NOVEL NDE

Methods for Materials

Edited by
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FOREWORD

Because of an acute need for increasing national productivity, material durability and reliability, and establishing retirement-for-cause criteria, the importance of nondestructive evaluation (NDE) of structural materials has steadily increased in recent years at an unprecedented rate. Recognition of this need may be illustrated using the gas-turbine engine components where 99% of the components are prematurely rejected because of our lack of knowledge in accurately determining their useful life. This is only one of numerous cases where better life prediction through NDE is essential. Furthermore, an increased emphasis on NDE in recent years is also in part due to demands on enhanced performance of structures and systems and development of new classes of materials using novel processing and fabrication technologies. The new materials, such as powder consolidates, composites, and ceramics require new and reliable detection methods for evaluation of fine flaws and defects, which has thus far not been possible by the conventional NDE methods.

The major thrust of this symposium was to highlight behavior of materials as well as response of innovative techniques which have excellent potential for development of new NDE methods and procedures. Recent studies have indeed demonstrated the use of long-wavelength neutrons, positrons, x-rays, lasers, Rayleigh waves, and vibrothermography for nondestructive evaluation of flaws and defects in solids. The papers presented in this symposium will provide a single source for scientists and engineers on further exploration and application of new methodology to NDE.

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CONTENTS

POSITRON ANNIHILATION – A NON-DESTRUCTIVE PROBE

FOR MATERIALS SCIENCE

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A number of topics of interest to a material scientist
will be covered in this review. The traditional non-destruc-
tive use of positrons is to study various kinds of defects in
the lattices of metals and ionic crystals. Problems arise when
one tries to urge a specific interpretation on the results and
in general a consensus has not been obtained. There are
effects which do not correlate well with annihilation at
defects in the bulk of a solid. The experiments in many cases
however, were not done carefully enough to exclude the strong
influence of the free surface of the solid as well as the
contamination on internal "surfaces" such as voids and/or
grain boundaries. Specimens in the past were not always well
characterized. Surface effects may have plagued interpreta-
tion.

This effect of the annihilation near the surface may
indeed be an important advantage of using positrons. The posi-
tron has a negative work functions and thermalized ones tend
to drift to a free surface. Apparently they reside there for
a short time before annihilating. If that is the case, they
could be a powerful probe of the condition of the surface and
of any species adsorbed on it.

In the case of either "high energy" electrons or posi-
trons, they penetrate much deeper than the top surface layers.
In principle, the positrons do not have one advantage that the
electrons do for surface analysis, – the electron which can be
detected outside emerge from a shallow layer, roughly 1 to 10

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nanometers thick. The energy associated with adsorption or disappearance of the bulk of the electrons is readily dissipated in the lattice. On the other hand, when most of the positrons annihilate deep in the bulk of the lattice two relatively hard photons are emitted which can readily be detected several meters away from the specimen; this is a distinct advantage. They can traverse high pressure gases, the thick walls of a container and thus transmit information of an atomic or molecular nature, without leads or transducers, to detection equipment well outside the furnace, creep "stand" or vacuum enclosure.

However, one need not be limited to bombarding the specimen with the high energy positrons normally available. The new cadre of experiments involve thermalizing them in some solid and accelerating those which emerge through focussing lenses. They arrive at the specimen surface with a small tunable kinetic energy and are trapped at the surface even after slightly entering the solid. In this way, they become very strong non-destructive probes of surface conditions.

In this review, the author will try to put one interpretation on some of the conflicting data. To some extent, it represents a bias on his part. Whether it is correct or eventually supportable is another matter. The purpose is to focus attention on possible experiments which might lead to a better understanding. The second reason is to amplify the remarks by the speaker just before who had lectured on positron annihilation. He will undoubtedly have discussed the more traditional approach and traditional interpretation and to an extent, this reviewer has relied on him to cover much of the ground work and fundamental matters.

In this review, although twenty or more metals have been studied with positrons, two metals will be discussed in more detail than any others, namely iron and to a lesser extent, molybdenum. The technological significance of iron is self-evident. The interest in Mo is primarily because of its response to irradiation. The BCC metals have been considered at one time or another as candidates for the front-wall material for fusion reactors. While Mo may no longer be a candidate, a considerable amount of data on electron and neutron irradiated specimens has been accumulated and positrons have played a significant role in the interpretation of these data.

