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Positron Annihilation and Its Application to Defect Studies in Metals*

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I. INTRODUCTION

Because the positron was the first antiparticle to be discovered, it is not surprising that the fundamentals of positron physics are by now well documented. Modern quantum electrodynamics is capable of providing an explanation for all of the observed properties of the annihilation process wherein a positron and an electron are replaced in the final state by n photons ($n = 1, 2, 3 \dots$). In the decade of the fifties, perhaps due to the renewed interest in positrons aroused by quantum electrodynamics, studies of the annihilation process in solids began in earnest. It is not the purpose of this paper to exhaustively review the work which has followed since then. Reviews of this nature are readily available in the open literature.¹⁻⁶ Instead, we will concentrate upon recent developments in the application of positron annihilation to studies of imperfect solids. In particular, we will consider the present status of this field as it applies to metallic solids. After a brief review of positron physics in section two, in section three we will turn to a description of positron behavior in perfect metals. Section four will deal with the basic measurements that are performed to extract information about the electronic structure of solids from the annihilation photons. In section five, we will examine the recent experimental results that reveal the connection between positron annihilation and defects in metals. The sixth section will be devoted to a discussion of the model currently in use to explain the observations described in section five. The last part of the paper will be confined to speculations and suggestions for future work.

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II. FUNDAMENTALS OF POSITRON-ANNIHILATION SELECTION RULES

Being conjugate particles, the electron and positron have opposite parity so that the intrinsic parity of the annihilating pair must be odd. Thus the two states 1S_0 and 3S_1 both have odd parity. Now considering the parity of the n-photon states which result from the annihilation process, one finds that when $J = 0$ and $n = 2$, states of even or odd parity are allowed. Therefore the 1S_0 state can decay into 2 photons each of energy mc^2 ($= 511$ keV). On the other hand, when $J = 1$ annihilation into 2 photons is forbidden. Thus, the 3S_1 state cannot decay into 2 photons, but must decay into 3 or more. One-photon annihilation can occur, but it is essentially a three-body event, and the probability of its occurrence relative to that of two-photon annihilation is $\leq 7 \times 10^{-5}$.⁷ Thus, although in principle, one-quantum annihilation could furnish information about electron-electron correlations in solids, in practice it has not become a useful effect.

Experimental measurements of lifetimes in gases lead to the discovery that a positron and an electron can form a bound state. This is positronium, P_s , which is a hydrogen-like system with an energy level scheme analogous to that of hydrogen, but with a reduced mass of $m/2$ instead of m where m is the electron mass. Thus the energy levels of P_s are given by the relation,

$$E_n = -\frac{me^4}{4\hbar^2 n^2} \quad (1)$$

The P_s ionization potential is $\frac{1}{2}Ry = 6.8$ eV, and positronium exists in a 1S_0 or 3S_1 1S state. The lifetime of the singlet (para) 1S_0 state is 1.25×10^{-10} sec. whereas that of the triplet (ortho) 3S_1 state is 1.4×10^{-7} sec. The spin averaged lifetime $= 5 \times 10^{-10}$ sec. The ratio of the number of two-photon events to three-photon events is determined by the respective annihilation rates and statistical weights:

$$\frac{\text{2-photon annihilation rate}}{\text{3(3-photon annihilation rate)}} = \frac{1}{3} (1115) \approx 372.$$

Positron Sources

A search of the periodic table reveals that there are very few usable positron sources. A usable positron source in the present context is one that can be produced easily by neutron capture or through a charged-particle reaction, and that has a reasonably long half-life. A measure of the latter criterion is, of course, the ratio of the half-life to the duration of an experiment. Using these two criteria, one finds that the sources listed in Table I are of experimental value.

Table I. Positron Sources

Isotope	Half-life	Means of Production	End-point Energy
^{22}Na	2.58 a	$^{25}\text{Mg}(p, \alpha)^{22}\text{Na}$	0.54 MeV
^{65}Zn	245 d	$^{64}\text{Zn}(n, \gamma)^{65}\text{Zn}$	0.33 MeV
^{64}Cu	12.8 h	$^{63}\text{Cu}(n, \gamma)^{64}\text{Cu}$	0.66 MeV
^{58}Co	71 d	$^{58}\text{Ni}(n, p)^{58}\text{Co}$, $^{65}\text{Mn}(\alpha, n)^{58}\text{Co}$	0.48 MeV
^{55}Co	18.2 h	$^{58}\text{Ni}(p, \alpha)^{55}\text{Co}$, $^{56}\text{Fe}(p, 2n)^{55}\text{Co}$	1.50 MeV
^{69}Ge	40 h	$^{69}\text{Ga}(d, 2n)^{69}\text{Ge}$	1.22 MeV
^{57}Ni	36 h	$^{56}\text{Fe}(^3\text{He}, 2n)^{57}\text{Ni}$	0.85 MeV
^{90}Nb	14.7 h	$^{90}\text{Zr}(p, n)^{90}\text{Nb}$, $^{90}\text{Zr}(d, 2n)^{90}\text{Nb}$	1.50 MeV

Typical source strengths used in experiments range from the order of μCi to a few mCi .

The most frequently used member of this group is ^{22}Na . It is readily available albeit expensive in large strengths. Its long half life makes it ideal for all of the typical positron annihilation experiments. A less expensive alternative is ^{58}Co which can be produced in a nuclear reactor.

Recently,⁸ a series of experiments was performed in which each positron source was created in the interior of the metal under investigation. The purpose of this technique was to eliminate possible contributions to measured positron lifetimes arising from source and surface effects. Using photonuclear reactions, Souder was able to produce internal positron sources in Sc, Zn, Ni, K, Mo, Ag and Na. While some differences were noted in those cases where a comparison could be made, the experimental difficulties encountered tended to introduce new uncertainties. The method, of course, does not lend itself to such widespread usage as the conventional external source technique. Weisberg has studied and discussed the role of surfaces in his thesis.⁹

III. BEHAVIOR OF POSITRONS IN METALS

Thermalization

Note that the end-point energies of the positrons emitted from the sources listed in Table I of the preceding section are all of the order of a few tenths of an MeV. As they enter a metal, then, the positrons are moving rapidly, and one must ask how they lose their energy. The relevant questions are: how much time does a positron require to reach thermal energies, and how does this time, τ_T , compare with the lifetime against annihilation?

These questions were first investigated analytically by Lee-Whiting.¹⁰ His calculation predated the modern many-body techniques and neglected all correlations. Carbotte and Arora¹¹ re-examined the process using standard propagator formalism. Considering only positron

electron interactions, they assumed that the positron loses energy only through the creation of electron-hole pairs. The rate of energy loss is then given by the imaginary part of the positron self-energy operator. We note that Carbotte and Arora only calculated the energy-loss rate for low-energy positrons ($E_e \gtrsim 5$ eV), and thereby neglected plasmon creation. In fact, plasmon creation is the dominant mode of energy loss in the kilovolt region.

Carbotte and Arora found that most of the thermalization time occurs toward the end of the positron range. They also noted that the thermalization time increases with increasing electron density. This is because screening increases with electron density, and the stronger the screening the weaker the coupling of the positron to the electronic system.

