

Theoretical Calculations of Positron Lifetimes for Metal Oxides

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Our recent positron lifetime measurements for metal oxides suggest that positron lifetimes of bulk state in metal oxides are shorter than previously reported values. We have performed theoretical calculations of positron lifetimes for bulk and vacancy states in MgO and ZnO using first-principles electronic structure calculations and discuss the validity of positron lifetime calculations for insulators. By comparing the calculated positron lifetimes to the experimental values, it was found that the semiconductor model well reproduces the experimental positron lifetime. The longer positron lifetime previously reported can be considered to arise from not only the bulk but also from the vacancy induced by impurities. In the case of cation vacancy, the calculated positron lifetime based on semiconductor model is shorter than the experimental value, which suggests that the inward relaxation occurs around the cation vacancy trapping the positron.

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1. Introduction

Positron annihilation spectroscopy is a sensitive tool for vacancy-type defects in solids. In a perfect crystal, the positron wave function is distributed in the interstitial region because of the repulsion from the ion cores. If vacancy-type defects exist in solids, the positron wave function is localized at the defect where the electron density is lower than the other regions. The localization of the positron at the defect results in a longer lifetime of the positron compared to the lifetime in the bulk state because the positron lifetime is inversely proportional to the electron density where the positron annihilated. In the case of that several types of defects can be considered to exist, a combination with theoretical calculations of positron lifetimes allows to characterize measured positron lifetimes. One of the important factors in positron lifetime calculations is a description of the effect of the pileup of electrons around a positron. In general, the effect is taken into account by the enhancement factor. It has been confirmed that the enhancement factor based on the many-body calculations for a positron in a homogeneous electron-gas gives reliable positron lifetimes for metallic systems.¹⁻³⁾ However, it was pointed out that the electron-gas picture cannot be applied to semiconductors and insulators because the polarizability or the screening efficiency of the electrons is less than those in metallic systems.⁴⁾ In order to describe the electron-positron correlation in semiconductors and insulators, two models were proposed and their validities were examined by comparing the calculated positron lifetimes to the experimental results.⁴⁾ One of the two models, the insulator model, was formulated to reproduce the reported experimental results for insulators including MgO. However, our recent positron lifetime measurements revealed that the bulk positron lifetime in MgO is much shorter than the previously reported lifetime.⁵⁾ It is, therefore, worth to reconsider about the enhancement factor for insulators using more accurate experimental results. In this work, we have performed positron lifetime calculations for the bulk and vacancy states in MgO and ZnO based on first-principles electronic structure calculations. In order to discuss the validity of the enhancement factor for insulators, the

calculated results are compared with the experimental positron lifetimes that can be considered more reliable than previously reported values.

2. Computational Method

In order to obtain the electron density and potential, the DV-X α cluster method using a program code SCAT^{6,7)} is employed. In this first-principles calculation, the molecular-orbital wave function is expressed by a linear combination of atomic orbitals (LCAO) and is written as

$$\phi_l = \sum_i c_{il} \chi_i, \quad (1)$$

where c_{il} 's are coefficients. As the basis function χ_i , we use the numerical atomic orbitals obtained by solving the radial part of the Schrödinger equation for each atom in a given environment. 1s-3d, 1s-4p and 1s-2p atomic orbitals are used for Mg, Zn and O atoms, respectively. The model clusters composed of 135 and 144 atoms are used for the bulk state of MgO and ZnO, respectively. The central atom is extracted for the calculation of the vacancy state. All model clusters are embedded in Madelug potential generated by point charges outside the cluster.