Also, in this review much more attention will be devoted to an analysis of positron lifetimes than to the Doppler Broadening and line shapes. Only passing reference will be made to the important subject of Angular Correlation since it is primarily a tool for measuring the momentum of electrons in

a crystal and therefore for the determination of the Fermi surface. The latter subject does not figure prominently in the analysis of defects in metals and hence in the present topic of non-destructive evaluation.

Before launching into the meaty parts of the subject, another area of evaluating condensed matter non-destructively will be mentioned - namely problems of studying polymers and ceramics. At this stage, it seems to be easier and more productive to study the glass transition temperature in polymers than to study the densification of ceramic bodies. The pores left during sintering are too large in many cases to exploit the full power of this probe - that is, changes in lifetime with the number of atom vacancies in the cluster become saturated when the number approaches 125 - this could be a "spongy" region 15 nm on a side. The interesting size of a single condensed void in ceramics is about 1000 nm in diameter. The former size may not be easily seen with an electron microscope.

It is admittedly more traditional to discuss defects in metals, but the details of lattice vacancies and interstitials are well established and controllable in ionic materials. The electrostatic field associated with a specific defect is simple to calculate. Alkali halides being transparent have been studied by a wide variety of optical and resonance techniques. There seems to be a consensus even about the more complex color centers and structural relaxation effects. Possible traps for positrons can be evaluated even at positions which are not lattice sites (i.e. from the Ewald potential.) That is not so for metals, where there are several types of defects, such as vacancies, edge and screw dislocations, jogs or kinks. The macroscopic manifestations such as slip or cross slip, etc. are readily seen, but the atomic positrons near an edge or screw dislocation are not known with any certainty. This is because the force law between atoms is not well known. The Johnson interatomic potential (1) is used widely; it is a power series $\sum a_n r^n$ where the exponents n are positve numbers 1 to 6. A maximum range i.e. a cut-off at $r=r_c$ prevents the expression from diverging. The set of coefficients $\{a_n\}$ are adjusted to give a good fit to a set of experimental data. This power series is an oscillating function of interatomic distance. Various alternative interatomic potentials which have been used were recently discussed by de Hosson (2).

The atomic positions near the core of a dislocation are strongly dependent on the coefficients chosen for the power series. The relaxed positions of the atoms near jogs and kinks have scarcely been studied. But they may well be the ones that material scientists should be studying. This is the

justification for starting with the ionic salts and primarily the alkali halides before going to the metals.

Positron Annihilation in Ionic Crystals

Positron annihilation experiments have been conducted with ionic crystals for almost 20 years. An Italian group, Bisi, Fiorentini and Zappa (3) observed that positrons passing through ionic salts decayed in several ways. The experiments of Brandt et al (4) to elucidate color centers in alkali halides, did lead to the observation that lattice defects influenced the mode of positron decay. The latest in a series of reviews by Dupasquier (5) was presented at the Varenna conference last year and the reader is referred to it for both the early and the most recent experimental results and inter- pretations as well as literature citations to other signifi- cant reviews.

It has been apparent for a number of years that the lifetime spectrum is complex and contains more components than the numbers of distinct lattice defects which are likely to be present at the same time in different alkali halides. This fact has stimulated much research but has not yet lead to a resolution of the problem. Bussolati et al (6) conducted a systematic study of 19 alkali halides from LiF to CsI. The specimens were single crystals of ordinary chemical purity i.e with low defect concentrations - occasionally large grained samples were used when single crystals were not readily avail- able. For 14 of them, there were three components. The shortest lifetime, θ_1, range from 137 for LiF to 313 pico- seconds for KBr. This is for cases where at least 85 percent of the total intensity has been assigned - [the label here may be slightly different from the one they assigned], since they tended to call the shortest one θ_0 when it no longer was the one which accounted for most of the decay. Even for the long- est of the θ_1 values the annihilation was by the low momentum electrons in the bulk of the solid. In a recent theoretical study by Kunz and Waber (7), the lifetime for annihilation in the bulk was calculated and found to be in excellent agreement with experimental data and these data are compared in Table I.