For positron energies $\leq \sim 0.1$ eV, they obtained an expression identical to Lee-Whiting's when the Thomas-Fermi screening length for the electron gas is used as the screening parameter in Lee-Whiting's formula. Their more exact treatment reveals that at room temperature τ_T for Na and Al are much shorter than the lifetime for annihilation. In fact this is true for Na throughout the temperature range from 110K to 600K. However, for Al, $\tau_T > \tau_{\text{Annih.}}$ at 110K. Thus thermalization is not complete in this case. On the other hand, Carbotte and Arora pointed out that the time required for a positron to fall to an energy of ~ 0.1 eV is very short compared to typical lifetimes. Therefore, they assert, it is generally a good assumption that the positron momentum is negligible at the instant of annihilation.

Recently, consideration has been given to effects of the positron-phonon interaction in metals by Mikeska.¹² He has investigated the role of this interaction in the thermalization process as well as its effect upon the positron effective mass. His treatment considers positrons in thermal equilibrium with the electrons and phonons. He finds that although the phonon contribution to the effective mass is

negligible, for thermal energies the phonon contribution to the momentum distribution of the positrons can become much larger than the electron contribution. The rate of energy loss due to phonon emission at $T = 0$ is,

$$R_{ph}(p)_{T=0} = \frac{\eta\pi}{k_F} C^2 p^3, \quad (2)$$

where C is the velocity of sound, k_F is the wave vector at the Fermi energy, p is the momentum of the positron, and η measures the strength of the positron-phonon interaction and is of order unity.

The rate of energy loss to electrons in the same region according to Carbotte and Arora is:

$$R_{elec.-hole\ pairs} = \frac{1}{105} \frac{\pi}{k_F} \frac{p^6}{m^2 k_F} \quad (3)$$

Comparing Eq. 2 and Eq. 3, Mikeska observed that in the case of sodium, for example, $R_{ph} > R_{eh}$ for $p^2/2m < 230K$.

Moreover, he found that the positron momentum distribution is not Boltzmann-like. If one identifies the 2nd moment of the momentum distribution with the observed minimum temperature of the positron then for the Mikeska distribution function,

$$\left\langle \frac{p^2}{2m} \right\rangle \approx 1.8 \left(\frac{3}{2} kT \right)$$

Therefore the mean energy of the positron is larger than that predicted on the basis of a Boltzman distribution.

It turns out theoretically that the positron effective mass is nearly equal to unity, but an apparent effective mass closer to two has been deduced experimentally on the incorrect assumption that the

positron momentum is described by a Boltzmann distribution. Thus, Mikeska's results apparently explain most of the discrepancy between the theoretical effective mass derived neglecting positron-phonon interactions, and that deduced from the observed thermal smearing of the experimental momentum distribution

Charge Density Enhancement

A natural quantity to investigate in studying positron annihilation in metals is the annihilation rate, or its reciprocal, the lifetime. In metals one expects that this quantity will provide information about the electron density at the positron. Generally, in this field, electron density is described in terms of a dimensionless parameter r_s , the radius of the sphere which contains just one electron. Thus, if n is the number of valence electrons per cm^3 then

$$n = \left[\frac{4}{3} a_0^3 r_s^3 \right]^{-1} \quad (4)$$

where a_0 is the radius of the first Bohr orbit.

From Sommerfeld's free electron theory one finds that

$$\lambda_{\text{Somm.}} = 12 r_s^{-3} \times 10^9 \text{ sec}^{-1}.$$

This result predicts a rather strong variation of lifetime with electron density. However, this dependence is not observed. In fact, the variation of annihilation rate with r_s is found to be rather small; most metals exhibit lifetimes of about $1.5\text{--}2.0 \times 10^{-10}$ sec. The reason for the failure of the Sommerfeld theory is the strong Coulomb interaction between the electrons and the positron. Thus, it is not the average electron density that is important, but rather the electron density at the positron position. Calculations taking into account this fact have been performed by several authors.¹³⁻¹⁵

Most recent is the work of Sjölander and Stott¹⁵ in which a new method for handling screening effects is used to account for the strong electron-electron correlations. The electron distribution is given in terms of the positron-electron static pair-correlation function $g^+(r)$. Figure 1 taken from their paper illustrates the effect of the strong positron-electron attractive potential. The figure clearly shows that a positron in a metal becomes surrounded by its own polarization cloud. The total induced charge is unity however, so that total charge neutrality is preserved. The annihilation rates calculated on the basis of this theory are in good agreement with experiments in aluminum and in the alkali metals, except for cesium which corresponds to an r_s of about 5.7. The results become unrealistic beyond an r_s of about 5.

At present, there is no reason to believe that positronium is formed in metals. If it were, a so-far unobserved long lifetime should arise from 3S_1 annihilation. Or else, a rapid triplet-singlet conversion could give rise to an unobserved lifetime equal to four times the 1S_0 lifetime, i.e., 5×10^{-10} sec. The primary reason given for the absence of positronium is that a positronium-like bound state cannot form at normal metallic electron densities, but only at densities such that $r_s \geq 8.6$.¹⁶ For real metals $1.8 \leq r_s \leq 5.5$.

IV. EXPERIMENTAL METHODS OF INVESTIGATING POSITRON

ANNIHILATION IN SOLIDS

General Remarks

Since the two antiparticles disappear during an encounter, all information about the event is carried away by the photons. We have noted earlier that two-quantum annihilation is most common, and it is the event most often studied in metals.

Basically there are three types of measurements commonly performed.

One is a measurement of the positron lifetime, another is the Doppler broadening of the annihilation line, and the third is a measurement of the angular-correlation of two-photon annihilation radiation.

Suppose that $\Gamma^2(p)dp$ is the probability per unit time that annihilation into two photons whose total momentum lies between p and $p+dp$ takes place. Then it has been shown¹⁷ that if the electron is in a state ψ_i , and the positron in state ψ_t ,

$$\Gamma_i^{2\gamma}(p)dp = \frac{\alpha^3}{4\pi^2} \left| \int \psi_i(r) \psi_t(r) e^{ip \cdot r} dr \right|_{\hbar}^2 dp, \quad (5)$$

where atomic units have been used and the atomic unit of time is 2.42×10^{-17} sec. The annihilation rate into any total momentum then must be,

$$\Gamma_i^{2\gamma} = \int \Gamma_i^{2\gamma}(p) dp = \frac{\alpha^3}{4\pi^2} \int \left| \int \psi_i(r) \psi_t(r) e^{ip \cdot r} dr \right|_{\hbar}^2 dp. \quad (6)$$

By Parseval's theorem this becomes

$$\Gamma_i^{2\gamma} = 2\pi\alpha^3 \int |\psi_i(r) \psi_t(r)|^2 dr = 2\pi\alpha^3 \int |\psi_i(r)|^2 |\psi_t(r)|^2 dr, \quad (7)$$

the partial annihilation rate, λ_i . Summing over all occupied electron states we obtain the total annihilation rate, the reciprocal of which is the lifetime of the positron:

$$\tau^{-1} = \sum_{\text{occ. } i} \Gamma_i^{2\gamma}. \quad (8)$$

Angular-Correlation Measurements

Now let us consider a typical angular-correlation experiment. The sample and positron source are located, as shown in Figure 2, midway

between a pair of photon detectors. Generally a linear slit is placed in front of each detector and the sample-detector distance is made long enough so that the angular resolution is between 0.5 and 1.0 mrad. Appropriate lead shielding is placed around the source so that the detectors see only photons created in the sample.

