Electron and Positron Densities and the Temperature Dependence of the Positron Lifetime in a Vacancy in Aluminum

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The results of an augmented-plane-wave calculation of the electron and positron density distributions in a vacancy in Al are reported. The environment of the vacancy was simulated by a super cell with a volume 27 times that of the primitive unit cell. These results show that jellium-model calculations overestimate the electron density in a vacancy. The variation of the positron lifetime associated with thermal expansion of the lattice is also presented.

Positron-annihilation experiments have the unique capability to probe the electronic structure of materials containing atomic defects, since positrons are very sensitive to the variations of the electron density in the crystal and prefer regions of low-electron density away from the ion cores. Positrons are trapped at vacancies in metals and this localization results in a positron lifetime which is ~(20–50)% longer than in its untrapped state in the crystal. Previous theoretical investigations of positron localization at vacancies in metals have been limited to simple metals to which the jellium model,[1-5] or modifications to it,[6] could be applied. The jellium-model calculations ignore the existence of the ionic lattice and, as a result, the electron density inside the vacancy sphere tends to be substantially overestimated.[6] Hodges[7] has attempted to include explicitly the lattice using a pseudopotential approach and has calculated the positron-vacancy binding energy for a number of simple metals.

The results of an augmented-plane-wave (APW) calculation[8] of the electron and the positron density distributions associated with a vacancy are presented here; this the first time that a realistic band-structure approach has been used to investigate this problem. Although aluminum was chosen as a test case, the technique is rather general and can be used to study both simple and transition metals with the same degree of accuracy. The inadequacy of jellium models has been recognized,[3,6] even for a polyvalent, simple metal such as Al. The vacancy formation energies calculated within the jellium approximation[3,9] are found to be erroneous, since the jellium model does not correctly represent the electron density inside a vacancy. The present approach attempts to remedy these difficulties.

The atomic environment of the vacancy was simulated by using a large fcc unit cell (super cell)[10] with a lattice constant three times that of the normal Al lattice. The vacancy is represented by the absence of an Al atom, as shown in Fig. 1. The presence of a vacancy causes the various surrounding shells of Al atoms to see different environments and, hence, these shells have been treated accordingly. This amounts to using four different species in the super cell. The crystal potentials for the electrons and positron were obtained in the usual manner by superposition of the atomic charge densities[11] and the atomic potentials were derived from the solution of Poisson's equation. The exchange and correlation contribution to the electronic potential was included using the $X\alpha$ method with the Slater exchange parameter $\alpha = 1.0$. For the positron potential the Slater term was not included. The crystal potential was made spherically symmetric inside each muffin-tin sphere, but was not as-

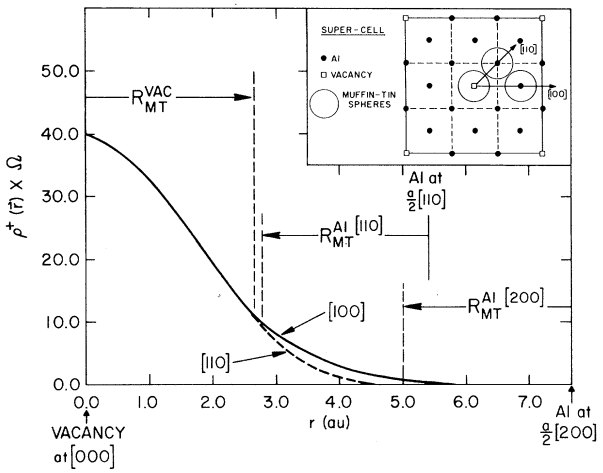

FIG. 1. Positron density $\rho^+(\vec{r})$ in the vacancy-trap state along the [100] and [110] directions multipled by Ω, the volume of the super cell. R_{MT} denotes the radius of the muffin-tin sphere. The (100) face of the face-centered cubic super cell is shown in the inset.

sumed constant in the interstitial region between the spheres.

