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Positron annihilation as a probe for impurities trapped by vacancy clusters

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The electronic structure of impurity atoms trapped by metal vacancies and vacancy clusters is examined by analyzing the positron annihilation characteristics. It is shown that the binding energies and lifetimes of positrons attached to impurity-vacancy complexes can provide a measure of the spatial character of electrons.

The electronic structure of impurities is often characterized by the charge transfer between the impurity and host atoms. In a metallic environment the charge state of an impurity cannot be determined unambiguously since the impurity charge is screened by the conduction electrons. In this Communication we show that the binding energy and lifetime of positrons attached to impurity-vacancy complexes bear a distinct signature of the impurity's electronic structure. Furthermore, in the limit of large vacancy clusters, the trapped impurities are found to exhibit the rudiments of the conventional rule of electronegativity.

It is well known that vacancies and vacancy clusters (voids) provide an attractive potential well which trap the positron.[1] The binding energy of a positron inside a monovacancy in Al, for example, is about 2 eV and increases steadily as the vacancy grows in size. If an impurity is introduced at the vacancy site, the positron would experience a different potential well. Consequently, the binding energy and lifetimes of positrons attached to the impurity-vacancy complex will be affected. Thus, the difference between the positron binding energy and lifetime in the impurity-vacancy complex and in the pure vacancy can be used as probe of the impurity's electronic structure.

The problem now at hand is to find out if a positron can be bound to an impurity-vacancy complex. A bound state is possible if there exists a solution to the Schrödinger equation for the positron, namely,

$$H\psi_+(\vec{r}) = -\epsilon_+\psi_+(\vec{r}) \quad . \tag{1}$$

Here H, ϵ_+, and $\psi_+(\vec{r})$ are, respectively, the Hamiltonian, binding energy, and eigenstate of the positron. The positron Hamiltonian is given in atomic Rydberg units by

$$H = -\nabla^2 + V_{\mathrm{es}}^{+}(\vec{r}) + \{V_{\mathrm{corr}}[n(r)] - V_{\mathrm{corr}}[n_0]\} - V_0\Theta(\vec{r}-\vec{a}) \quad , \tag{2}$$

where $V_{\mathrm{es}}^{+}(\vec{r})$ is the electrostatic potential experienced by the positron due to all the charges in the material. $V_{\mathrm{corr}}^{+}[n(\vec{r})]$ is the correlation potential[2] between the positron and electrons of density $n(\vec{r})$ in the local density approximation and is measured with respect to the correlation potential $V_{\mathrm{corr}}[n_0]$ for the average background. V_0 is the zero-point energy[3] of the positron in the perfect host. The Heaviside function Θ is zero for $r < a$ and unity for $r > a$, where a is the radius of the vacancy. The electrostatic potential of the positron is simply negative of the electrostatic potential V_{es} felt by the electron.

The density distribution of the inhomogeneous electron gas around a defect and the corresponding electrostatic potential are determined in the density-functional theory[4] by solving the following set of equations self-consistently (all quantities are in atomic Rydberg units):

$$\{-\nabla^2 + V_{\mathrm{es}}(r) + V_{\mathrm{xc}}[n(r)] - V_{\mathrm{xc}}[n_0]\}\psi_k(r) = E_k\psi_k(\vec{r}) \quad , \tag{3}$$

$$n(r) = \sum_k^{\mathrm{occ}} |\psi_k(r)|^2 \quad , \tag{4}$$

$$\nabla^2 V_{\mathrm{es}}(r) = -8\pi[n(r) - n_{\mathrm{ext}}(\vec{r})] \quad , \tag{5}$$

$$n_{\mathrm{ext}}(\vec{r}) = Z_I\delta(\vec{r}) + n_0\Theta(\vec{r}-\vec{a}) \quad . \tag{6}$$

Here, $V_{\mathrm{xc}}[n(\vec{r})]$ is the exchange-correlation potential of the electrons in the local density approximation. The external perturbation $n_{\mathrm{ext}}(\vec{r})$ on the positive charge background, due to a defect complex, is modeled through Eq. (6) by inserting an impurity nucleus containing Z_I protons at the center of a vacancy of radius a. For a monovacancy, a is equal to the Wigner-Seitz radius and can be increased to simulate the effect of vacancy clusters or voids. For $Z_I = 0$ and $a = R_{WS}$, Eq. (6) would correspond to a pure monovacancy.