If the annihilating pair were at rest in the center-of-mass system, then the two quanta would be emitted precisely in opposite directions in the laboratory system. We have concluded in our earlier discussion of thermalization that for most purposes one may assume that the positron is thermalized and, hence, it is essentially at rest. The annihilating electron, however, is not. Therefore, the center of mass of the annihilating pair is in motion, and the two photon directions deviate slightly from 180° relative to one another in the laboratory system. This slight deviation is what gives rise to the demand for high angular resolution. In practice one arm of the instrument shown in Figure 2 is held stationary while the other is moved in small angular increments in the z direction, for example. In order to obtain sufficient sensitivity with the available positron sources, one employs large-volume detectors whose long dimension is parallel to the collimating slits. Thus, the detectors are insensitive to the x and y components of momentum, and the experiment determines only one component, say p_z . From the figure we see that to a good approximation for the small angular range under consideration (roughly 0-50 mrad.) $p_z = mc\theta$ ($= c\theta$ in atomic units). In terms of the expressions given in the previous section the rate of annihilation into the momentum region between $p_z = c\theta$ and $c(\theta+d\theta)$ becomes,¹⁸

$$N_z(\theta) = \sum_i c \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \Gamma_i(p_x, p_y, c\theta) dp_x dp_y, \quad (9)$$

and the area under the angular correlation curve is,

$$\int_{-\pi/2}^{+\pi/2} N_z(\theta) d\theta = \sum_i c \int_{-\infty}^{\infty} \Gamma_i(p_x, p_y, c\theta) dp_x dp_y d\theta, \quad (10)$$

a quantity proportional to the total annihilation rate.

Of course, in practice, the area under the actual measured angular-correlation curve is just equal to the total number of coincidence counts collected. But if the normalization factor were known this area could be converted into an annihilation rate or a total lifetime.

If one calculates electron wave functions for the electrons in various shells of an atom or for valence electrons, and if one also knows the positron wavefunction, then it is possible to generate a theoretical angular-distribution curve. This can be normalized to a measured distribution, and one then can make some assessment of the relative contribution which electrons in different states make to the observed annihilation process. An example of the method applied to aluminum is shown in Figure 3 taken from the work of Berko and Plaskett (Fig. 12, Ref. 18). The theoretical curves, shown as solid lines, have been normalized to the experimental counting rate at 0° . The open circles are the experimental points. The parabolic curve corresponds to the angular distribution arising from annihilation with the three valence electrons, while the other curve represents the contribution from L-shell electrons. This illustrates the high-momentum contribution to the angular distribution which comes from core annihilations.

Considering annihilation in a gas of free electrons, it is easy to see how the parabolic valence-electron distribution in Figure 3 comes about. We know that the momentum of the photons comes from the electrons since the positron is essentially at rest. The electron momenta are distributed uniformly throughout a sphere whose radius is the Fermi momentum. The conventional method of measuring an angular distribution corresponds to taking a slice through the sphere at a

transverse momentum $k_z = mc\theta$. The area of this slice as shown in Figure 4 is going to be proportional to the rate of annihilation into the angular region θ to $\theta + d\theta$. But this area is proportional to $k_F^2 - k_z^2$, and so the expected distribution for a Fermi gas is an inverted parabola. Many metals exhibit this form of low-momentum distribution (aluminum, for example in Figure 3). Consequently one usually speaks of this portion of an angular-distribution curve as the valence or conduction-electron part. We shall learn shortly that it has become common practice to resolve a measured distribution into a parabolic and a Gaussian part for the purposes of analysis. This is an approximation that is valid for some solids but it assumes, among other things, that the valence electrons make no contribution to the high-momentum tail of the angular-correlation distribution.

Doppler Broadening

We noted in the preceding section that the detectors used in angular-correlation experiments are insensitive to the component of electron momentum lying along the direction of the emitted photons. This component gives rise to the usual Doppler broadening of the annihilation photon at 511 keV. If E_0 is the rest mass of the electron, then the broadening ΔE is given by the relation

$$\Delta E/E_0 = (v_{c.m.})_x/c$$

Assuming that the positron is at rest, we find that the velocity of the center of mass, $v_{c.m.}$ equals $1/2 v_e$, the electron velocity. Thus,

$$\Delta E/E_0 = \frac{1}{2}(v_e)_x/c \quad (11)$$

or

$$\Delta E = (p_x/2m_0 c) E_0, \text{ where } p_x \text{ has its usual meaning.}$$

If the medium is isotropic with respect to the annihilation process, then all momentum components are equivalent. This means that p_x is equivalent to $p_z = m_0 c \theta$ as determined in the usual angular-correlation experiment.

Thus,

$$\Delta E = (m_0 c \theta / 2 m_0 c) E_0 = \frac{1}{2} E_0 \theta = 255.5 \theta \text{ eV}, \quad (12)$$

where θ is in milliradians and ΔE in electron volts. So we see that a one milliradian angular resolution corresponds to a Doppler broadening of 255.5 eV, and in principle, the two experimental techniques can furnish the same information. If the instrumental resolution is unfolded from the Doppler-broadened annihilation peak, then the electron momentum distribution will be recovered.

The method of performing these experiments is to use a Ge(Li) detector as part of an energy spectrometer. The instrumental resolution function $f(E, E')$, is determined by least-squares fitting of a multiparameter analytical expression to the shape of an unbroadened line from a known decay scheme at an energy conveniently near 511 keV. If the true energy distribution in the Doppler-broadened line is $N(E)$ then the convolution function

$$g(E) = \int N(E) f(E, E') dE' \quad (13)$$

can be calculated and compared with the experimental data point by point using least-squares analysis. This procedure yields the true distribution $N(E)$. Most of the difficulty in obtaining a good fit arises from the determination of the resolution function. Nevertheless, the unfolded angular distributions agree well with angular-correlation data as can be seen in Fig. 5 taken from the work of Rama Reddy and Carrigan on copper and zinc.⁷ They have prepared a table in which a

comparison of the two techniques is made. That table is reproduced here as Table II on the following page.

The limiting factor in these experiments at present is the FWHM of the Ge(Li) detector. The best available detector has a FWHM of about 1.1 keV; this corresponds to an angular resolution of about 4 mrad, not very good by comparison with angular-correlation instruments. The FWHM of these detectors is given by,

$$\text{FWHM} = 2.36\sigma(E\epsilon)^{1/2} \quad (14)$$

where σ is the statistical width, E the energy of the photon, ϵ the energy required to produce a charge pair, and F is a characteristic of the charge-pair creation process called the Fano factor. It is a measure of the fraction of the total number of electron-hole pairs created that is statistically independent. If the FWHM were smaller then there would be real promise for this method. We shall see in a later section that MacKenzie and his colleagues are even now using Doppler broadening successfully to study imperfect metals and alloys. No doubt others will follow their lead in the near future.

The method has one distinct advantage. It requires only one detector and no coincidence circuitry. Data can be collected rapidly and the statistics are, therefore, very good. Stabilized electronics are essential, however.

Lifetimes

The measured lifetimes of positrons in metals are all around 0.2 nsec. There are now commercially available electronic components that can be assembled to measure such short times. They operate near the limit of their capability, however, and great care is required to achieve reproducible results.

Table II. Comparison of 2-Photon Angular Correlation and Doppler-Broadening Techniques (Ref. 7).

