Theoretical study on the positron annihilation in Rocksalt structured magnesium oxide*

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Based on the atomic superposition approximation (ATSUP) and first-principles pseudopotential plane-wave methods, the bulk and Mg mono-vacancy positron lifetime of magnesium oxide were calculated using Arponen–Pajamme and Boroński–Nieminen positron-annihilation-rate interpolation formula respectively. The calculated values are in good agreement with experimental values and the first-principles method gives more convincing results. The positron annihilation density spectra analysis reveals that positrons mainly annihilate with valence electrons of oxygen atoms when the magnesium-vacancy appears within magnesium oxide.

Keywords: magnesium oxide, positron annihilation, momentum distribution

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1. Introduction

The rocksalt structured magnesium oxide (MgO) is a well-known mineral in the Earth's lower mantle and has been the object of theoretical and experimental studies for many years.[1,2] MgO has a relatively simple structure and has historically served as a model of the wide band gap oxide crystals. MgO belongs to the group of radiation resistant materials. Much attention has been paid to the MgO-based ceramic system to study the radiation damage due to the fact that it is of interest to control the solubility of radionuclides,[3] such as transuranic waste, which needs to be stored safely for long periods of time. Thus it is necessary to research the irradiation-related defects. In addition, the origin of ferromagnetism in undoped MgO has also been studied and the result shows that Mg vacancies can induce local moments in MgO while O vacancies cannot, irrespective of the concentration.[4] More generally, there is a consensus that the ferromagnetism is related with native defects. In ionic systems such as MgO, the dominant intrinsic defect is the pair vacancy with Mg and O sites vacant.[5] Analysis of the defect feature can help us better understand the physical properties of MgO.

Positrons have been widely used to study the crystal structure and the important applications of positron annihilation methods in condensed matter are the numerous studies on various vacancy-type defects.[6] Experimental methods based on positron annihilation give valuable information on the electronic and ionic structures of condensed matter. The positron traps at vacancy defects are experimentally observed by an increase in positron lifetime and a narrowing of the momentum of the annihilation electron–positron pairs.[7] Although there have been some positron annihilation experiment results for MgO, the conclusions or interpretations are contradictory. Tanaka *et al.*[8] studied the ultradilute dopants in ceramics and found that the undoped MgO sample shows the shortest lifetime of 141 ps. Nitesh *et al.*[9] studied the defect-induced ferromagnetism in MgO nanoparticles and obtained that the positron lifetime of bulk MgO is about 161 ps.

In this paper, the theoretical calculations of positron annihilation in rocksalt structured MgO are carried out employing the ATSUP[10] and first-principles pseudopotential plane-wave method.[11] The bulk and mono-vacancy positron lifetimes of MgO are obtained using the Arponen–Pajamme[12,13] and Boronski–Nieminen[14] formula, respectively. And the calculations based on this scheme agree with Tanaka's[8] experimental data. We also calculate Doppler-broadening spectrum for MgO and the results show that positrons mainly annihilate with 2 valence

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electrons of oxygen atoms in MgO.

2. Method

The description of the state of thermal positrons in a defect-free bulk crystal or of the positron trapped in a defect requires the solution of the Schrödinger equation. Here, the essential thing for a valid theory is that it gives a realistic description of the positron distribution and energy in the solid. In order to evaluate the positron wave function, we assume that there is only one positron for many electrons. As a result, there is no exchange part because there is no positron–positron interaction. Thus the total positron potential can be expressed as[15]

$$V_{\mathrm{p}}(r) = V_{\mathrm{i}}(r) + V_{\mathrm{e}}(r) + V_{\mathrm{ep}}(r), \tag{1}$$

where V_{i} is the potential due to the ion core, V_{e} is the potential due to the electrons and V_{ep} is the electron–positron correlation potential. A practical form for V_{ep} is the parameterisation by Boroński and Nieminen.[14]