The three-dimensional potential $V_+(r)$ sensed by positron is constructed as a sum of the electron static potential $V_C(r)$ due to the nuclei and the electrons, and a correlation potential $V_{\text{corr}}(n_-(r))$ describing the electron-positron correlation:

$$V_+(r) = V_C(r) + V_{\text{corr}}(n_-(r)), \quad (2)$$

where $n_-(r)$ is the electron density. For the density dependence of $V_{\text{corr}}(n_-(r))$ we have used the interpolation formula of Bronski and Nieminen⁸⁾ based on the result of many-body calculation.⁹⁾ The Schrödinger equation for the positron is solved by the finite-difference method¹⁾ employing the periodic boundary conditions for delocalized positron wave function in the bulk state. In the case of the localized positron at the vacancy, the boundary conditions are the vanishing of the positron wave function on the surface of a large polyhedron.

The positron lifetime τ is calculated as the reciprocal value of the positron annihilation rate λ by

$$\lambda = \pi r_0^2 c \int n_+(r) n_-(r) \gamma(r) dr, \quad (3)$$

where r_0 is the classical electron radius, c is the speed of light, $n_+(r)$ is the positron density and $\gamma(r)$ is the enhancement factor describing the short-range pileup of the electron at the positron. For the enhancement factor in metallic systems, interpolation forms based on free-electron gas calculations have been used.¹⁻³⁾ In insulators and semiconductors, the existence of the band gap is considered to reduce the effect in comparison with metallic systems. Two models are proposed by Puska *et al.* for the enhancement in compounds having the band gap.⁴⁾ One is called semiconductor model using the dielectric constant. The other is called insulator model based on atomic polarizability. The calculated positron lifetimes for bulk state in MgO reported by Puska *et al.* are 119 ps within the semiconductor model and 167 ps within the insulator model. In the insulator model, adjustable parameters are included and determined in order to reproduce the experimental lifetime of several insulators including MgO. However, our recent positron lifetime measurements revealed that the positron lifetime of bulk state in MgO is much shorter

than previously reported value of 166 ps.¹⁰⁾ It is suggested that this longer positron lifetime may reflect the defect component introduced to compensate the extra charge by impurities. Therefore the insulator model parameterized using unreliable experimental results is not appropriate even for MgO. In this work, as the conventional enhancement factor called the BN model, we have used the interpolation formula by Puska *et al.*¹¹⁾ based on Lantto's data.¹²⁾ In addition, the semiconductor model formulated by Puska¹³⁾ are also employed. As the high-frequency dielectric constant ϵ^∞ that appears in the semiconductor model, a value of 3.0⁴⁾ and 4.6¹⁴⁾ are used for MgO and ZnO, respectively. Partial annihilation rates are obtained using the results of the Mulliken population analysis.¹⁵⁾

3. Results and Discussion

3.1 Positron lifetimes for bulk state

Figures 1 and 2 show the electron densities, positron densities and potentials sensed by a positron in bulk MgO and ZnO, respectively. In metallic systems, the positron in a perfect crystal tends to be distributed in the interstitial