Feature	Conventional 2-photon angular correlation	Doppler broadening
1) Basic measurement	angular correlation	line broadening
2) Resolution	very good; 0.5 mrad typical (4 mrad/1 kev.) No convenient calibration in this method	not very good yet, best FWHM $\sim$ 1.1 kev at present
3) Electronic circuitry	fast coincidence	linear pulse analysis
4) Measured parameter	transverse pair momentum	longitudinal pair momentum
5) Applicability	<ul style="list-style-type: none"> a) useful for 2-γ decay only b) desired portion of curve can be scanned at will c) slow counting rate in "tail" 	<ul style="list-style-type: none"> a) useful for 1,2,3 photon decay b) entire energy spectrum obtained at once c) may be better for "tail" data because counting rate is high
6) Sample constraints	a problem - limits angular resolution, counting rate, etc.	no problem in working with high pressures, variable temperatures, electric and magnetic fields, etc.
7) Data acquisition rate	slow	about 10 times faster with weaker sources than for angular-correlation method.

The standard method of measuring lifetimes employs delayed-coincidence counting, and a typical system is shown in the block diagram of Fig. 6. The system includes a time-to-amplitude converter by means of which the elapsed time between the emission of the positron and its annihilation in the sample is converted to a proportional pulse which is stored in a multichannel analyzer. The distribution of time intervals, and therefore pulse heights, is an exponential whose decay time is the mean life, τ , provided that the natural delay is long compared to the width of the prompt resolution curve. The time resolution is determined by measuring the pulse-height distribution from a source that emits two coincident gamma rays, for example ^{60}Co . The typical spectra would appear as in Fig. 7. The lifetime equals the difference in the centroids of the two curves shown in Fig. 7. Newton has shown that it also can be determined from the slope of the tail of the delayed coincidence spectrum. However, generally the analysis is performed by computer fitting of a sum of exponentials to that part of the delayed curve corresponding to large positive delays. The prompt resolution curve is approximated by a Gaussian and folded with the exponentials in a least-squares calculation. In the case of metals, it is generally assumed that the delayed curve consists of only two exponentials. One exponential corresponds to the desired lifetime while the other is of weak intensity ($\sim 2-5\%$) and arises from annihilation within the source. The latter usually yields a lifetime of ~ 0.5 nsec. In the next section we shall learn that it is of interest to look for two real lifetimes that are close to one another in metals. However, successful attempts to resolve them have not been reported to date.

The use of delayed-coincidence circuitry requires that care be taken to achieve good electronic stability. The major problem arises from the so-called "walk" effect in fast-pulse spectrometry. Walk arises because pulses of the same rise time but different amplitude cross the zero-level discriminator at slightly different times. Thus,

the timing has an inherent error in it. Methods have been devised for reducing this effect and are now in common use. The stability of the electronic system is both temperature and humidity sensitive. It is essential that the experiments be conducted in an area where good control over these ambient conditions exists. Recent developments in integrated circuitry may reduce the problem, for small IC chips lend themselves to temperature regulation through the use of cooling devices such as thermoelectric coolers.

V. POSITRON ANNIHILATION IN IMPERFECT METALS - EXPERIMENT

Defects in Metals

A perfect metal is an idealization that is not realized in nature, although in some special cases it can be closely approximated. Nevertheless, many properties of real metals are determined by their defect structure. The defects may take the form of vacant lattice sites, interstitial atoms of the host or of an impurity, dislocation networks, grain boundaries, or foreign precipitates, for example.

In recent years, it has been discovered that positrons are extremely sensitive to the presence of certain kinds of lattice imperfections. Because an understanding of defects in solids is so vital to an understanding of the behavior of solids, the prospect of a new probe for studying defects has excited great interest. In sections V-VI we shall examine these recent developments, discussing first the experimental observations, and second the models that have been proposed to explain the data. The field is in its infancy, and in the next few years we will determine the extent of its usefulness. Already there are those who believe that positron annihilation offers the best hope for measuring vacancy formation energies accurately.

We need not discuss defects themselves in detail for the purposes of our discussion. The literature covering this subject is extensive and readily available.¹⁹⁻²¹ Moreover, in confining our discussion to positron-defect interactions we are aware that we are omitting a large body of experimental results dealing with the behavior of positrons in metals. In fact, the effects to be described have a direct bearing upon these other studies. For it quickly will become apparent that the results of angular-correlation or lifetime measurements are affected by the state of the sample as regards deformation and temperature, to mention two important parameters. Thus, the interpretation of data must take into account the history of a sample as well as the conditions that applied during its use in an experiment.

By now a number of investigators have confirmed the role of defects in positron annihilation and we need only summarize some of the results in this paper. Several years ago, Dekhtyar²² published a review in which he described many experimental observations of positron annihilation in metals and alloys containing lattice defects. For a more complete review of experimental data one may refer to his paper.

Experimental Results

Plastic Deformation. It was probably Dekhtyar and his colleagues²³ who first noted that plastic deformation measurably altered the shape of a two-photon angular-correlation curve. Their investigation began with iron and iron-nickel alloys, but it subsequently extended to a number of cubic metals and alloys. In every case they observed that after deforming the samples by rolling to 70-80% reduction two changes took place:

- 1) The maximum counting rate increased, and
- 2) The FWHM decreased.

Taken together these two changes were interpreted as being due to a decrease in positron interactions with core electrons and an increase in their interaction with conduction electrons. This might arise from some redistribution of electrons in the s and d bands due to the strain introduced by deformation.

Several years elapsed before Berko and Erskine²⁴ investigated the 2-quantum angular correlation in plastically-deformed aluminum, and confirmed Dekhtyar's observations. Their aluminum samples had a purity of 99.99% and were 0.1 in. thick. After undergoing an annealing treatment at 600°C for 3 hours and a slow cooling to room temperature the samples were hammered to reduce their thickness from 10-16%. These samples exhibited a narrowing for small values of θ and a smearing at θ_F (the angle corresponding to the Fermi cutoff) relative to the annealed state. Reannealing produced complete overlap of the data with those from the original annealed state of the sample.

To eliminate possible surface effects Berko and Erskine used two positron sources with different end-point energies: ²²Na, 59 keV, and ⁶⁹Ge, 1.22 MeV. The results were indistinguishable thus proving that the effect was associated with the volume and not the surface of the sample.

The results of these experiments suggested that positrons annihilate preferentially in regions of lowered electron density near defects. Berko and Erskine pointed out that the positrons could be preferentially attracted toward the dislocations produced by deformation and might even become bound. This idea appears plausible in view of the earlier calculation of Cottrell, Hunter and Nabarro²⁵ who showed that the strain field around an edge dislocation induces a charge redistribution and a consequent electric dipole at the dislocation. The potential due to a dilatation Δ was found to be $V \sim 4/15 (\pi^2 k_F^2 / 2m) \Delta$. This is the electrical interaction energy of a unit charged particle placed in any part of the strain field. If the positron wavefunction peaks in the vicinity of the

dipole, or if, indeed, the increased kinetic energy due to localization is outweighed by the interaction energy, thereby leading to a bound state, then this effect might help to explain the changes observed. It does not, however, suggest why fewer annihilations with high-momenta electrons should occur in the vicinity of the dislocation.

Berko and Erskine also pointed out that vacancies are produced during plastic deformation, and could serve as positron traps. They suggested that if this were so then the same defect might explain the increased lifetimes observed by McKee *et al.*²⁶ in deformed aluminum, and the change in angular correlation with temperature observed earlier by MacKenzie *et al.*²⁷ for example.

