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Positron annihilation in metal-vacancy—hydrogen complexes

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Using a self-consistent density-functional theory we find that a positron is bound to a metal monovacancy even if it contains a hydrogen atom. While the positron binding energy in the hydrogen-vacancy complex does not differ markedly from that in a pure vacancy, the corresponding lifetimes and angular correlation curves are quite different from those in bulk as well as in pure vacancies. The implications of these results are discussed.

It is well known[1] that the positron-annihilation studies in defected materials provide a measure of the electron and positron density profiles around the defect. The annihilation characteristics around metal vacancies and voids are well understood from *ab initio*[2] as well as model calculations.[3,4] In this Communication we consider a rather novel aspect of this problem, i.e., the behavior of a positron in vacancies containing hydrogen. This is an important problem not only because the simultaneous interaction of electrons with the positron, vacancy, and hydrogen illustrates interesting physical concepts, but because it may also have some practical implications concerning hydrogen trapping. For example, it is believed that the migration of hydrogen to crack tips facilitates the embrittlement process. Thus, suitable trapping centers for hydrogen may prevent this migration, at least at low temperatures. The addition of impurities in certain hosts is also known to increase the solubility of hydrogen—a process of interest in storage problems. The analysis presented here reaffirms the optimism that positrons can be used as convenient probes for studying the trapping of hydrogen by intrinsic metal defects.

We present the first theoretical study of the positron annihilation characteristics in metal-vacancy—hydrogen complexes. We have chosen aluminum and copper hosts for our investigation for the following reasons: There is evidence[5-8] that protons are trapped by vacancies in these materials at low temperature. Furthermore, a proton-vacancy complex in monovalent Cu would provide no net positive external charge perturbation, while in trivalent Al it would correspond to the removal of two net positive charges from the Wigner-Seitz sphere. Consequently, a study of positron binding energy, lifetime, and angular correlation between annihilation photons would provide deeper insight into not only the effects of different electrostatic interactions but also the feasibility that positrons could probe trapped hydrogen in monovalent as well as polyvalent metals.

We find that the positrons are bound to monovacancy-hydrogen complexes. The binding energies of positrons in vacancies containing hydrogen are not markedly different from those in pure vacancies. However, there are substantial differences in the corresponding positron lifetimes and angular correlation curves. These results which bear the signature of the electron and positron density profiles are well within the reach of present-day experimental capabilities.

The response of the host conduction electrons to external perturbation caused by a vacancy or vacancy-hydrogen complex was calculated *self-consistently* within the framework of the density-functional theory.[3,4,9] The external charge perturbation $n_{\text{ext}}(\vec{r})$ is given by

$$n_{\text{ext}}(\vec{r}) = Z\delta(\vec{r}) + n_0\Theta(\vec{r} - \vec{R}_{\text{WS}}) \quad , \tag{1}$$

where $Z = 1$ for the proton and n_0 is the ambient homogeneous density of the host medium. The second term in Eq. (1) simulates a vacancy by creating a spherical hole of radius R_{WS} (the Wigner-Seitz radius) in the background positive charge distribution. In Figs. 1(a) and 1(b) we have plotted, respectively, the electron density distribution (solid curve) around a pure vacancy and a vacancy containing a proton at its center in Al host. Because of the strong attractive interaction between the proton and the electrons, there is a sharp pileup of the electron charge around the center of the vacancy-hydrogen complex. On the other hand, the electron density at the center of a pure vacancy is minimum and about two orders of magnitude smaller than that at the proton site. Because of the screening of the proton within a radius of about $2a_0$, the differences in the electron density profiles between a vacancy and a vacancy-hydrogen complex are quite small for distances beyond the Wigner-Seitz sphere.

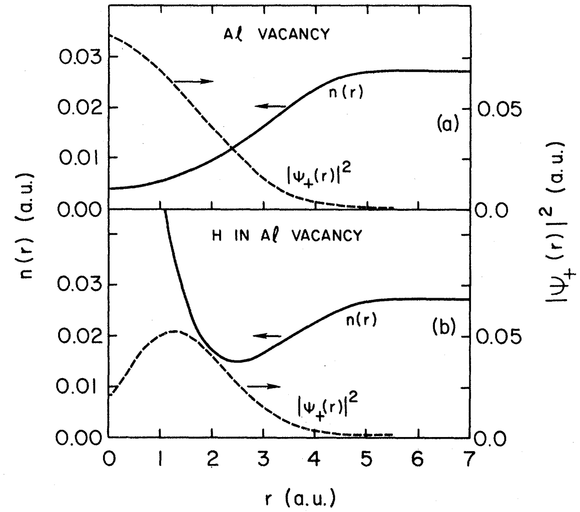

FIG. 1. Electron (solid line) and positron (dashed line) density profiles around (a) vacancy and (b) vacancy-hydrogen complex in Al.