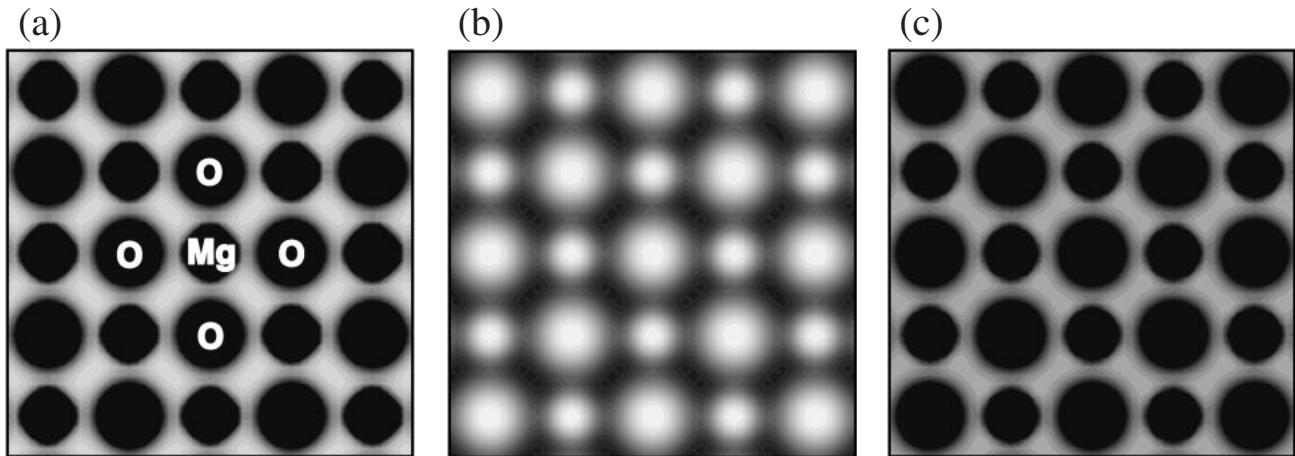


Fig. 1 Electron density (a), positron density (b) and potential sensed by positron on (001) in the bulk MgO. The plot range is from 0 to 0.1, 0 to 0.003 and -0.25 to 0.3 (a.u.) for (a), (b) and (c), respectively.

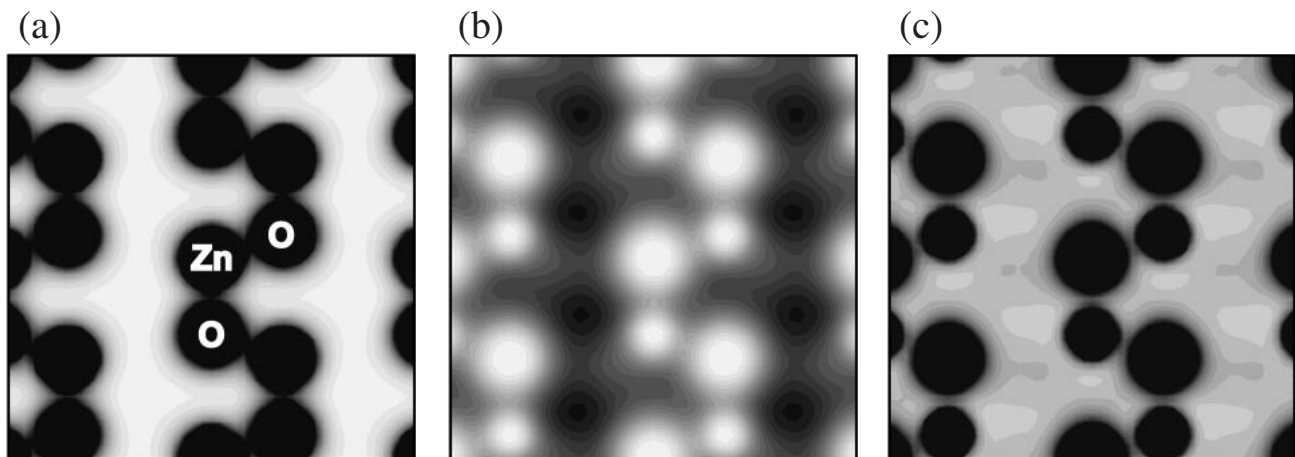


Fig. 2 Electron density (a), positron density (b) and potential sensed by positron on $(11\bar{2}0)$ in the bulk ZnO. The plot range is from 0 to 0.1, 0 to 0.003 and -0.25 to 0.3 (a.u.) for (a), (b) and (c), respectively.

regions because of the coulomb repulsion from the ion cores. In ionic compounds such as MgO and ZnO, the coulomb repulsion around the anion atoms is more screened by the electrons than that around the cation atoms. As seen in Fig. 1(c) and Fig. 2(c), the potentials around O atoms are lower than those around Mg/Zn atoms. Consequently, the positron distribution spreads into the sphere of O atoms. In MgO, there is only one type of interstitial site and the positron density is uniformly distributed into each interstitial site. On the other hand, tetrahedral sites and octahedral sites exist in ZnO. The positron density at the octahedral sites is higher than that at the tetrahedral sites because the octahedral sites have larger free volume than the tetrahedral sites in ZnO.