Dekhtyar *et al.*²⁸ also reported the first study in single crystals, using deformed molybdenum crystals with (110) or (100) faces. They cold rolled the specimens to produce a deformation of 17% and then annealed them after each experiment, first to 1000°C, then to 1500°C and finally to 1800°C. When positrons were incident on the (110) face the 2-photon angular-correlation curve exhibited the expected narrowing and increase in peak height (by ~ 20%). By decomposing the distribution into a parabola plus a Gaussian, Dekhtyar *et al.* were able to define the relative probability of annihilation with conduction electrons as the ratio of the area under the parabola to the total area. They found the surprising result that the ratio for 17% deformation in the single crystal seemed to be equivalent to that caused by 80% deformation of polycrystals. Also the changes were much larger in the (110) than in the (100) sample. Annealing caused the distribution curves to return to the shape arising from the initial undeformed crystal. Dekhtyar and his colleagues suggest that one should investigate changes in the shape of the Fermi surface in deformed crystals. These experiments and others similar to them confirmed the relationship between plastic deformation and angular-correlation data. Similar and related

effects were observed at about the same time in lifetime and Doppler-broadening experiments.

For example, Grosskreutz and Millett²⁹ introduced dislocations and vacancies into copper and aluminum by means of cyclic deformation. The 4-9 aluminum was cycled 8000 times at room temperature while 2-9 copper sustained 3000 deformation cycles at the same temperature. Measurements at room temperature showed the following changes in mean lifetime:

<u>Metal</u>	<u>Treatment</u>	<u>τ</u>
Al	1) annealed	204 psec
	2) fatigued (8000 cycles)	258 psec
Cu	1) annealed	177 psec
	2) fatigued (3000 cycles)	259 psec
	3) fatigued and annealed for 15 min @ 375°C	259 psec

It is known that the annealing treatment at 375°C does not remove the equilibrium dislocation distribution in fatigued copper although it will remove prismatic loops and perhaps vacancies. Grosskreutz and Millett thus concluded that the observed enhancement in lifetime had its origin in the dislocation network, but that the specific morphology of the network was unimportant, at least in copper. They suggested that one should observe two lifetimes in deformed metals if they can be resolved.

Doppler-broadening experiments also have been directed toward examining the behavior of positrons in imperfect metals. Using a Ge(Li) spectrometer with a resolution of 1.2 keV at 514 keV, MacKenzie³⁰ was able to distinguish differences in lineshapes in different metals and changes in lineshape for a given metal under different strains. He cold-rolled samples of aluminum, gold and copper to double their

initial area and found definite changes in lineshapes. In each case the line broadening diminished, the largest effect being observed in copper. On the other hand, indium exhibited no narrowing following deformation but a marked narrowing with increasing temperature. We will say more about the temperature effect shortly. Since the Doppler broadening is only sensitive to changes in the core contribution to the momentum distribution, MacKenzie concluded that the line narrowing must arise from trapping of positrons at vacancies and dislocations where they annihilate more frequently with low-momentum electrons than they do in the perfect metal. MacKenzie and his colleagues³¹ extended their investigations to high-purity copper and to an aluminum alloy known as 6061. They defined a lineshape parameter,

$$S = \frac{\sum \text{counts in fixed no. of channels in the center of the peak}}{\text{Area of the peak}}. \quad (15)$$

The numerator was chosen so that $S \approx 0.5$. An interesting point noted by these investigators is that the good statistical properties of Doppler-broadening measurements compensate for the small changes in S usually observed. For example, S changed by only 3.5% between the annealed and the severely cold-worked specimens. However, because the quantity S follows a binomial distribution rather than the usual Gaussian distribution, the error for 5×10^5 counts in the peak was only 0.35%. The resolution of the spectrometer was 1.6 keV for the 514 keV line of ⁸⁵Sr. On the assumption that the value of S is linearly related to the fraction of trapped positrons, η_t , MacKenzie et al. found that,

$$\eta_t = A + B \log D \quad \text{for} \quad 20\% < \eta_t < 95\% ,$$

where D is the percent deformation. They were also able to measure the surface hardness of their specimens, and found that it correlated

very well with the values of η_t derived from lineshape changes for $D < \sim 34\%$ (Fig. 8). Thus, these data held out the promise of determining dislocation densities from Doppler-broadening. However, the authors pointed out, correctly, that a quantitative link depends upon a theory of positron-defect interactions, and that the predictions of such a theory are sensitive to the form of the interaction chosen. Various groups have used different models of the positron wavefunction, treating the positron as a plane wave, a diffusing wave packet or a classical particle in thermal equilibrium with the sample. Each model can lead to a different interpretation of the point-defect density present.

Temperature Effects. Perhaps the first detailed examination of the temperature dependence of positron annihilation in metals was that conducted by MacKenzie and his collaborators.²⁷ They found that indium, cadmium, and zinc exhibited markedly narrower angular-correlation distributions at elevated temperatures. An increase in peak heights was accompanied by a decrease in the intensity in the tails of distributions. Some of the metals investigated did not respond in the same manner, however. For example, lead, tin, aluminum and bismuth showed only small variations with temperature. These could be understood in terms of the lattice thermal expansion. At the time, the role of defects was not fully appreciated. Nevertheless, these authors did point out that certain metals evidently exhibit some of the disorder properties of their liquid state before reaching their melting point.

Somewhat later, MacKenzie and his associates³² reexamined the temperature effect using mean lifetimes as an indicator rather than angular distributions. They obtained data from cadmium, indium, zinc, aluminum and copper. With the exception of copper, whose temperature sensitivity was relatively very weak, all of the metals studied showed effects analogous to the earlier angular-correlation data. Plots of

the annihilation rates versus temperature exhibited shapes that were similar to plots of the tail intensity versus temperature in the angular-correlation work. As usual, a weak second component of lifetime (2-3%) was observed, and was attributed to surface effects following Weisberg and Berko.³³ The intensity of the weak component was determined at room temperature and at high temperature, and the average value was used to correct data at intermediate temperatures. Because of the absence of any hysteresis in their data MacKenzie et al. concluded that the effect they observed could not be attributed to dislocations. In general, the lifetimes increased with increasing temperature, and tended to reach a plateau at some elevated temperature. The only physical change that MacKenzie et al. could link with the observed effect was the variation in the equilibrium vacancy concentration with temperature. They, therefore, came to the conclusion that a positron-vacancy interaction must exist, and that the lower electron density expected in the vicinity of a vacancy must account for the longer lifetimes associated with positrons in these defects. They did not, however, anticipate that vacancies actually would form bound states at vacant lattice sites.

Shortly thereafter, Brandt and Waung³⁴ demonstrated that sodium and gallium showed large changes in their major lifetime component upon melting. These authors pointed out that the prediction of the free-electron theory for electron-density changes on melting are much too small to account for their results. They, too, suggested that observed changes were due to annihilation at vacancies with mostly low-momenta electrons (as required by angular-correlation data on liquid metals). Brandt and Waung pointed out that if vacancies were responsible for what they observed then the lifetime change would be positive if the vacancy concentration, C_v , were such that

$$C_V = \left(\frac{\Delta V}{3V} - \frac{\Delta a}{a} \right) > 0 \quad \text{in the liquid.}$$

V representing the sample volume, and a, the lattice parameter. In gallium, $\Delta V/3V < 0$ so that $\Delta a/a$ must be even more negative to account for the observed increases in lifetime. According to Brandt and Waung this requirement is consistent with x-ray data that suggest clustering in liquid gallium. Such a phenomenon could yield a negative $\Delta a/a$ and would diminish at increasing temperatures in the melt. This, in turn, would cause the lifetime increment to decrease as was observed at temperatures well above the melting point.

