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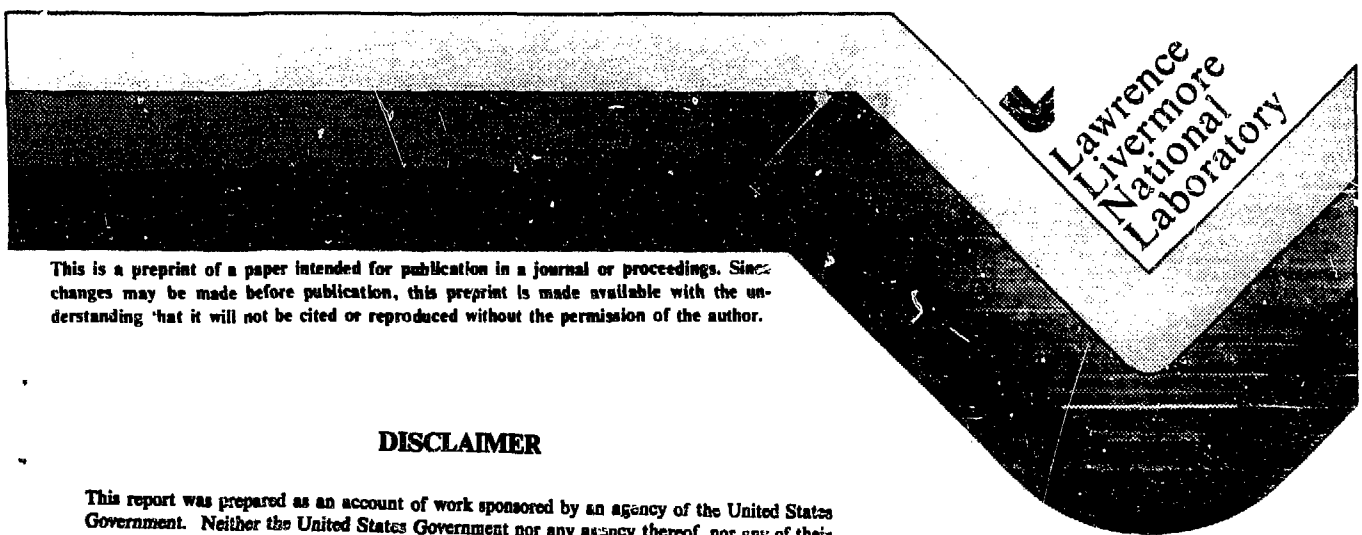

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ON THE RESOLVABILITY OF DEFECT ENSEMBLES WITH POSITRON ANNIHILATION STUDIES*

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ABSTRACT

Recent advances in the use of positron annihilation to study defect ensembles in and on the surfaces of metals, are pointing the way towards studies where particular positron-electron annihilation modes may be identified and studied in the presence of one another. Although a great deal is understood about the annihilation of positrons in ostensibly defect free metals, much less is understood when the positron annihilates in complex defect systems such as liquid metals, amorphous solids, or at or near the vacuum-solid interface. In this paper the results of three experiments, all of which demonstrate means by which we can resolve various positron annihilation channels from one another, will be discussed.

DIVACANCIES IN ALUMINUM

It is generally, although not universally accepted that the mechanism for enhanced high temperature self-diffusion in aluminum is a consequence of a significant equilibrium divacancy population. Aluminum is an ideal candidate material for a study of the resolving power of positron annihilation techniques for small defect clusters, in this case the separation of monovacancy and divacancy positron annihilation signals. The comparatively large total vacancy concentration at melting ($C_V(T_m)$-10^{-3}) in aluminum results in a wide temperature where >90% of the annihilations take place from positron-vacancy trapped states associated with an increasing divacancy population. Sufficiently high resolution two dimensional angular correlation of annihilation radiation (2D-ACAR) studies on single crystals of Al will eventually reveal the detailed anisotropies that may be associated with trapping in divacancies. However, recent 2D-ACAR experiments [1] performed at Brandeis University were only of sufficient resolution to allow one to follow the narrowing of the ACAR distribution with increasing temperature and to verify that lattice expansion alone could not explain the observed temperature dependence of the observed momentum distribution changes at high temperatures. Thus, one was forced to introduce an additional experimental argument, temperature (T), to compensate for the lack of resolving power in these experiments.