Aluminum at 250°C, with lattice constant $a = 7.6950$ a.u., was initially considered. Two states of the positron at the zone center were found: a bound state in the vacancy with energy $E_v = -3.31$ eV and a higher state, usually referred to as the Bloch state with energy $E_B = 0$ with respect to the bottom of the positron conduction band. This gives a binding energy of the positron trapped in a vacancy in Al at 250°C of $E^B = 3.31$ eV, a value similar in magnitude to those from earlier calculations. The maximum depth of the trapping potential V_t that the positron experiences at the center of the vacancy is 10.27 eV, as measured from the bottom of the positron conduction band. This potential varies by ~2.7 eV from the center of the vacancy to the surface of its muffin-tin sphere.

In Fig. 1, the positron charge-density variation, calculated from the positron wave function in the trapped state, is shown from the center of the vacancy along the [110] and [100] directions. A substantial localization of the positron density within the muffin-tin sphere of the vacancy is seen in Fig. 1. The positron density drops off rapidly as one approaches the center of the nearest-neighbor muffin-tin sphere (i.e., along [110]) containing the Al ion core. A detailed analysis of the positron density distribution in the super cell shows that roughly 0.5 of the positron is located within the muffin-tin sphere of the vacancy, in contrast to the volume of this sphere which is only 2.7% of the volume of the super cell. Approximately 0.2 of the positron lies inside the twelve nearest-neighbor muffin-tin spheres surrounding the vacancy (each containing about 0.0165 positron), and the remaining 0.3 lies in the interstitial region. It is noteworthy that the remaining fourteen muffin-tin spheres inside the super cell contain almost no positron density (i.e., <1%). The positron density inside the vacancy sphere shows relatively little anisotropy. However, the anisotropy is rather substantial in the interstitial region surrounding the vacancy, as expected from its atomic environment and shown in Fig. 1.

The electron density was calculated from the Bloch functions by summing over all states below the Fermi level. In the present case there are 78 electrons in the unit cell and hence 39 bands to be filled up. The electron density obtained along the [110] direction is shown in Fig. 2. The density at the center of the vacancy is only about 6% of the uniform density $\rho_0 = 78/27\Omega_0$, where Ω_0 is the volume of the primitive unit cell of the Al lattice. This is roughly a factor of 3–4 smaller than obtained from jellium-model calculations.[2-5] The effect of including the ionic lattice has been to decrease the electron density in the vacancy. The vacancy muffin-tin sphere, which has a volume roughly two-thirds that of the Wigner-Seitz sphere, contains about 0.8 electrons.

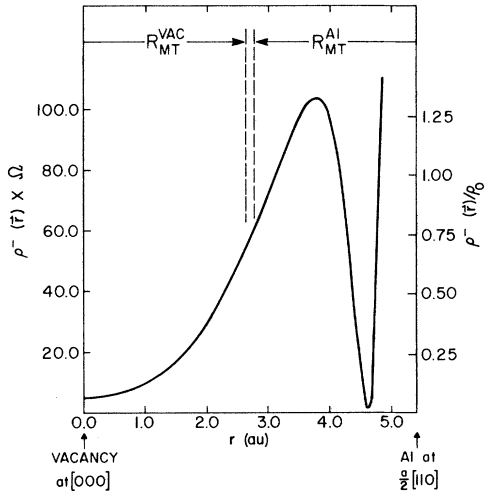

FIG. 2. Electron density $\rho^-(\vec{r})$ at a vacancy shown along a [110] direction. Ω is the volume of the super cell and ρ_0 is defined in the text.