The calculated and experimental positron lifetimes are listed in Table 1. The experimental positron lifetime of bulk state was obtained by measuring the sintered specimens made of ultra-high purity MgO and ZnO powder.⁵⁾ Recently it was reported that the positron lifetime in the bulk state of ZnO is 170 ps at 300 K.¹⁶⁾ Comparing with our experimental lifetime of 153 ps the lifetime of 170 ps seems to be affected by a defect state. The calculated positron lifetimes of the semiconductor model are about 10 ps longer than those of the BN model because of the decrease of the enhancement effect. In the both cases of MgO and ZnO, the semiconductor model reproduces the experimental positron lifetimes better than the BN model. Table 2 shows positron annihilation rates of each orbital in MgO and ZnO. O atom has a larger annihilation rate than Mg or Zn atoms. This is because O atom has a larger ionic radius and negative charge that attracts a positron. By comparing MgO and ZnO, the positron annihilation rates of O atom in MgO are larger than those in ZnO. This is because

Table 2 Positron annihilation rate λ for the bulk states in MgO and ZnO.

		Annihilation rate, λ/ns^{-1}				Annihilation Fraction (%)
		λ_{core}	λ_s	λ_p	λ_d	
MgO						
	Mg	1.077	0.305	0.440	0.292	32.7
	O	0.018	1.320	4.263	—	67.3
ZnO						
	Zn	0.353	0.421	0.568	1.304	43.0
	O	0.020	0.895	2.996	—	57.0

the ionicity of O atom in MgO is greater than that in ZnO. According to the Mulliken population analysis, the net charge of O atom in MgO is -1.24 and that in ZnO is -1.08 . On the other hand, the covalent bonding, which mainly arises from the interaction between Zn 3d and O 2p orbitals, can be seen in ZnO.

3.2 Positron lifetimes for vacancy state

Figure 3 shows the calculated positron densities around Mg vacancy in MgO and Zn vacancy in ZnO. In contrast to the bulk state, the positron is localized at the vacancy site because of the missing of the ion cores and the negatively charged O atoms around the vacancy site. In ionic compounds such as MgO and ZnO, an anion vacancy hardly traps a positron owing to the Coulomb repulsion force from the neighboring cation atoms around the anion vacancy.

The positron lifetimes for the vacancy states calculated are listed with experimental positron lifetimes in Table 1. The experimental positron lifetime of Mg vacancy in MgO was obtained by measuring Ga-doped MgO.⁵⁾ For the measurement of positron lifetime of the Zn vacancy in ZnO, non-doped ZnO was irradiated with 1 MeV electrons up to $1.5 \times 10^{19} \text{ e}^-/\text{cm}^2$. Although the calculated positron lifetime of the bulk state using the semiconductor model shows an excellent agreement with the experimental values, those both of the Mg vacancy in MgO and Zn vacancy in ZnO are longer than the experimental values. This discrepancy mainly arises from neglecting the lattice relaxation around the vacancy in

Table 1 Calculated and experimental positron lifetimes (ps) for the bulk and vacancy states in MgO and ZnO.

	BN Model	Semiconductor model	Exp.
MgO bulk	121	131	130
Mg vacancy	180	201	185
ZnO bulk	144	153	153
Zn vacancy	200	217	202