In this Communication we report calculations for impurities H, He, Li, Be, B, C, N, and O ($Z_I = 1$, 2, 3, 4, 5, 6, 7, and 8, respectively) located at the center of 1-, 2-, and 4-spherical vacancy clusters in aluminum matrix. The first stage of the calculation involves the self-consistent solution of the density-functional Eqs. (3)–(6). The purpose of choosing Eq. (6) to represent an impurity-vacancy complex is threefold: (i) We avoid using ambiguous pseudopotentials for the impurity. (ii) The core and the scattering electrons of the impurity ion are computed in the metallic environment. (iii) The repulsion of the positron from the impurity nucleus is explicitly incorporated in the electrostatic potential.

The electrostatic potential obtained from Eq. (5) was then substituted into Eq. (2) after reversing its sign. Using[3] $V_0 = 4.9$ eV, Eq. (2) was solved to search for possible bound states of the positron. Since the sample may contain only one positron at a time, the ground state with $l = 0$ needs to be considered. We found s-wave bound states for positrons in pure vacancies as well as in all the impurity-vacancy complexes studied here.

For the purpose of the present paper, it is convenient to discuss the difference in the positron binding energies, $\Delta\epsilon_+$ between pure vacancies $[\epsilon_+(V)]$ and impurity-vacancy complexes $[\epsilon_+(I\text{-}V)]$, namely,

$$\Delta\epsilon_+ = \epsilon_+(V) - \epsilon_+(I\text{-}V) \ . \tag{7}$$

A negative $\Delta\epsilon_+$ would therefore mean that the impurity ion provides an additional *attractive* potential for the positron. The converse is true if $\Delta\epsilon_+$ is positive.

The results of $\Delta\epsilon_+$ are plotted in Fig. 1 for impurities H, He, Li, Be, B, C, N, and O embedded inside clusters of 1, 2, and 4 vacancies in Al. The sharp deviation of $\Delta\epsilon_+$ from zero in all cases studied is a clear indication that the impurity has a substantial influence on the positron's binding energy. There are several interesting features to be noted in Fig. 1. First, lithium has the maximum destabilizing effect on the binding of a positron to lithium-vacancy complexes. For example, a positron is barely bound in a Li-monovacancy complex. This is consistent with the strong affinity of lithium ions for attracting electrons. Second, as the vacancy clusters grow in size, impurities such as hydrogen, nitrogen, and oxygen help to strengthen the binding of positrons to these complexes. It is known, from many calculations[5] based upon widely different models, that there is charge transfer from host atoms to hydrogen. Thus hydrogen remains in an "anioniclike" form in metals. This tendency would certainly enhance positron trapping. To understand the trend of $\Delta\epsilon_+$ for nitrogen and oxygen trapped in large vacancy clusters, we note that the local electron density inside a void decreases and the isolation of impurity ion from host atoms increases and the void gets bigger. In the limit of large voids the ionicity of nitrogen and oxygen would tend to be negative. Thus nitrogen and oxygen impurities would enhance positron trapping in a manner similar to hydrogen.

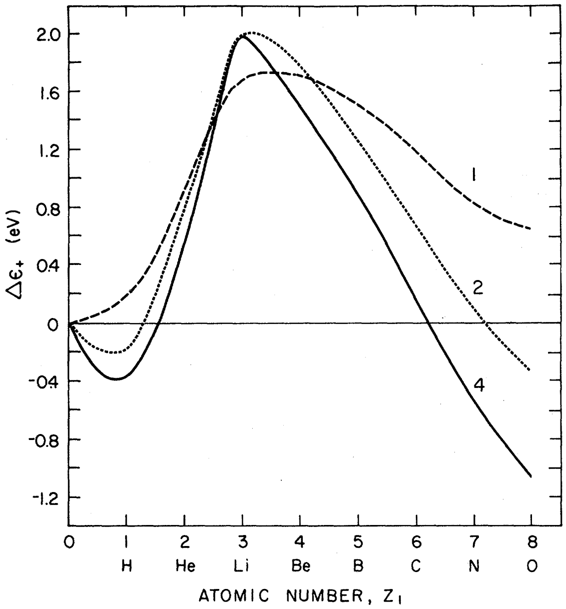

FIG. 1. Difference between the binding energy of a positron in pure vacancy and in impurity-vacancy complex $\Delta\epsilon_+$ Eq. (7) as a function of the impurity's atomic number. The curves labeled 1, 2, and 4 correspond, respectively, to impurities located inside 1-, 2-, and 4-vacancy clusters in Al.