The second component θ_2 ranged from 297 for LiF to 755 picoseconds for KBr. This assignment is slightly more tenuous because it is not clear whether it is properly θ_2 or really θ_3 for the bromides. If one restricts the list to the fluorides and chlorides, what is called θ_2 represents 45 to 66 percent of the spectra, and the percentage of events assigned θ_1 range

Table I Calculated and Experimental
Lifetimes for Annihilation in the Bulk
(After Kunz and Waber)

	Calculated	Experimental
NaF	300 psec	297psec
NaCl	365	313
NiO	150	150
CaO	218	240
MgO	210	203

from 30 to 27. Study of the five iodides they worked with
showed that the most frequent events had lifetimes from 327 to
425 psec with percentages ranging down from 85 to 53. For
three of these five plus CsBr, the so called θ_0 values are 126
to 183 psec. with percentages 26 to 15 percent. For LiI and
NaI, the θ_0 values are not listed and perhaps were not separ-
ated from the next component in the analysis of the data. The
question is to what should this most probable lifetime compo-
nent be assigned.

     Somewhat more puzzling is the remaining 5 to 20 percent
in the fluorides and chlorides. The values of θ_3 range from
1210 (I=5%) for CsCl to 744 psec for RbF. For the high mole-
cular weight set CsBr, KI, RbI and CsI the third longest
component range from 686 to 980 psec. and with intensities
ranging from 22 down to 4 percent. This subdivision has been
made because they have the CsCl rather than the NaCl crystal
structure although no reason is apparent why their lifetime
spectra should have an additional component.

     Then there remains the problem of the longest lifetime
which is frequently called the tail with percentages amounting
to 1 to 2 percent. The lifetimes range from 1870 (LiF) to
2430 (KCl) to 4220 (NaI) psec. Since these values are very
hard to explain, experimenters have doubted that their compu-
ter fitting procedure is reliable enough to extract this low
slope, low fractional intensity portion of the data when one
makes a plot of the number of counts versus the lapsed time.
The expression for the number of positrons remaining at time t
is

$$N(t) = N(0) \sum I_i \exp(-t/\theta_i). \tag{1}$$

     Analysis of the "tails" have been distrusted and they
have been ignored and/or not recorded by their authors. Three

5

lifetimes are hard enough to explain why include the fourth and most inaccurate especially when it represents only a minor fraction of the annihilation events? That is a reasonable viewpoint.

The fourth lifetime is usually longer with a powder than with a single crystal of the same substance. The ratios θ_4(powder)/θ_4(crystal) are for example, (4050/2430) and (3600/1440). The pertinent intensity ratio, namely- I_4(powder)/I_4(crystal) is numerically smaller, i.e., 0.8/1.3 and 1.3/1.6. Times in excess of 1000 psec can reasonably be associated with the positron residing in a surface state - probably as positronium. This reflects the reviewer's opinion.

Let us turn aside from the speculation here and look back at the second component which for low molecular weight crys- tals is from 300 to 450 (and possibly up to 628 psec) For the heavier alkali halides the second component is 339 to 425 psec. Grouped in this way the range is small and the similar values suggest that θ_2 might not be associated with bulk properties of the individual chemical species. This is of course not the conventional explanation; usually it is asso- ciated with cation vacancies. Although the vacant site will vary from a small size in the case of lithium to large for cesium; this observation would seem to require that the elec- tronic charge density vary from only 1 to 1.5 arbitrary units to have the same lifetimes. It would seem possible, but if it is true, it is remarkable.

Before continuing this topic, it is worthwhile to re- view the lifetime spectra of various oxides and chalcogenides. For 17 compounds Bertolaccini et al (8) found that the short component θ_1 ranged from 148 to 334 psec. For most of them the percentage was 85 to 10 percent. The second component, θ_2 ranged from 315 to 910 psec. Most of the compounds were of the AB type but five were A_2B where A is monovalent. As indicated above these authors ignored the tail components θ_2 or θ_4. In their Table II, lifetimes and intensities for 27 alkali and alkaline earth halides are listed. These are more recent values than Bussolatti et al. The range of θ_1 was 207 to 364 and for the alkaline earth halides 204 to 352. For the A_2B oxides, θ_2 ranged from 315 to 584 for AB oxides 351 to 909 psec. For alkali halide θ_2 ran from 297 to 685 and for the A_2B halides 347 to 538 psec. Without going into details, these values tally well with the earlier values if one ignores θ_0, θ_3 and θ_4 components which would require a new labelling. That was done above. But it is not feasible here since the percentage I_1 and I_2 are not given - they might be inferred by matching the numbers preented by Bussolatti et al (6). The small range of θ_2 discussed a few paragraphs earlier is nei- ther confirmed or denied.