It is well known that by following the temperature dependence of the positron-electron annihilation signal it is possible to determine various vacancy point defect properties, particularly the vacancy formation enthalpy for monovacancies (H^F_{1v}). (For an overview of the various positron experimental methods the reader is directed to reference [2].) An example of such a study for aluminum is shown in Fig. 1. The temperature dependent "S" shaped curve was obtained from a 1D-ACAR experiment by measuring the peak counting rate. The full 2D-ACAR spectra for the positron Bloch and positron vacancy trapped states are shown as well so as to emphasize the overall spectral changes which occur upon trapping of the positron. As noted by Fluss and co-workers [3] it is

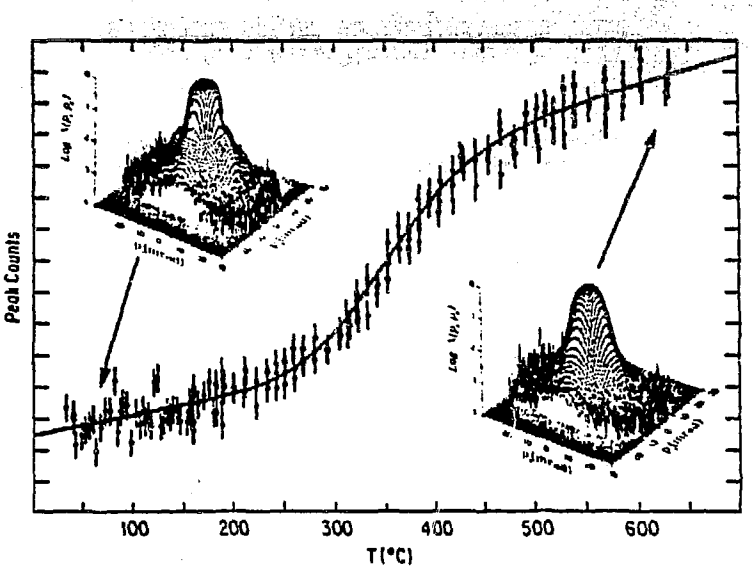

Fig. 1. One and two dimensional angular correlation data obtained from an aluminum single crystal, illustrating the peak count rate and 2D-ACAR experimental techniques. (From reference [1,3].)

possible to determine divacancy properties, which will manifest themselves in the high temperature region of the data shown in Fig. 1, if a priori information exists about the annihilation signal from monovacancy and divacancy trapped positrons. Since such theoretically derived information was available for positrons in aluminum [3,4] the present application was possible.

With several experimental and analysis constraints a mono-divacancy model analysis of the data could be obtained which was unique, and which yielded a divacancy binding energy of 0.30 ± 0.13 eV. The constraints used were:

1) the independent determination of H^{F}_{1v} from lifetime experiments at low temperatures, where the contribution from divacancies to the positron signal could be expected to be minimal,

2) the theoretically predicted peak count rates from 1D-ACAR experiments for positrons in monovacancies and divacancies, along with the predicted temperature dependencies from lattice expansion, and

3) a simultaneous or global analysis of data taken for three different crystal orientations.

The most important lesson learned in this analytical analysis was the critical role played by the last of these constraints. By "viewing" the temperature dependent signal from several crystal orientations differences in response were obtained. These differences apparently imposed a much more stringent set of criteria for for the model fit than that which would have been obtained by simply repeating the same experiment three times at the same orientation. Such tomographic constraints are not new to the use of positron ACAR data, but this application to defect studies is! The sensitivity of this analytical method is illustrated in Fig. 2. Here, for the purpose of demonstration, the divacancy binding energy is fixed at either 0.2 or 0.3 eV for three independent analyses of data from three crystal orientations. Since a physically sensible analysis requires defect concentrations to be independent of crystal orientation, it is concluded that the analyses where the divacancy binding energy is 0.3 eV is preferable to the one where it is 0.2 eV. This demonstrates the value

of the tomographic constraint which was imposed by simultaneously minimizing the mono- divacancy model to the temperature dependent data obtained from the three crystal orientations.

Such a general method should be very important in future experiments where similar resolving power may be required. Extension to other defect systems is anticipated, particularly vacancy-solute clusters. High resolution 2D-ACAR experiments may also eventually be able to "finger print" defect species, however, one will usually be forced to deal with the superposition of two or more positron annihilation exit channels.