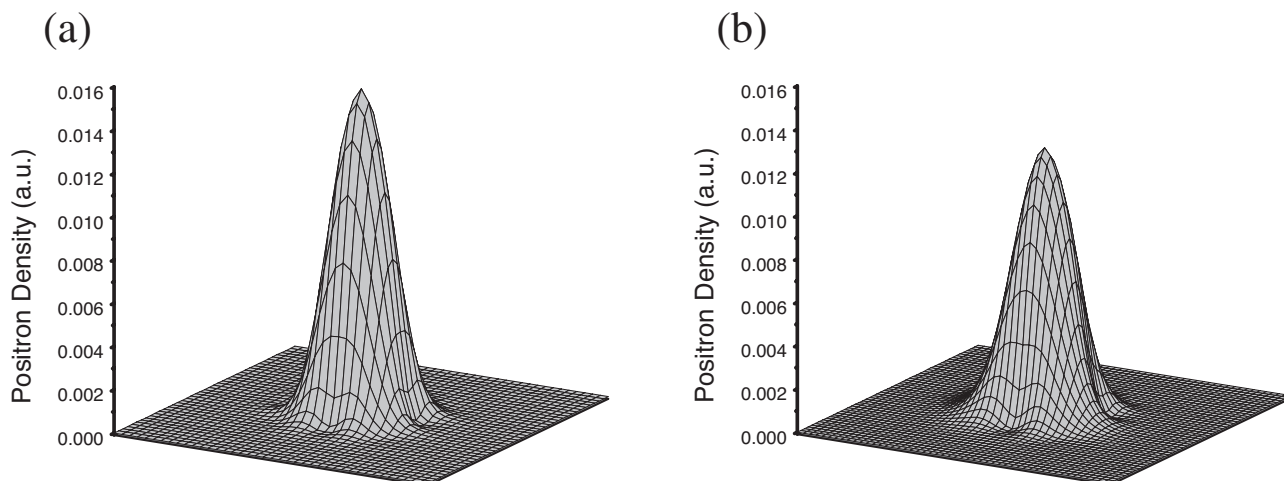


Fig. 3 Positron density around the Mg vacancy on (001) in MgO (a) and Zn vacancy on (11 $\bar{2}$ 0) in ZnO (b).

the positron lifetime calculation. As seen in equation (3), the positron lifetime is inversely proportional to the electron density and the lattice relaxation around the vacancy affects the positron lifetime. The longer calculated positron lifetimes than the experimental values for the vacancy suggest that the inward relaxation occurs around the vacancy. In ionic compounds, the Coulomb repulsion between neighboring atoms around a vacancy has an effect to induce the outward relaxation. In the case of the O vacancy in MgO, the occupation of electrons on the defect level, which is mainly composed of Mg 3s orbitals, increases the electron density at the O vacancy and reduces the Coulomb repulsion force. The outward relaxation around the O vacancy, therefore, decreases with the increase in the charge state of the O vacancy.¹⁷⁾ On the other hand, the defect level induced by the Mg vacancy is mainly composed of the O 2p orbitals that are distributed not at the Mg vacancy but at the neighboring O atoms. As a result, the relaxation around the Mg vacancy is insensitive to the charge state.¹⁷⁾ The distribution of the positron is also hardly affected by the charge state of the Mg vacancy. However, the positron trapped at the Mg vacancy is expected to reduce the Coulomb repulsion force between neighboring O atoms and decrease the outward relaxation, because the positron density is strongly localized at the Mg vacancy as seen in Fig. 3. Taking the lattice relaxation induced by the positron into account could reduce the discrepancy between calculated and experimental positron lifetimes for the Mg/Zn vacancy.

4. Conclusions

We have calculated positron lifetimes for bulk and vacancy states in MgO and ZnO based on first-principles electronic structure calculations. The experimental positron lifetimes for the bulk state both of MgO and ZnO are well reproduced by the semiconductor model. Regarding the vacancy state, the calculated positron lifetimes using the semiconductor model are longer than the experimental values. This result suggests that the inward relaxation occurs around the Mg and Zn vacancy. The localization of the

positron at the Mg/Zn vacancy reduces the Coulomb repulsion between Oxygen atoms around the Mg/Zn vacancy, which may leads to the inward relaxation of Oxygen atoms.

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