In order to see if a positron can be bound to a vacancy-hydrogen complex, we have constructed the positron potential using the pseudopotential picture of Stott and Kubica,[10] namely,

$$V_+(\vec{r}) = \phi(\vec{r}) - E_0\Theta(\vec{r} - \vec{R}_{\rm WS}) + E_{\rm corr}[n(r)] - E_{\rm corr}[n_0] \ . \qquad (2)$$

Here $\phi(\vec{r})$ is the positron electrostatic potential (which is simply the negative of the electrostatic potential felt by the electrons) and is obtained from our self-consistent calculation. E_0 is the kinetic energy of the positron in the perfect host[11] (4.9 eV in Al and 4.8 eV for Cu) and $E_{\rm corr}$ is the positron-electron correlation energy[12] in the local-density approximation. Using the potential in Eq. (2) we have solved the appropriate Schrödinger equation.[3,4] The binding energies of the positron in a vacancy-hydrogen complex in Al and Cu are, respectively, 1.61 and 0.27 eV. The corresponding binding energies in pure vacancies in Al and Cu are, respectively, 1.80 and 0.24 eV. At first it may seem surprising that the positron binding energies in vacancy-hydrogen complex are not markedly smaller than those in pure vacancy as a result of the substantial positron-proton repulsion. The calculated small differences between these binding energies are due to two main reasons. The large electron-proton attraction results in an over screening of the proton over short distances and consequently there is a charge transfer from the metal ion to hydrogen. Secondly, the electron charge pileup as well as the electrostatic potential around the proton, although large, are of short range and therefore undermine the strength of the positron-proton repulsion. On the other hand, the attractive interaction between the vacancy and the positron is long range in comparison.

In spite of these similarities in the binding energies, the positron density profiles in a pure vacancy and a vacancy-hydrogen complex are very different as can be seen from Figs. 1(a) and 1(b). While the positron density profile peaks at the center of a pure vacancy, it is maximum around $1.5a_0$ from the center of a vacancy-hydrogen complex. These features of the electron-positron density profiles are responsible for the predicted changes in the positron-annihilation characteristics around defect-trapped hydrogen.

The annihilation rate λ of positrons in an inhomogeneous electron gas is calculated in the local density approximation,[13]

$$\lambda = \int d\vec{r}\, |\psi_+(\vec{r})|^2 \Gamma(n(\vec{r}))\ , \qquad (3)$$

where $\psi_+(\vec{r})$ is the wave function of the bound positron and

$$\Gamma(n) = (2 + 134n) \times 10^9 \ {\rm s}^{-1} \qquad (4)$$

is the annihilation rate for a homogeneous electron gas of density n. The annihilation rate with the core electrons of the host metal is included[14] by replacing the electron density outside the vacancy cell by $n(r) + (\Gamma_c/\Gamma_v)n_0$, where Γ_c and Γ_v are the annihilation rates with core and valency electrons, respectively. We have used $\Gamma_c/\Gamma_v = 0.154$ for Al and 2.16 for Cu which yield bulk lifetimes of 162 ps in Al and 137 ps in Cu. These values agree closely with the experimental values[15] of 161 ps in Al and 132 ps in Cu. Using computed positron density $|\psi_+(r)|^2$ and electron density $n(r)$ in Eq. (3), we find the positron lifetimes $\tau = 1/\lambda$ in vacancy-hydrogen complex in Al and Cu to be 188 and 153 ps, respectively. These values are significantly smaller than the calculated lifetimes of 239 ps in Al vacancy and 170 ps in Cu vacancy. This marked decrease in the positron lifetime is the result of a simultaneous increase in the number of electrons, and decrease in the number of positrons inside the Wigner-Seitz sphere of the vacancy-hydrogen complex. For example, the fraction of positron (and number of electrons) inside the vacancy and vacancy-hydrogen complex in Al are, respectively, 0.618 (1.241) and 0.577 (2.325). The corresponding values in Cu are 0.292 (0.525) and 0.282 (1.604).

To our knowledge no experimental data on positron lifetimes in vacancy-hydrogen complex are available at the present time. Therefore to assess the accuracy of our predicted values, it is worth noting that the calculated positron lifetime inside the vacancy in Al of 239 ps is in remarkable agreement with experimental value of 242 ps. Similar agreement[3,4] between theory and experiment has been found for several metallic hosts. It should be noted that the annihilation rate with the hydrogen screening cloud was calculated using the same enhancement as for the electron gas in Eq. (4). In reality the enhancement within the range of rapidly varying electron density around hydrogen could be smaller than that prescribed in Eq. (4). Thus the positron lifetime in the vacancy-hydrogen complex could represent an underestimate. Since this rapidly varying density is confined to only a narrow region, we do not expect the predicted lifetimes to be significantly different from experimental values when available.