6

One reason Bertolacini et al (8) constrained their data was because they used the two state trapping model and analysis. They assumed that at time t_o either:

a) all the positrons were in the state 1 and 2 characterized by different electronic densities; then I_1 would rep sent the state populations.

b) all the positrons are thermalized and migrating in the bulk of the crystal state and portions of them become trapped in State 2.

They present a method for getting the rate of transition from state 1 to 2 called k_{12}. Only case (b) permitted them to ascribe a common fate to the positrons annihilating in the wide range of some ionic and covalent salts they studied. For annihilation rates $(r_1 = \theta_1^{-1})$ is a linear function of the density of negative ions per unit volume, n^*. This number is calculated as follows

$$n^* = v_- \ (pA/M)[1 - 4\pi R^3/3 v_+]$$

(2)

where p is the density, A is Avogadro's number, M is the molecular weight and the v's are the stoichiometric numbers in the formula $C_{v_+} A_{v_-}$. This model is based on a simplified picture of ionic solids namely that all the electrons associated with the cation C are found within a sphere of radius R_{cat} and that the electrostatic potential outside this radius of a cation is positive. Hence the positron would never penetrate R_{cat} and would only be annihilated by the electrons of the anion. The theoretical analysis discussed below yields plots of the probability of finding a positron along the shortest anion-cation line. Contrary to the hard ball model just discussed, the positron has appreciable probability of being found in a region where the electronic charge densities of both the anion and cation are also appreciable. That is the positron overlaps both regions with significant electronic density. That point is not greatly significant at this point in the review. What is interesting is that r_1 is well correlated with n^*. They found that r_2 (or $1/\theta_2$) did not correlate with n^*. It would seem quite plausible that it should if θ_2 corresponds to the lifetime in a cation vacancy. Their argument assumes that the volume occupied by the cation sublattice are disjoint "regions inaccessible to the positron". A positron trapped in a hole (relatively speaking, in a negative region) would not have been scattered by the cations but would have better access to the electrons of the nearby an-

ions.

The correlation they found was that θ_2 is related to both the anion and cation populations and was relatively independent of the properties of the crystal namely

$$\theta_2 = (C_s/4)(pA/M)(v_+f_+ + v_-f_-) \qquad (3)$$

where f_+ and f_- are the effective numbers of electrons "available" from the cation and anion, C_s is Dirac fundamental interaction rate of a positron in the singlet state and the factor $1/4$ corrects for the statistical weight of the singlet.

Independent of the details, this second decay mode is distinct from the first. They conclude that "the positron in the second state can be annihilated. Either with the positive ion or the negative ion, (a) the number of electrons per ion effective for annihilation seems to be higher when the ion size is larger" Also they conclude (8) that the positron wave function "in the second state must differ deeply from that in the first". They offer the observation that the transition rate (what we would suggest is the trapping rate) seem to increase with the formation energy of a Schottky defect. At this stage, any identification of θ_2 with a positron trapped in a cation vacancy is inferential. But the point could be reinforced by looking at the behavior when positrons are implanted in crystals which have been doped to enhance the cation vacancy concentration. Interestingly, interstitial anions do not seem to have been considered in the treatments this reviewer has read. The case of AgBr would be desirable to study since Frenkel pairs are commonly formed defects. The effect of introducing dislocations by deforming the ionic crystals is another interesting topic since they are effective traps. Unfortunately, the results to date are not too convincing. Radiation by ionizing particles does so much damage that we will not use that information. In short, positron annihilation can be likened to a two-edged sword. It is sensitve to small changes in defect concentration but the experimental difficulties in characterizing the specimens tend to become the stumbling blocks to getting results reproducible by another research group and it does not lead to unequivocal interpretations.