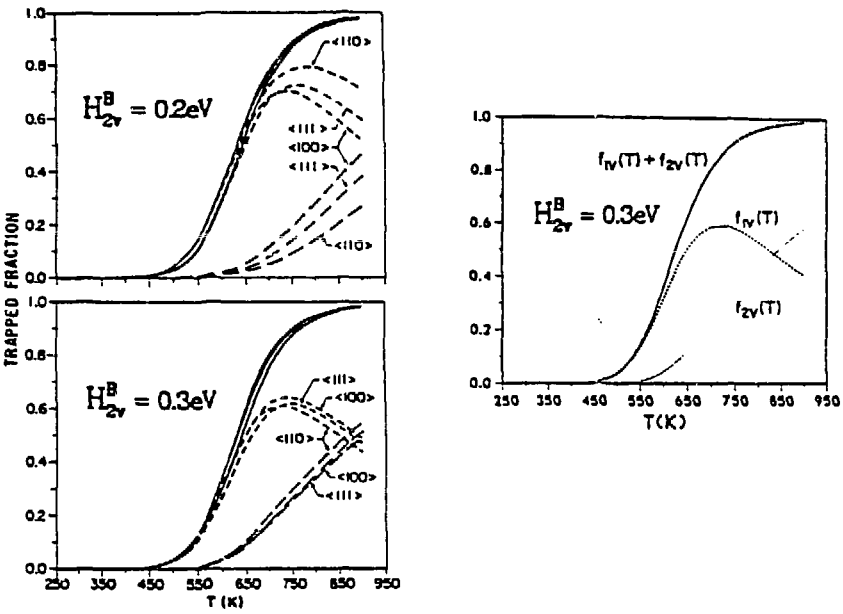

Fig. 2. Comparison of constrained mono-divacancy analyses for three crystal orientations in aluminum. The analyses results are presented in the form of the fraction of the positron population annihilating from monovacancies, f_{1v}, and divacancies, f_{2v}, and the total fraction, f. (From reference [3].)

AGE VS MOMENTUM

The size of the vacancy site from which a positron annihilates effects not only the observed momentum distribution, but the lifetime of the positron as well. The combination of momentum and lifetime measurements can be used to advantage in achieving defect spectroscopic resolution. A good example of such an experiment has been reported by Kishimoto and Tanigawa [5] for annihilation of positrons in liquid and solid metals. The goal of these experiments was to identify if more than one positron state was present for the liquid metal case. Fig. 3a shows the positron mean lifetime, τ_m, in gallium as a function of T. Above the melting point, T_m, there is a dramatic increase in τ_m indicative of trapping in open regions of the liquid. By studying the correlation between age and momentum additional information is obtained as shown in Fig. 3b. Here, for the solid state, the flat τ_m vs momentum (shown in energy units for the Doppler shift) indicates a single positron state. All elements of the momentum density will exhibit the same lifetime if there is only one positron state extant in the system. For the liquid

case, however, the authors discovered a lifetime-momentum correlation indicating that not only was the positron trapped in open regions, as evidenced by the overall increase in τ_m, but that there is a background of annihilations in solid clusters as well. In contrast, a similar experiment for the melting of indium yielded a different result. Fig. 3c shows the τ_m vs T for indium, and Fig. 3d the corresponding τ_m vs momentum. Again, at low temperatures only a single state is present in the bulk. At 85°, where ~75% of the positrons are trapped, a two component system consisting of trapped positrons and the delocalized Bloch state could reasonably be anticipated. In the region just below the melting point the size of the average trapped state appears to change rapidly with T and the τ_m vs momentum correlation implies that this is due to a mixture of vacancy states, most likely mono-, di-, and trivacancies. Upon melting, however, the system returns to a single state indicative of monovacancy size trapping sites for the positron. With the availability of theoretical models for the various positron states, this experimental technique may prove itself to be a valuable way to strip the superposition of positron states observed in the momentum spectra in the presence of defect ensembles.

