the Cd (0001) recrystallized approximately 10° off the original axis. Although it may turn out that more advanced crystal-preparation techniques yet to be determined lead to even more strongly negative dependences of D_+ on T, it is already clear even in these low-temperature measurements that they are stronger than $T^{-1/2}$ by a factor of $\simeq 2$ or more.

As discussed prior to Eq. (6) the positron implantation profile assumed for the present data analysis was exponential. Recent theoretical[9] and experimental[10] results indicate that a more appropriate description is the Makhovian profile, which looks something like a skewed derivative of a Gaussian. It was demonstrated in both Refs. 9 and 10 that the magnitude of D_+ or L_+ deduced from Ps-fraction data is significantly affected by the choice of profile (the exponential profile yields values which are too low); however, we have found in both this and other studies[4,11] that systematics observed (including temperature dependence) are not affected by the choice of profile. It is possible that the implantation profile would itself be a function of temperature as suggested by Nieminen and Oliva,[12] although we expect that this would be a relatively small effect. In the present analysis we have deliberately fixed the exponent $n = 1.6$ in the absence of a detailed description of the effect of temperature on the stopping profile.[9,12] Fitting Eq. (6) to the data with a different n produces very little change in the derived temperature dependence of D_+. In addition to changing the profile shape in the analysis we changed the parameters R_0, R_1, and P_1/P_0 [Eq. (5)] well outside the expected limits of experimental uncertainty. In all cases we

found that the slope measured for $\log_{10}(L_+)^2$ vs $\log_{10}(T)$ changed by less than $\pm 10\%$.

A further degree of caution must be exercised in comparing the absolute values of D_+ for the different specimens shown here, since not only is the magnitude of D_+ influenced by the stopping profile, but also by the geometrical details of the experiment. As an example, our test of varying P_1/P_0 by $\pm 25\%$ from the "best" value of 0.4 indicated that the temperature dependence of D_+ was not affected much at all, as we mentioned above. However, this same variation did lead to $\approx 50\%$ changes in the values deduced for D_+. The data compared here were taken at different times (Table I), often with different sample/detector geometries, which we have shown[13] can lead to significant deviation. In all cases, however, a value of D_+ of the order 1 cm^2/sec at room temperature was found. Comparison of relative magnitudes of D_+ for various orientations and/or materials would certainly be of interest, particularly in light of the data presented here. Such a study would, however, require a consistent sample-geometry, handling and data analysis.

The observation that D_+ is more strongly dependent on temperature than $T^{-1/2}$ was quite unexpected. Electron scattering would lead to a temperature dependence of T^{-1}, which is closer to what we observe, but the conclusion[1] that it is much weaker than acoustical phonon scattering seems reasonable. That implies that either phonon scattering has been incorrectly calculated or that the diffusion is limited by a much more complicated mechanism than has so far been described. The model of Ref. 1 includes the assumption that the deformation potential [Eq. (3)] is independent of temperature. The neglect of lattice expansion, which is suggested by this, may account for some of the discrepancy observed.[14] A more careful estimation of $E_d(T)$ would be useful before the temperature dependence of the positron diffusion can be accurately described.

In conclusion, we have presented data for the positron diffusion coefficient D_+ in a variety of metals which clearly demonstrate that positron motion in these samples is a much stronger function of temperature than expected. The data also show that the dependence of diffusion coefficient on temperature is anisotropic in Cd, suggesting that the simple relaxation-time approach for calculating positron diffusion may not be sufficient for this case. It is expected that future detailed measurements of other materials will reveal similar anisotropies.

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