All of the foregoing experimental observations seemed qualitatively consistent with the concept of a strong positron-vacancy interaction. As early as 1965, Brandt³⁵ had proposed a simple rate theory to explain a related phenomenon. This model subsequently was applied to metals in more explicit terms by several groups. It has become known as the "trapping model".

VI. THE TRAPPING MODEL

Bergerson and Stott, and Connors and West in similar treatments described a phenomenological model of positron annihilation in metals, assuming that vacancies act as positron traps.

Suppose that there are two annihilation rates associated with a metal, λ_1 , corresponding to the decay rate in the perfect metal and λ_2 corresponding to the positron decay rate in vacancies. Suppose also, that the rate at which positrons are trapped at vacancies is given by the relation

$$\kappa = \mu c(T), \quad (16)$$

where μ is presumed to be a constant of the material and $c(T)$ is the

vacancy concentration at temperature T. Then the rate equations describing the time dependence of the number of free and trapped positions are, respectively,

$$\begin{aligned}\dot{n}_1 &= -\lambda_1 n_1 - \mu c n_1, \text{ and} \\ \dot{n}_2 &= -\lambda_2 n_2 + \mu c n_1,\end{aligned}\tag{17}$$

where, initially, $n_1 + n_2$ equals N, and $n_2(0) = 0$. Solving these equations one obtains for the rate of annihilation $R(t)$ at time t , the expression,

$$\begin{aligned}R(t) &= -N^{-1} \frac{d}{dt} (n_1 + n_2) \\ &= \frac{\lambda_2 \mu c \exp(-\lambda_2 t) + (\lambda_1 - \lambda_2)(\lambda_1 + \mu c) \exp[(-\lambda_1 - \mu c)t]}{\lambda_1 + \mu c - \lambda_2}.\end{aligned}\tag{18}$$

At time $t = 0$,

$$\begin{aligned}R(0) &= \frac{\lambda_2 \mu c (\lambda_1 - \lambda_2)(\lambda_1 + \mu c)}{\lambda_1 - \lambda_2 + \mu c} = \frac{\lambda_1^2 - \lambda_1 \lambda_2 + \lambda_1 \mu c}{\lambda_1 - \lambda_2 + \mu c} \\ &= \lambda_1 \frac{(\lambda_1 - \lambda_2 + \mu c)}{\lambda_1 - \lambda_2 + \mu c} = \lambda_1, \text{ the "free" decay rate.}\end{aligned}\tag{19}$$

The mean lifetime predicted by this model turns out to be

$$\bar{\tau} = \lambda_2^{-1} (\lambda_2 + \mu c) / (\lambda_1 + \mu c).\tag{20}$$

The mean life consists of contributions from the two decay modes which are characterized by the lifetimes λ_2^{-1} and $(\lambda_1 + \mu c)^{-1}$. Bergersen and Stott³⁶ pointed out that these two decay modes make equal contributions when

$$\mu c \approx \lambda_1 - \lambda_2 . \quad (21)$$

Now the vacancy concentration at any temperature T is given by a Boltzmann expression, viz.,

$$c(T) = B \exp(-E_{IV}^F / k_B T) \quad (22)$$

where B is a factor arising from the configurational entropy of the vacancy in a particular lattice structure, k_B is Boltzmann's constant, and E_F is the formation energy of the vacancy. If λ_1 and λ_2 are known from low- and high-temperature data, respectively, then the experimental temperature dependence of $\bar{\tau}$ can be used to determine the "critical" temperature at which

$$\bar{\tau} = \frac{\lambda_1}{\lambda_2(2\lambda_1 - \lambda_2)} , \quad (\mu c \approx \lambda_1 - \lambda_2) . \quad (23)$$

Knowing this temperature, Bergersen and Stott evaluated the associated "critical" vacancy concentration by using assumed values for the vacancy formation energy, E_{IV}^F . They allowed B to be unity whereas it is often ~ 10 , and they used somewhat arbitrary values of E_{IV}^F . Nevertheless, even if the correct values of B and E_{IV}^F are used in the expression for c , one still arrives at their conclusion that positrons are very sensitive to the presence of vacancies in fractional concentrations as low as 10^{-6} . This suggests that positrons offer an opportunity to study equilibrium concentrations of vacancies in metals.

Using the same model, Connors and West³⁷ have drawn equivalent conclusions. They proposed, following earlier work³, that the constant μ can be equated to $\sigma_c \bar{v}$ where σ_c is the capture cross section of the vacancy and $\bar{v}$, the thermal velocity of the positron ($\alpha T^{1/2}$).

Hautojärvi et al.³⁸ applied the trapping model to the measurement of positron lifetimes in deformed aluminum. They reasoned that since deformation produces vacancies and dislocations, the trapping model should be applicable. Their paper is especially valuable because it illustrates the difficulties encountered in analyzing data on lifetimes in terms of two competing decay modes. Hautojärvi et al. found that attempts to fit their data with two exponentials plus a source term failed. In fact after subtracting a source term of about 2%, and using a one-exponential fit they still found that the variance had reasonable values only for the undeformed and highly-deformed specimens. They concluded that these results again verified that only one lifetime exists at each extreme, and that intermediate lifetimes are a mixture of these two states. Recognizing that κ is the only parameter in the trapping model once λ_1 and λ_2 are determined, they followed a fitting procedure to obtain values of κ as a function of deformation from the experimental annihilation rates. The values of the variance were reasonable, but not as good as they had anticipated.

Since vacancies make a negligible contribution to the positron lifetime in aluminum at 300K where the data were taken, Hautojärvi and his colleagues concluded that their observations were affected only by dislocations. However, their attempts to relate the trapping rate, κ , to the dislocation density by electron microscopy were not especially noteworthy.

Of course, similar attempts have been made to explain angular-correlation data on the basis of the trapping model. These include the work of Dekhtyar on deformed metals,^{22,28} Connors et al.^{39,40} on quenched cadmium and Kusmiss et al.⁴¹ on electron-irradiated platinum.

In all cases, the changes in the angular-correlation distributions were the same as those arising from increases in sample temperature. Most of the results have been published in brief form. However, two complete papers have appeared recently. In the first, Snead *et al.*⁴² discussed the influence of defects on the angular-correlation distribution in electron-irradiated and in deformed iron. In the second, Connors *et al.*⁴⁰ considered the effects of vacancies on positron annihilation in cadmium.