The electron density and the positron potential are calculated at the grid points of a three-dimensional mesh. For the ATSUP method, the electron density of the solid is approximated by the superposition of the charge densities of free atoms. For first-principles method, the electron density of the solid is obtained by pseudopotential plane-wave method. The calculations for localized positron states at defects in MgO are based on the 'conventional' scheme in which the positron does not affect the average electron density around the defects. When the potential sensed by a positron is obtained, the corresponding Schrödinger equation can be solved. Once the positron and electron densities are known, the positron annihilation rate can be calculated

$$\begin{aligned}\lambda &= \pi r_0^2 c \int \mathrm{d}r \cdot n_{\mathrm{p}}(r) \cdot n_{\mathrm{e}}(r) \cdot \gamma(n_{\mathrm{e}}) \\ &= \int \mathrm{d}r \cdot n_{\mathrm{p}}(r) \cdot \Gamma(n_{\mathrm{e}}),\end{aligned} \tag{2}$$

where r_0 is the classical electron radius, c is the speed of light, $\gamma(n_{\mathrm{e}})$ is called the enhancement factor of the electron density at the positron and $\Gamma(n_{\mathrm{e}})$ is the positron annihilation rate in a homogenous electron gas with density n_{e}.

The enhancement factor is a manifestation of electron–positron interactions and it is always a crucial ingredient when calculating the positron lifetime.[16] Many-body calculations for a positron in a homogeneous electron gas have been used to model the electron–positron correlation.

For the positron annihilation rate $\Gamma(n_{\mathrm{e}})$, Arponen and Pajamme give the following form (AP model):[12,13]

$$\begin{aligned}\Gamma(n_{\mathrm{e}}) = {} & \pi r_0^2 c n_{\mathrm{e}} [1 + 1.23 r_{\mathrm{s}} - 0.0742 r_{\mathrm{s}}^2 \\ & + (1 - 1/\varepsilon) \cdot (r_{\mathrm{s}}^3/6)],\end{aligned} \tag{3}$$

where r_{s} is the electron density parameter,

$$n_{\mathrm{e}} = 3/(4\pi r_{\mathrm{s}}^3) \tag{4}$$

and ε is the high-frequency dielectric constant. In the model of Boroński and Nieminen (BN model),[14] the annihilation rate is replaced by

$$\begin{aligned}\Gamma(n_{\mathrm{e}}) = {} & \pi r_0^2 c n_{\mathrm{e}} [1 + 1.23 r_{\mathrm{s}} + 0.8295 r_{\mathrm{s}}^{1.5} - 1.26 r_{\mathrm{s}}^2 \\ & + 0.3286 r_{\mathrm{s}}^{2.5} + (1 - 1/\varepsilon) \cdot (r_{\mathrm{s}}^3/6)].\end{aligned} \tag{5}$$

In the calculations of MgO, the experimental lattice parameters of $a = b = c = 4.211$ Å (1 Å=0.1 nm) were adopted.[17] For the first-principles method, the calculations were performed using generalized gradient approximation (GGA), the valence configurations were $3s^2$ and $2s^2 2p^4$ for Mg and O, respectively. An energy cutoff of 500 eV was set for the plane wave basis. For the Brillouin-zone sampling, 4×4×4 Monkhorst–Pack k mesh[18] was used for the electron density calculation.

3. Results and discussion

3.1. Positron lifetime

Positrons are sensitive to sites with less electron density such as defects and may become trapped by them. Positrons implanted into a material rapidly reached thermal equilibrium with the medium and enter a Bloch state from which they may annihilate directly with a characteristic lifetime τ_{b} or from which they can trap to defect states prior to annihilation. The decomposition of the positron lifetime spectrum is explained by the trapping model which gives the rate equations for the positron annihilating in delocalized states and in localized states.

Theoretically calculated positron lifetimes using ATSUP and first-principles methods in defect-free MgO and with V_{Mg} (mono-vacancy of magnesium), V_{O} (mono-vacancy of oxygen) are shown in Table 1 and these values are in good agreement with the recent research.[8,19] In the defect-free MgO, positrons are delocalized (as shown in Fig. 1) and annihilate