We have also calculated the angular correlation between the annihilation quanta which measures the momentum distribution of the annihilating electron-positron pair. In the independent-particle model,[3] the momentum density is given by

$$\rho(p) \propto \sum_i \left| \int d\vec{r}\, e^{-i\vec{p}\cdot\vec{r}} \psi_+(\vec{r}) \psi_i(\vec{r}) \right|^2 , \qquad (5)$$

where ψ_i is the wave function of the conduction electron in ith state and the summation is carried over all occupied states. In a conventional angular correlation or Doppler-broadening experiment, one measures only one momentum component. For an isotropic distribution, the counting rate is

$$I(p_z) \propto \int_{p_z}^{\infty} dp\, p\rho(p) , \qquad (6)$$

where p_z is given by $\theta = p_z/m_0c$, θ being the angle between the two x-ray quanta.

In Fig. 2 we have plotted the angular correlation curve for hydrogen-vacancy complex in Al and compared it to that in pure vacancy. The decrease of about 7% in the peak counting rate, concomitant with an increase in the full width at half maximum (FWHM) for hydrogen-vacancy complex, originates from a broadening of the positron distribution. It is quite clear that the angular correlation curve, just like the positron lifetime will be intermediate between the pure vacancy and bulk annihilation. Our prediction concerning the systematics in the angular correlation curves is in agreement with the experimental observation in Zr-H (Ref. 16) and Ni-H (Ref. 17) alloys containing vacancies.

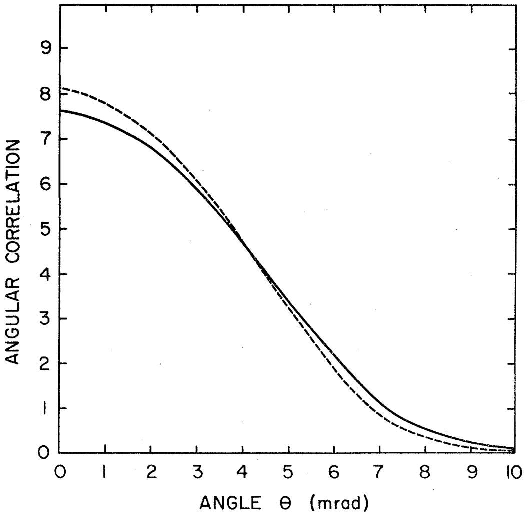

FIG. 2. Angular-correlation curves for positron annihilation in a hydrogen-vacancy complex (solid line) and in a pure vacancy (dashed line) in Al.

Lengeler *et al.*[8] have studied hydrogen-vacancy complexes in Cu. They see a clear change in the Doppler broadening parameter when the vacancies are occupied by hydrogen, and interpret this change by postulating a reduced trapping rate for positrons. Our results for the positron binding energy suggest that the trapping rate should be essentially the same for a pure vacancy as for a hydrogen-vacancy complex. Since Lengeler *et al.*[8] do not get exactly the bulk annihilation parameter for samples containing hydrogen, there is room for an alternate interpretation that the positron trapping rate remains the same as for pure vacancies, but the annihilation parameter for the vacancy-hydrogen complex is different from that for the pure vacancy (being closer to the bulk value). This would be in agreement with our calculated lifetimes.

In conclusion, we have presented the first theoretical study of the positron annihilation characteristics in hydrogen-vacancy complexes in metals. Several interesting results have emerged. (1) Contrary to earlier suggestion,[8] the binding energy of the positron in a vacancy-hydrogen complex is not very different from that in a pure vacancy. (2) There are significant differences in the positron lifetimes and angular correlation curves between bulk, pure vacancy, and vacancy-hydrogen complex. These result from the corresponding changes in the electron and positron density profiles. (3) The differences in the lifetimes between bulk, vacancy, and vacancy-hydrogen complex suggest interesting effects during annealing studies, since hydrogen, vacancy, and vacancy-hydrogen complex are expected to have different diffusive properties at elevated temperatures.

We hope that this work would stimulate further experimental research in this area not only because of the role positrons can play in probing trapped hydrogen but one can also estimate the activation energy of hydrogen associated with the trap from annealing studies. Further theoretical and experimental work on trapping of hydrogen and helium by both point and extended defects in metals would be quite valuable for understanding fundamental as well as technologically important problems.

ACKNOWLEDGMENT

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