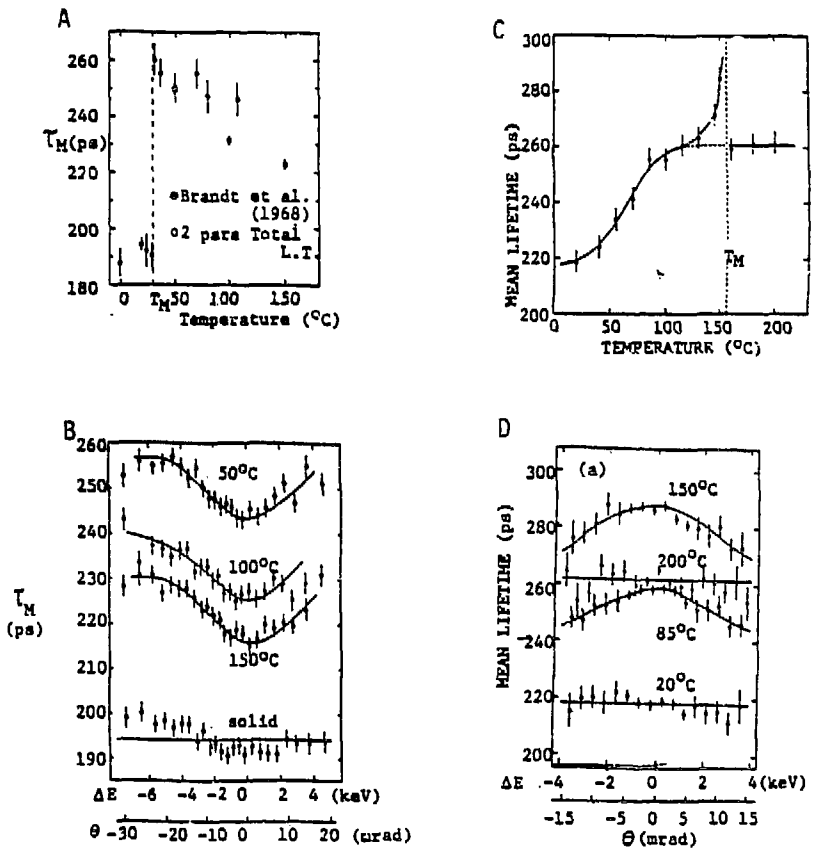

Fig. 3. (a) Mean lifetime, τ_m, vs temperature for gallium, (b) τ_m, vs Doppler shift energy (momentum) for selected temperatures in gallium, (c) τ_m, vs temperature for indium, and (d) τ_m, vs Doppler shift energy (momentum) for selected temperatures in indium. (From reference [5]).

SURFACE ANNIHILATION STUDIES

With the recent development of intense, monoenergetic, variable energy positron beams at Lawrence Livermore National Laboratory, it is now possible to study electron momentum densities at the surfaces of solids using positron annihilation techniques. Moreover, when the positron is energetically ejected from the surface into the vacuum as positronium (Ps) it is shifted into the forward hemisphere by an energy approximately equal to the work function energy for the Ps production process. This particular positron exit channel can also be studied using time-of-flight (TOF) techniques. This mode of annihilation may be of particular importance since the information about the surface properties of the sample is carried into a volume of space where it can be easily separated from those annihilations which take place from positrons localized or trapped in the near surface region.

Positron beams at LLNL are obtained by moderating high energy positrons produced by pair production in a tungsten target irradiated by a pulsed electron beam at the LLNL 100 MeV Electron Linac [6,7]. The high energy positrons are moderated in tungsten vanes and a small fraction are emitted from the moderator surface due to the negative work function of the tungsten. These positrons are then electrostatically accelerated and transported along a magnetic guiding field to a UHV (2×10^{-10} torr) chamber. TOF and 2D-ACAR experiments are used to resolve the annihilation events from Ps in flight and positrons bound to the surface. The first experiments have been designed to explore what surface sensitivity this new technique may posses; that is, what information about the surface of a solid is acquired and then released by the annihilating positron-electron pair.

Fig. 4 shows the 2D-ACAR spectra obtained for positron beams incident on a [121] plane of Cu. Beam energies of 18 keV and 740 eV were used, the 18 keV data exhibited a spectrum indicative of the Fermi surface of Cu, while the spectrum from the lower energy positron beam shows a high degree of asymmetry indicative of energetic Ps annihilating in flight. The Ps component was resolved from this latter, and is shown in the top of Fig. 5. A simple model, which was calculated for a free electron gas, is shown for comparison. The momentum distribution of the Ps is determined by kinematics, the positron-electron interaction, and the electronic density of states. Underlying this spectrum is what is believed to be a spectrum from positrons which are trapped or bound at the surface. The asymmetry observed in this spectrum, which is shown in the bottom of Fig. 5, compared to the high energy spectrum, apparently arises from the localization of the electrons perpendicular to the surface and the delocalization parallel to the surface.

Fig. 6 is the corresponding TOF spectrum for the 740 eV incident positron beam. Here, the annihilation of Ps travelling away from the surface is detected by a collimated detector 10 cm from the Cu sample. Momentum resolutions similar to that achievable with ACAR are possible. It is noteworthy that the general features of the TOF spectra obtained to date confirm the 2D-ACAR distributions obtained for the same energetic Ps component.