The rate of positron annihilation, λ, is given by the integral of the overlap of the electron and positron densities[12]

$$\lambda = \pi r_0^2 c \int \rho^-(\vec{r}) \rho^+(\vec{r}) d^3r, \quad (1)$$

where r_0 is the classical electron radius, c is the velocity of light, ρ^- and ρ^+ are the electron and positron densities in the crystal, respectively, and the integral is evaluated over the unit cell. Using Eq. (1) the annihilation rate of the positron in the Bloch state, λ_B, has been calculated in two separate ways: (1) A calculation of the electron and positron densities using the standard primitive unit cell of Al was performed and the annihilation rate from valence electrons was 1.290 ns^{-1}. A calculation of λ in the super cell without a vacancy was in excellent agreement with this value. (2) A second calculation using the electron density of the super cell with a vacancy and the Bloch state of the positron resulted in $\lambda = 1.239$ ns^{-1}. Clearly the annihilation rate from this second calculation is smaller than that from the first, since there are now three less valence electrons participating in the annihilation process (78 electrons versus 81 in the first), due to the

presence of a vacancy in the unit cell. Although the two results agree quite well and this agreement will improve as the size of the super cell is increased, the discrepancy can be removed by simply normalizing the second value to 81 electrons; i.e., by multiplying by a factor $\frac{81}{78}$. This procedure yields $\lambda = 1.287\ \mathrm{ns}^{-1}$, in very good agreement with the value of $1.290\ \mathrm{ns}^{-1}$ obtained in the first calculation. This procedure has been used to correct all the calculated annihilation rates for the finite size of the super cell. The total contribution to λ_B from the core electrons was $0.222\ \mathrm{ns}^{-1}$, which is roughly 17% of the valence-electron contribution. The contribution from the 1*s* electrons of the core was almost negligible, and the 2*s* and 2*p* electrons contribute roughly equally per electron to the annihilation rate. Using the Brandt-Reinheimer[13] formula for the enhancement due to electron-positron correlation, the enhanced valence-electron annihilation rate is $5.433\ \mathrm{ns}^{-1}$, giving an enhancement factor of 4.2. Assuming an enhancement factor of 1.6 for the core-electron contribution,[14] the total annihilation rate of the Bloch-state positron $\lambda_B = 5.792\ \mathrm{ns}^{-1}$, which yields a positron lifetime $\tau_B = \lambda_B^{-1} = 172.6$ ps at 250°C. This is in excellent agreement with the experimentally observed value[15] of 172 ps at 250°C in Al.

The unenhanced valence and core contributions to the positron annihilation rate in the vacancy-trap state were 0.8384 and $0.0574\ \mathrm{ns}^{-1}$, respectively. Approximately 30% of the valence-electron contribution to the annihilation rate comes from the muffin-tin sphere of the vacancy, 30% from the surrounding twelve Al-atom muffin tins and the remaining 40% from the interstitial region. Again using the Brandt-Reinheimer formula for the enhancement of the contribution from valence electrons, and the same enhancement factor of 1.6 for the core contribution, the lifetime of the positron in the vacancy $\tau_v = \lambda_v^{-1} = 231$ ps was obtained. The Brandt-Reinheimer formula actually does not correctly account for the enhancement of the electron density in a vacancy,[13] since the electron density there is low and varies rapidly. The valence enhancement was therefore reduced by 5.5% in order to obtain agreement with experiment. This resulted in $\tau_v = 244.2$ ps at 250°C as compared with the experimental value of 244 ps in Al.[15]

It was additionally possible within the present framework to consider the variation of τ_B and τ_v with lattice expansion due to increasing temperature. It has generally been assumed that τ_B increases roughly in proportion to the volume expansion, whereas τ_v remains essentially constant (as discussed in Ref. 15). In an effort to study the positron-lifetime variations associated with the thermal expansion of the lattice, the calculations were repeated for two additional lattice constants corresponding to Al at 450 and 650°C. It was found that with increasing lattice constant, the positron trapping potential was slightly shallower, resulting in a small decrease in the positron-vacancy binding energy. The calculated fractional increase in τ_B and τ_v as a function of the fractional increase in the volume of the lattice is shown in Fig. 3. The positron lifetime in the vacancy, τ_v, increases rather slowly compared with thermal expansion, changing only by half as much. On the other hand, the lifetime in the Bloch state, τ_B, increases more rapidly, about 75% that expected from thermal expansion. It is interesting to note that over a 400°C range both lifetimes have increased by ~5 ps. The variation in τ_v with temperature, T, thus calculated is fully consistent with measurements of $\tau_v(T)$ in Al.[15] However, the experimentally observed temperature dependence of τ_B in Al is more complex[15] and requires the inclusion of phonon-coupling effects[16] in addition to lattice expansion to explain even the observations below ~350°C.