Since the electrostatic potential of the positron is calculated in the jellium approximation, one may wonder about the effect of the lattice structure on the positron binding energy. Several calculations[6] for the positron binding to aluminum-metal vacancy exist in the literature. For example, the non-self-consistent supercell band-structure calculation of Gupta and Siegel[7] yields 3.31 eV for the positron monovacancy binding energy in Al. This has to be compared with 1.75 eV obtained in our calculation. Recently, Chakraborty[8] has carried the supercell calculation of Gupta and Siegel[7] to self-consistency and finds the corresponding positron binding energy to be 2.3 eV. In this paper we are, however, interested in the difference binding energy $\Delta\epsilon_+$ and do not expect the solid-state effects to significantly alter the systematic trend in Fig. 1.

To gain further insight into the nature of screening, we have calculated the change in the total net electronic charge inside the vacancy when the impurity is added, namely,

$$\Delta Z = Z_{I\text{-}V} - Z_V \ . \tag{8}$$

Here, $Z_{I\text{-}V}(Z_V)$ is the net electron charge inside the cavity of an impurity-vacancy complex (pure vacancy). These are calculated by integrating the induced charge in Eq. (4) up to a radius a defined in Eq. (6). In Fig. 2, we have plotted $\Delta Z/Z_I$ for various impurities located inside 1-, 2-, and 4-vacancy clusters. The impurities appear to have a negative (positive) charge on them inside a vacancy if $\Delta Z/Z_I > 1$ ($\Delta Z/Z_I < 1$). In all impurity-vacancy clusters studied, Li continues to have the maximum positive charge on it. This is

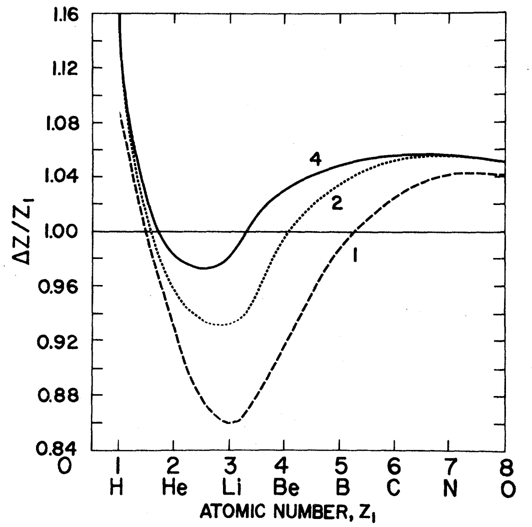

FIG. 2. Effective charge on an impurity as a function of atomic number of impurities located inside monovacancy (curve 1), 2-vacancy complex (curve 2), and 4-vacancy complex (curve 4) in Al. See Eq. (8).

consistent with the results of Fig. 1. However, it is difficult to find one-to-one correspondence between the results in Figs. 1 and 2 since the binding energy of a positron is not solely determined by the amount of charge inside a vacancy cluster. These charge transfers would have significant effect on the core level shifts obtained from x-ray photoemission spectroscopy measurements. We have also analyzed the spatial character of the electron and positron denstiy profiles around impurity-vacancy complexes. The pileup of electrons around the impurity nucleus increases with the increase in the impurity's atomic number. Correspondingly, the positron density decreases sharply in the vicinity of the impurity. These profiles are reflections of the changes in the electrostatic potential when impurities are added to a vacancy.

The overlap between the electron and positron density profiles determines the lifetime τ of the positron. In the local density approximation,[9] the annihilation rate $\lambda = 1/\tau$ is given by

$$\lambda = \int d\vec{r}\, |\psi_+(\vec{r})|^2 \Gamma[n(\vec{r})] \ , \tag{9}$$

where

$$\Gamma[n] = (2 + 134n) \times 10^9 \ \mathrm{sec}^{-1} \tag{10}$$

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 in a manner suggested by West.[10] There are two factors in Eq. (9) that influence the variation of the positron lifetime for various impurity-vacancy complexes. As the atomic number of the impurity inside the vacancy grows, the electron density simultaneously increases. Thus, if this factor were the only important term, one would expect the positron lifetime to decrease monotonically with the atomic number of the impurity. However, the results of the variation in the binding energy of Fig. 1 suggests that the spatial extent of the positron distribution should also play a significant role.