(d) Thermal Effects in Ionic Crystals. The θ_1 value in NaCl only increases by 13 percent when heated from room temperature to 973°K which is 100° below the melting point (9). When KCl was cooled to liquid nitrogen (77° K), θ_1 increased slightly (about 10% due to cooling). Both θ_2 and θ_3 essen-

8

tially did not change but I_3 was a few percent smaller at liquid nitrogen temperature then at room temperature. Measurements at the temperature of liquid nitrogen seem to show less regular changes than measurements made at room temperature (or 77 K) following a quench from high temperature. The resolved
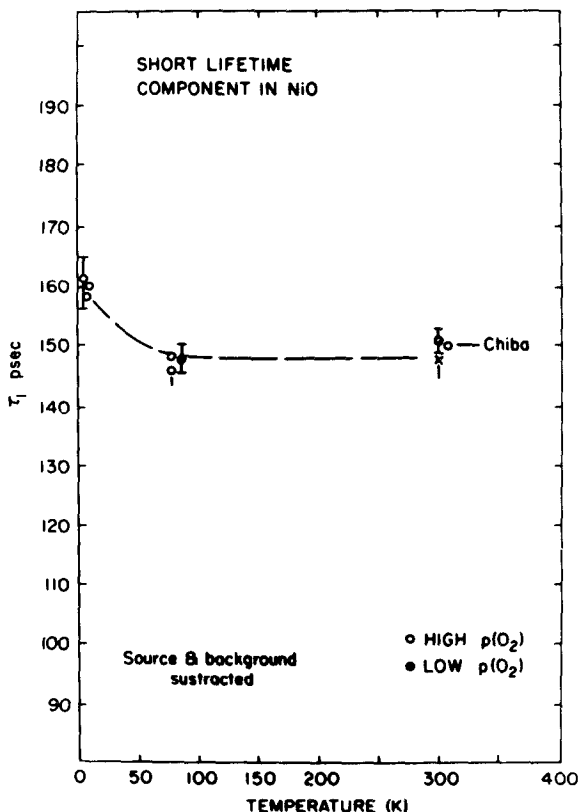

Figure 1- Variation of the shortest lifetime θ_1 of monocrystalline NiO with temperature and cation vacancy concentration produced by annealing above 1200° C
(after Waber, Snead and Lynn)

9

ℓ_1 (measured at room temperature) for KCl increased from about 185 psec when quenched from 550°C to 235 following quenching from 750°. For 77° K measurements the same values are 210 psec increasing to 260. The authors (10) kept ℓ_2 = 464 and ℓ_3 = 774 psec. This is scarcely strong evidence for thermal detrapping especially since I_2 decreased from 50 to 40 percent while ℓ_1 was climbing.

It is not easy to increase the vacancy concentration above about 1 ppm by heating to 700° K. This number of defects is equivalent to minimum content of impurities in the typically high purity material. At 1000° C, thermally generated defects might reach 40 ppm.

Doping KCl with divalent Ca ions produces very little effect apparently - (See section 5.2.3 of Ref. 5). This statement does not strengthen the association of ℓ_2 with trapping and annihilation at such traps.

This thermal behavior of the alkali halides is very consistent with the recent results of Waber, Lynn and Snead (10) on NiO. The shortest lifetime (mean value 150 psec) plotted in Figure 1 showed a negative temperature coefficient in the range of liquid-hydrogen to room temperature. The experiment was planned to determine whether shallow traps might be detected. This increase to 160 psec below 77°K might have that intepretation. The intensity I_1 was essentially constant. More signifcant is the fact that this high purity single crystal was one of a set used by Petersen et al (11) at Argonne National Lab to measure cation diffusion and the control of the concentration of cation vacancies by varying the oxygen pressure is well known (12,13). Actually, NiO is one of the very ionic systems which have been well studied by a variety of experimental methods. In short, the cation vacancy concentration should have increased from less than 1 part in 10^6 for 760 Torr oxygen, to 15 ppm at the low relative oxygen gas concentration of 1.6 ppm. The data in Figure 1 do not show significant changes from reannealing at T > 1200°C the crystal in the latter gas. The latter cation vacancy concentration should readily exceed any preexisting effects due to the small number of impurities in the sample. Cation vacancies seem to have very little effect on the lifetime. On the basis of the theoretical calculations the value of 150 psec for annihilation in the bulk NiO is in very good agreement with the experimental ℓ_1 cited.

An intermediate component of approximately 350 psec has not been reported since the number is close to that of the polymer Kapton (14), namely 382 psec, which had been used to encapsulate the source. The relative intensity of this source

was essentially constant at 22 to 23 percent throughout the
set of experiments. It would be tempting to attribute this to
annihilation in the para-positronium (or singlet state).