The future for the use of positron beams seems to be a rich one. Lifetime, TOF, and momentum studies (Doppler broadening and ACAR) are all viable spectroscopic tools for such studies, and as has been demonstrated here, different positron annihilation channels can be resolved from one another. Future work will examine the effects of surface conditions, physical and chemical adsorbates, defects, roughness, and crystal orientation, as well as temperature on the annihilation spectra.

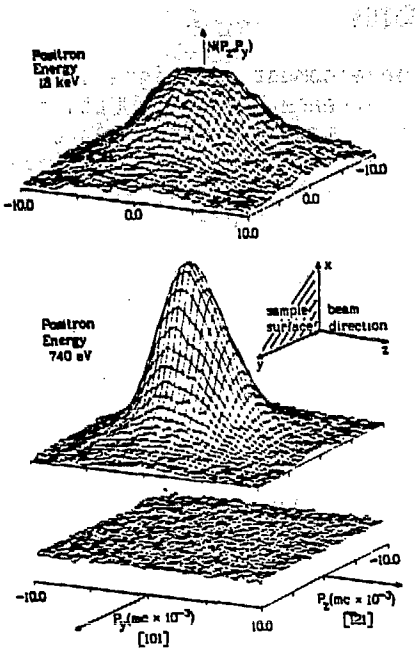

Fig. 4. The 2D-ACAR spectra for positron beams of 18 keV and 740 eV impinging on a single crystal of copper. The sample surface orientation and a typical background spectrum are also shown. (From reference [7].)

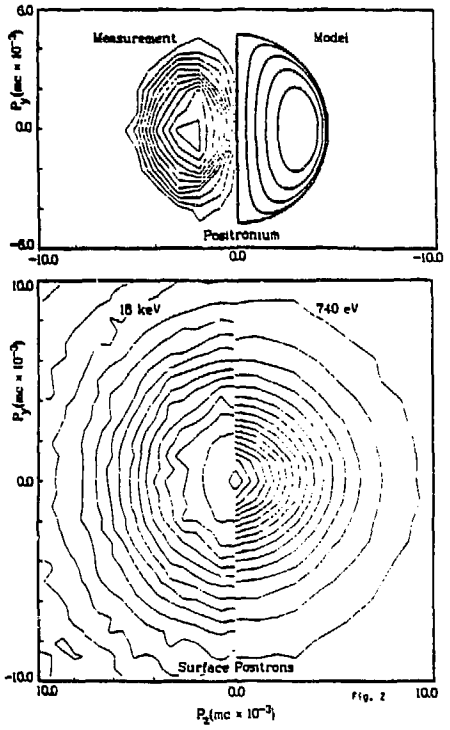

Fig. 5. Top) Contour maps comparing measured and computed momentum distributions for positronium ejected from the copper surface. Bottom) The bulk and surface trapped positron contours for the 18 keV and 740 eV beams. (From reference [7].)

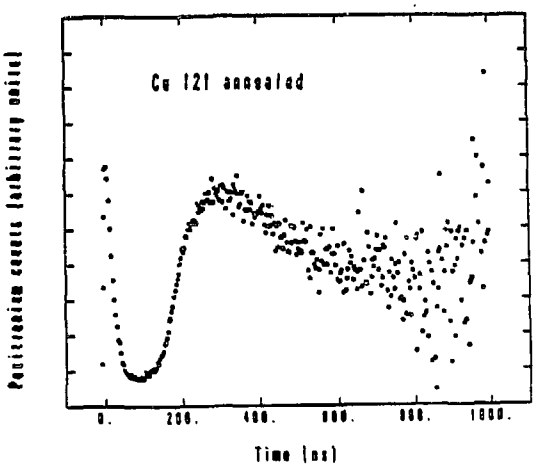

Fig. 6. Energetic positronium TOF spectrum for low energy positrons on Cu single crystal surface. The peak of the positronium distribution is in good agreement with the 2D-ACAR results and the maximum Ps energy of 2.6±0.3 eV is in good agreement with the negative Ps-work function.

SUMMARY

Three experimental methods for resolving positron annihilation exit channels and hence learning additional information about the defect ensemble in the bulk and at the surface of materials have been presented. The techniques developed for the analytical analyses in the case of the mono- divacancy studies in Al should prove of significant benefit in other positron experiments where it is desired to resolve the components of the vacancy defect population. Thus, one can reasonably anticipate improvement in the quantitative interpretation of crossed lifetime-momentum experiments and surface studies using positron annihilation techniques.

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* Work performed under the auspices of the U.S. Dept. of Energy by Lawrence Livermore Laboratory under contract W-7405-ENG-48.

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