Snead *et al.* have shown that one can deduce trapping cross sections from a combination of angular-correlation and lifetime data by using the trapping model. They have shown that if the angular correlation curve can be described by a combination of a parabolic and a Gaussian distribution, then the change in the peak height of the total curve can be expressed as

$$\Delta H = (\Delta H)_s \eta_t, \quad (24)$$

where $(\Delta H)_s$ is the difference in the peak heights for saturation and for "zero" vacancy concentrations, and η_t is the fraction of trapped positrons. The trapping model in turn requires that

$$\eta_t = \frac{\mu c}{\lambda_1 + \mu c}, \quad (25)$$

where these quantities have been defined in Eqs. 16 and 17. If one now assumes that $\mu = \sigma_c \bar{V}$ as suggested earlier by Connors and West,³⁷ then the capture cross section becomes,

$$\sigma_c = \lambda_1 [\Delta H / (\Delta H)_s] / \bar{V} c [1 - \Delta H / (\Delta H)_s] \quad (26)$$

In principle, to be able to calculate σ , one must measure the angular correlation for a series of specimens containing known vacancy

concentrations ranging from amounts too small to affect the distribution to quantities that totally control it (saturation). In the case of plastic deformation this is not possible at present, but for irradiated specimens it is in principle, because it is possible to irradiate specimens in such a manner as to create only vacancies. Combining irradiation and deformation experiments, Snead et al.⁴² were able to deduce the value $\sigma_c \approx 10 \times 10^{-16} \text{ cm}^2$ for Fe.

The effect of vacancies alone as compared to a combination of vacancies and dislocations was demonstrated clearly for the first time by the work on iron. The irradiation was performed at a temperature such as to introduce only vacancies. When the samples were annealed at 100C the changes in angular correlation caused by the irradiation disappeared (See Fig. 9), whereas those induced by the deformation showed no recovery. Vacancies are immobile at 100C, but Snead et al. argued that the carbon known to be present in the samples had migrated to the vacancies and eliminated them as trapping centers. The deformed samples only exhibited a change following an annealing treatment at 250C, a temperature where single and divacancies are believed to be mobile. After a 400C anneal further changes were observed due to the reduction of small clusters. Thus, the remaining deviation of the angular correlation distribution from that of a well annealed state could be attributed to dislocation along (Fig. 10). This technique of separating vacancy effects from those of other lattice defects should prove useful in future defect studies.

Connors, Crisp and West⁴⁰ have analyzed in detail the temperature dependence of two-photon angular-correlation data in their paper. They illustrate the application of the trapping model to the determination of the vacancy-formation energy. This may prove to be one of its most useful functions. They point out that much information can be derived from purely statistical considerations of carefully taken data. They maintain that changes in the angular distributions arise from a

decrease in annihilation with core-state electrons while to a first approximation the partial annihilation rate with conduction electrons remains essentially unchanged as the temperature increases. First, they normalize their data by fitting the angular-distribution curves to a single Gaussian at large angles. This has the effect of increasing the peak heights. Next, they define a function $h(T)$ much as Snead and his colleagues have done. The function $h(T)$ is given as

$$h(T) = \frac{\rho(p_z=0)}{\int \rho(p_z) dp_z}, \quad (27)$$

where $\rho(p_z)$ is the measured angular distribution. If positrons annihilate in normal regions of a metal to yield a normalized height, h_1 and in a vacancy to give the corresponding height, h_2 , then it can be shown from the trapping model that

$$\ln \left(\frac{h - h_1}{h_2 - h} \right) = \ln(aT^{1/2}) - E_{IV}^F/kT. \quad (28)$$

Thus, Connors et al. have plotted semi-logarithmically $\ln[(h - h_1)/(h_2 - h)]$ versus $1/T$ to obtain a straight line whose slope corresponds to a vacancy formation energy of 0.52 ± 0.05 eV. The value quoted in the literature from x-ray lattice parameter and length-change measurements is 0.44 eV. Since both types of experiments are equilibrium measurements, it is not easy to say at this point which is the more accurate. However, some speculations can be made. The curve of $h(T)$ vs. T reveals that in reality h_1 has a temperature dependence so that it must be replaced by $h_1(T)$ in the equation above. A linear dependence has been assumed by Connors et al. for the function $h_1(T)$. On the other hand, h_2 is assumed to be temperature independent. At this time one cannot completely justify these assumptions. The observed change in the total annihilation rate is attributed to a

decrease in core electrons around a positron in a vacancy. However, it is difficult to justify theoretically the identification of the Gaussian component of the angular distribution solely with core annihilations. The extrapolation of this distribution to $p_z = 0$ is also open to question. One difficulty that the positron and combined lattice parameter - length change experiments have in common is that at elevated temperatures the probability of divacancy formation is not altogether negligible. The positron experiments are analyzed by ignoring this fact, whereas the lattice-parameter length-change experiments have been interpreted with allowances for higher-order vacancy clusters. At the moment one would have to state that the latter method probably yields more correct formation energies. However, if the theoretical basis for the positron experiments can be strengthened, there is every reason to believe that they will rival other experimental methods for deducing the desired quantities.

As to which measurement, positron mean lifetime or two-photon angular correlation, is more sensitive to the presence of defects, Dekhtyar and Ciz̆ek⁴³ have recently argued in favor of the latter experiments. They have investigated the effect of temperature upon two-quantum annihilation in deformed 4-9's nickel at 77 and 300K. Their analysis consisted of deducing the parabolic part of each measured distribution and taking the ratio of this area (S_p) to the total area under the curve (S). They found that $S_p^{300}/S_p^{77} \approx 1.35$. On the other hand, substituting the appropriate data for κ^{300} , κ^{77} , τ_1 and τ_2 into the expression for the mean lifetime from the trapping model, they found that $\bar{\tau}^{300}/\bar{\tau}^{77} = 1.05$. Thus, they concluded that the temperature effect could not be detected readily by lifetime measurements, but could be observed easily in two-photon angular correlation experiments. Of course, one can combine data from both measurements and seek a self-consistent solution. This has been proposed by Triftshäuser et al.⁴⁴

We recall according to the trapping model that the rate of annihilation at time t and temperature T is:

$$R(t, T) = \frac{(\lambda_1 - \lambda_2)(\lambda_1 + \mu c)}{\lambda_1 + \mu c - \lambda_2} \exp [(-\lambda_1 - \mu c)t] + \frac{\lambda_2 \mu c}{\lambda_1 + \mu c - \lambda_2} \exp (-\lambda_2 t). \quad (29)$$

The intensities associated with the two decay modes are

$$I_1(T) = \frac{\lambda_1 - \lambda_2}{\lambda_1 + \mu c - \lambda_2}, \text{ and} \quad (30)$$

$$I_2(T) = \frac{\mu c}{\lambda_1 + \mu c - \lambda_2}.$$

Note that $I_1 + I_2 = 1$. Thus,

$$I_2/I_1 = \mu c / \lambda_1 - \lambda_2. \quad (31)$$

If $\mu c = \mu_0 \exp (-E_{IV}^F/kT)$, $\ln I_2/I_1$ vs. T^{-1} should give E_{IV}^F .

We already know from angular-correlation analysis that if we assume the distribution to be the sum of two distributions weighted by the fraction of free and trapped positions, respectively, then we may use any point on the distribution to find,

$$\ln \left[\frac{F(T) - F_1}{F_2 - F(T)} \right] = - \frac{E_{IV}^F}{kT} + \ln \frac{\mu_0}{\lambda_n}. \quad (32)$$

The angular correlation experiment can be performed by counting in the tail of the distribution for a long time, for example. The lifetime measurements, however, still demand the resolution of two very similar lifetimes, λ_1 and λ_2 .