The component for a positron with a lifetime in excess
of 1000 psec is plotted in Figure 2. Here some trends can be
seen. There are positive temperature coefficients, the in-
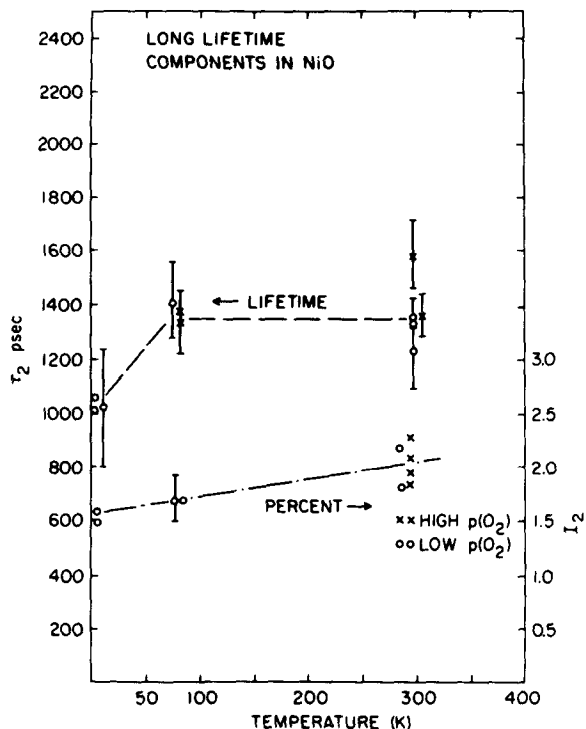tensity increases by several percent. The error bars repre-

Figure 2 - Variation of both the lifetime
θ_3 and the intensity I_3 of the same single
crystal with temperature and oxygen pres-
sure. (After Waber, Lynn and Snead)

sent variations between several determinations on the same
specimen in the same annealed condition. Then data were not
corrected for any source - surface contribution. This invest-
igation of NiO does not give any evidence of thermally acti-

vated desorption or shallow traps. There are two possibilities, one that almost all of the positrons are localized in deep traps or that diffusion was not sufficient for most of the positrons to reach the traps.

A recent calculation of the binding of a positron to a cation vacancy was made by Kunz and Waber (16). The binding energy was 8.1 eV in NiO and 9.1 in CaO, but only a fraction of an eV in several alkali halides such as NaCl. It was felt by the authors that because the latter cluster calculation was extremely sensitive to the basis set of atomic orbitals used, the results were unreliable. This nickel oxide value was consistent with the binding energy found in a theoretical study of the adsorption of H onto NiO carried out by Surratt and Kunz (16). The situation is ambiguous, the binding energy is so high that thermal desorption is very unlikely to be observed. The second (unreported) component might be due to annihilation in these traps. The long-life component is probably due to the annihilation of quasi-positronium (qPs) trapped in the bulk or in the surface of NiO.

In short, the usual interpretation of annihilation lifetimes and broadening dependent on cation vacancies trapping at internal interfaces such as between the colloidal metal and the host in colored and/or irradiated alkali halide is possible but seldom discussed. The evidence seems to be far from convincing. The possibility that many of the positrons are trapped at surfaces and annihilate due to pick-off or spin-flip processes is not excluded by the evidence. That must still be regarded as a speculative position for the reviewer to take.

(b) Properties of Ps and qPs. The lifetimes of Positronium and quasi-Positronium have emerged in the last few years as the significant problem to be understood in discussing the behavior of positrons in the alkali halides and in the oxides. Positronium Ps is a low atomic weight hydrogen atom. An electron is bound "loosely" to a positron (or antielectron) which replaces the proton in normal hydrogen or the deuteron in heavy hydrogen. A proton weighs roughly 1850 times as much as an electron, whereas a positron weighs no more than twice as much. Much of our intuition and insight into materials problems can be brought to bear on the treatment if we think of a positron as a lightweight hydrogen atom. This would be convenient if the "darned thing did not die so soon". The death of positronium is violent just as is the death of one of the partners, the positron. The two or three gamma rays which are created are the "fingerprint" of what conditions were like when the Ps atom self-annihilated. If