We have calculated the positron lifetimes in Eq. (9) by using the self-consistent electron density in Eq. (4) and the positron wave function in Eq. (1). The results are plotted in Fig. 3 for various impurities embedded in clusters containing 1, 2, and 4 vacancies. Two important features should be noted: (i) A hump in the lifetime distribution persists for all vacancy clusters. This hump, whose magnitude can be as large as 10 ps, indicates the important interplay between electron and positron density profiles. (ii) For monovacancy and divacancy clusters the lifetime of positrons in trapped state with N and O impurities can even be lower than the bulk lifetime of 161 ps.[11] In order to judge the reliability of our lifetime prediction, two points should be noted: (i) Our calculated positron lifetime of 239 ps in Al monovacancy compares very well with the experimental value of 242 ps. For impurity-vacancy complexes, the annihilation rate in the immediate vicinity of the impurity was cal-

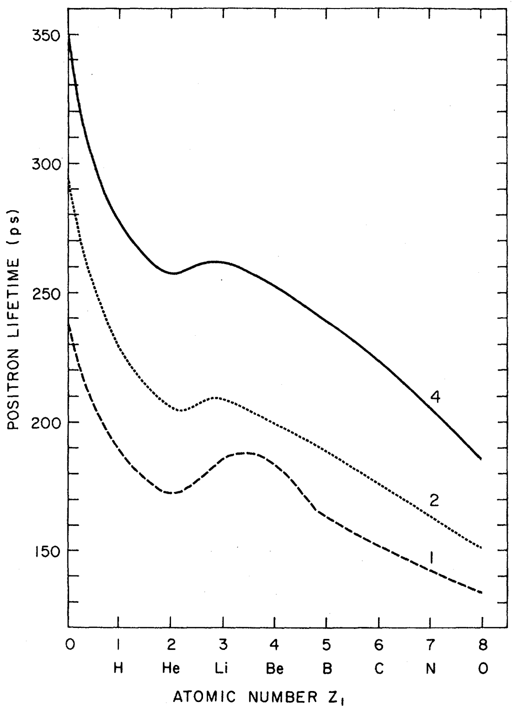

FIG. 3. The variation of positron lifetimes with respect to the atomic number of impurities located inside monovacancy (curve 1), 2-vacancy complex (curve 2), and 4-vacancy complex (curve 4) in Al.

culated using the same enhancement as for the electron gas in Eq. (10). As pointed out earlier,[12] this is not expected to significantly alter the predicted lifetimes, since the rapidly varying electron density in the vicinity of the impurity nucleus is confined to a narrow region. (ii) The 2- and 4-vacancy complexes are assumed to be spherical. Recently, McMullen *et al.*[13] have shown that the positron lifetime in an aspherical divacancy differs from that in a spherical divacancy by only 3%. We should again point out that the main interest here is in the variation of the lifetimes with the impurity's valence, and not as much in the absolute numbers.

The results discussed above correspond to impurities located centrally inside a vacancy cluster. While this is true for heavier impurities, as well as rare-gas atoms, for some of the light impurities such as hydrogen considered here, an off-center positron may be preferred.[14] We are presently studying the equilibrium configuration and binding energy of impurities associated with vacancies. The results will be published in due course. We do expect binding of positrons to impurity-vacancy complexes considered here in situations where impurities are off centered. The qualitative trends in systematics of the positron binding energies and lifetimes are, however, expected not to change.

In conclusion, we have demonstrated the possibility of studying the electronic structure of impurity atoms in metallic environment through a systematic measurement of the binding of a positron to impurity-vacancy complexes and the corresponding lifetimes. The results also indicate that the lifetimes of positrons in metal voids would continue to decrease as impurities, such as helium, accumulate inside the void. It is hoped that this work will stimulate experimental studies of positron annihilation spectroscopy in impurity-vacancy complexes.

ACKNOWLEDGMENT

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