Theory of Positron-Vacancy Interaction

Throughout this review we have alluded to the need for a theoretical basis for understanding the behavior of positrons at defects. Very little has been published so far to satisfy this need. Hodges⁴⁵ has attempted to explain the trapping process in terms of an effective potential well representing the vacancy. The depths of the well, V_t , is the difference between the bottom of the positron energy band in the solid and the potential felt by the positron inside the vacancy. The effective positron-ion interaction $V(r)$ is calculated by treating the positron and its polarization cloud as a neutral pseudo-atom interacting with lattice atoms through a pairwise potential. Positron-electron correlations are neglected so that their influence upon the binding of positrons to vacancies is not taken into account. The positron effective potential is determined by the expression

$$V_t(\vec{r}) = \sum_{\vec{R} \neq 0} V(|\vec{r} - \vec{R}|). \quad (33)$$

$V_t(\vec{r})$ has the behavior shown in Fig. 11. In the figure, the vacancy is at $r = 0$, and R_a is the radius of the Wigner-Seitz sphere surrounding the vacancy.

The salient features of the positron potential are:

- 1) Strong Coulomb repulsion near ion centers, and
- 2) Screening of the Coulomb interaction in the interstitial and vacancy regions.

Hodges' computation consists of searching for localized bound states at energies below V_t . Thus, the problem is equivalent to that corresponding to a trapping well of depth V_t and width R_a . Inclusion by Hodges of electron-electron correlations increases the efficiency of screening and reduces the lowest potential in the host lattice, $V_{W.S.}$. Hodges calculates values of V_t , the trapping potential, as well as the

binding energy, E_b , for a large number of common metals. E_b ranges from 0.01 Ry in the alkali metals to 0.15 in aluminum. Because some metals show no temperature-dependent lifetime, it is quite likely that inclusion of positron-electron correlations would produce zero or negative binding energies for them.

Hodges also estimated the trapping rate per unit vacancy concentration for aluminum using the calculated binding energy. The trapping process is similar to the thermalization process calculated by Carbotte and Arora.¹¹ The positron transfers its binding energy to the valence electrons by creating electron-hole excitations. Hodges finds that the trapping rate in aluminum is of the order of 10^{15} captures sec^{-1} (vac. conc.)⁻¹. Thus for vacancy concentrations greater than 10^{-5} the trapping lifetime is less than 10^{-10} sec, i.e., less than the annihilation lifetime. Therefore, all annihilations must take place in vacancies. The theory predicts that the trapping rates should vary in proportion to the binding energy. Recently, Kusmiss et al.⁴⁶ have analyzed the temperature dependence of angular correlation data for indium, cadmium, zinc, aluminum and copper in terms of the trapping model. Contrary to Hodges' suggestion, they find no correlation between trapping rates and binding energies. Moreover, the trapping rates exhibit a dependence upon temperature, decreasing as the temperature rises.

Kusmiss et al.⁴⁶ have pointed out an interesting feature of the trapping model analysis as applied to angular-correlation data. Noting that normalized curves cross over at some position, θ_c , (see Fig. 12, for example) they show that for a given sample, all curves must intersect at the same position. If they do not, there is some problem in the normalization procedure or elsewhere in the data.

VII. SPECULATIONS AND CONCLUSIONS

Hopefully, the foregoing review demonstrates that there is a growing worldwide interest in positron annihilation as a tool for studying defects in metals. This conclusion was reinforced by the discussions and papers presented at the recent Second International Conference on Positron Annihilation held at Queen's University in Kingston, Canada. It is now quite clear, however, that progress in the application of positron annihilation to lattice imperfections requires further theoretical underpinnings. For example, there remains the question of how one ought to treat the behavior of a positron in a metal. Should it be thought of classically as a free particle weakly interacting with the lattice, or quantum-mechanically as an extended wave packet? In the former case, one can speak of the positron capture cross section only of transition rates from free to bound states. The two viewpoints have been utilized, for example, by Brandt and Waung⁴⁷ and by Hodges,⁴⁵ respectively.

Another aspect of the interaction between positrons and electrons in metals has to do with the relative importance of annihilation with core and conduction electrons at defects. A complete theory must be able to sort out and to predict quantitative changes in these two annihilation rates due to positron-defect interactions. This requires a knowledge of changes in electronic structure arising from defects as well as a proper treatment of positron-electron interactions. At present it would appear that the pseudo-potential formalism can prove to be a powerful tool for such theoretical investigations.

There is evidence, too, that positrons can be used to probe chemical impurities in metals if the impurities possess charge states that are sufficiently different from the host lattice atoms. Equalization between the Fermi level at the impurity atom site and its value elsewhere requires a transfer of charge. In addition, there are size-effects

arising from the difference in atomic radii between host and impurity atoms. These two effects produce a local perturbation in electronic structure that can be detected by the positron. Recent calculations and experiments⁴⁸ on lithium-magnesium alloys appear to support these concepts. They suggest that positrons must be sensitive to very small clusters of impurity atoms which are, in effect, precipitation nuclei.

We would be remiss if we did not point out before concluding that there exists a growing body of work dealing with positron-defect interactions in nonmetals, e.g., sodium chloride, potassium chloride and quartz. These investigations illustrate a whole new approach to the study of color centers. They represent a complementary technique that should become increasingly important in the effort to understand defects in ionic crystals.

Thus, we conclude that the potential for useful research on the defect solid state which is presented by the phenomenon of positron annihilation will be realized and fully exploited in the next few years.

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FIGURE CAPTIONS

- Fig. 1. The static pair correlation function according to Sjölander and Stott (full line) and using linear response theory (broken line). (Ref. 15).
- Fig. 2. Schematic diagram of a typical 2-photon angular-correlation experiment.
- Fig. 3. Angular distribution for aluminum. The points are experimental data for the [111] direction in aluminum, and the solid curve is a theoretical one normalized to the experimental counting rate at 0° . (Ref. 18).
- Fig. 4. A slice through the Fermi surface for a free-electron gas showing how the parabolic angular distribution arises.
- Fig. 5. Comparison of pair momentum distribution spectrum from Doppler-broadening technique and angular-correlation technique; points (o) and (•) represent two methods of analysis of Doppler-broadening data; (Δ) are angular-correlation data from A. T. Stewart, Can. Jour. Phys. 35, 168 (1957). (Ref. 7).
- Fig. 6. Block diagram of slow-fast delayed coincidence method for time spectroscopy of annihilation photons.
- Fig. 7. Typical appearance of prompt and delayed spectra obtained by the delayed coincidence technique depicted in Fig. 6.
- Fig. 8. The correlation between hardness and positron trapping in copper of high purity. (Ref. 31).

Fig. 9. Angular correlation curves comparing irradiated iron with iron irradiated and then annealed at 100°C for 1 h. The dashed curve depicts the angular correlation for the annealed unirradiated specimen. (Ref. 42).

Fig. 10. The effects of deformation and annealing on angular correlation in iron. (a) compares iron plastically deformed to 16% with an undeformed annealed specimen and (b) compares the same deformed sample before and after annealing at 250°C for 1 h. (Ref. 42).

Fig. 11. The potential V_t (solid line), formed by the superposition of repulsive positron-ion interactions (dashed lines), plotted against distance r along a line of atomic centers from the vacancy center in Al. The horizontal dotted line represents the bottom of the positron energy band, and V_c , the equivalent trapping potential, is determined by the zero-point energy of the positron V_{zp} , and the lowest potential in the host lattice, V_{ws} . (Ref. 45).

Fig. 12. Angular-correlation results for In at 298K and 403K. Both curves are normalized to the same total area. The shaded portion (marked AA) is used in deducing the fraction of positrons which annihilate from traps. (Ref. 46).

FIG. 1

FIG. 2

FIG. 3

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FIG. 11

FIG. 10