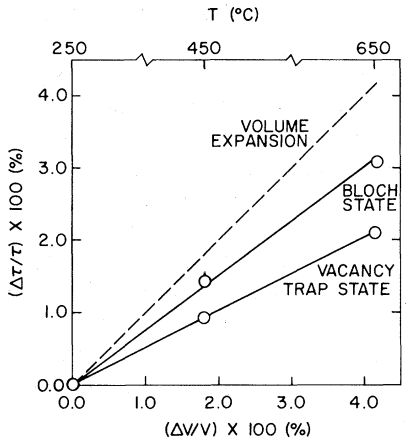

FIG. 3. Fractional variation of the positron lifetimes in the Bloch state (τ_B) and in the trapped state in the vacancy (τ_v) vs fractional change in volume, calculated for three different temperatures, compared with the variation expected from a simple volume-expansion model.

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Spin-Disorder–Induced Raman Scattering in Europium Chalcogenides

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The four independent symmetry components of first-order phonon Raman scattering in the paramagnetic phase of europium chalcogenides have been measured around the fundamental gap. The usually unobservable antisymmetric Γ_{15}^{+} component is found to be the largest one. The resonance enhancements of the different components, their relative intensities, and the scattered spectra are explained by a parameter-free microscopic theory which takes into account the spin disorder of the Eu^{2+} ions and the spin-orbit interaction of the $4f$ electrons.

Raman scattering (RS) of europium monochalcogenides EuX (X=O,S,Se,Te) has attracted considerable interest because of anomalous features, which seem to be unique to this class of magnetic semiconductors.[1-8] In the paramagnetic phase of fcc EuX one observes symmetry-forbidden first-order[1,3,7] RS with a broad peak at a frequency ω_0 between the zone-center TO and LO phonon frequencies. Contrary to previous measurements,[1-3] we arrive, on the basis of the polarization dependence of this peak, at definite conclusions about its origin, i.e., the scattering mechanism and the phonons involved.

In order to study this problem in more detail we have measured the polarization dependence of this mode in EuX at 300 K for laser frequencies above and below the fundamental gap. The measurements have been performed in back-scattering configuration for laser excitations from 1.5 to 2.8 eV, using the discrete lines of Kr and Ar lasers and an oxacine dye laser. Figure 1 shows the Raman spectrum for 2.41-eV (5145-Å) excitation on a (001) crystal face of EuS. The four different scattering components were taken in the configurations (Fig. 1 from top to bottom) $z(x+y, x-y)\bar{z}$, $\bar{z}(x,y)\bar{z}$, $z(x,x)\bar{z}$, $z(x+iy, x-iy)\bar{z}$. We observe a pronounced polarization dependence of the mode at $\omega_0 = 240$ cm^{-1} and, in particular, a strong antisymmetric Γ_{15}^{+} component.

Figure 2 shows the Γ_{15}^{+} and the Γ_{12}^{+}, Γ_{25}^{+} scattering components of EuS at 300 K measured as a function of the excitation frequency. Each individual component was evaluated from the measured areas under the peaks of the mode at $\omega_0 = 240$ cm^{-1} in the different scattering configurations. Particular care was taken for the corrections involved in the experiment, i.e., different responses of the circular and linear polarizers, spectrometer response, and background subtraction. The scattering cross sections have been corrected for absorption, measured on the very same sample used for the resonant RS experiment. In Fig. 2 we do not show the Γ_{1}^{+} component since it is zero within the experimental error. Figure 2