with a single bulk lifetime component. As for the bulk positron lifetime τ_b, reference [9] obtains even bigger value of about 166ps, and this value is somewhat between that of the bulk value and the mono-vacancy of magnesium of our calculated results. We analysed the reason for the discrepancy and concluded that these measured longer bulk lifetimes are the weighted average lifetime over bulk value and mono-vacancy values. Carefully analyse one time, we can find out that the change in lifetime from the bulk value is small for oxygen vacancies. A simple ionic model gives the local charge state of V_O as 2^+, so the isolated oxygen vacancy may not trap positrons.[20] Probably the most direct reason why the positron lifetime is increased is the reduction in average electron density in the lattice. When oxygen-vacancy arises, the open volume in the lattice increases and could also weakly localize the positron wave function. Sharma *et al.* calculated positron lifetimes in ZnO wurtzite supercell and also obtained similar results.[21] However, magnesium-vacancy is a deep potential well capable to confine the positron wave function and it can be clearly seen from Fig. 1 that positron states are localized at mono-vacancy of magnesium.

Table 1. Calculated positron annihilation lifetime in bulk (τ_b), in mono-vacancy of oxygen (τ_O) and magnesium (τ_{Mg}) of MgO.

	ATSUP method		First-principles method		expt.[19]
	AP model	BN model	AP model	BN model	
τ_b/ps	110	120	122	134	130
τ_O/ps	118	129	128	140	
τ_{Mg}/ps	154	171	167	186	180

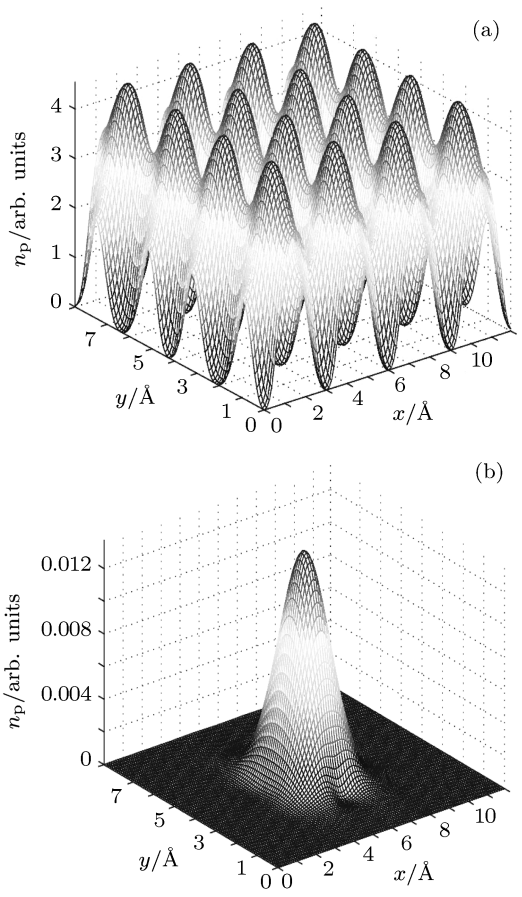


Fig. 1. Positron density map in MgO on [110] plane: (a) defect-free, (b) with V_{Mg}.

3.2. Momentum distributions

Figure 2 illustrates the calculated positron annihilation density spectra with momentum distributions in defect-free MgO with/without V_O or V_{Mg}. Based on analysing the annihilation probability density with core and valence electrons, it is easy to observe that positrons are mainly annihilated with valence electrons of oxygen within the low momentum range and core electrons of magnesium within the high momentum range in defect-free MgO. Once oxygen vacancies appear, the positron annihilation probability with electrons of magnesium increases slightly. However, the predominance of these annihilations is replaced in turn by electrons of oxygen within almost all momentum ranges in the MgO with mono-vacancies of magnesium.

The reconstructed positron annihilation probability density spectra are all shown in Fig. 2(d). Compared with defect-free MgO, the positron annihilation probability density for MgO with V_O decreases more prominently in low momentum range. Although the annihilation probability increases in high momentum range, the absolute value is small (as can be seen in Fig. 2(b)). Thus the positron lifetime of MgO with V_O

increases somewhat. On the contrary, although similar decrease appears in higher momentum range for MgO with $V_{\rm Mg}$, the situation is reverse in lower momentum range. This means that more positrons annihilate with valence electrons of oxygen which make a predominant contribution in lower momentum range. By comparison, we may safely draw a conclusion that positrons mainly annihilate with valence electrons of oxygen when the magnesium-vacancy appears within the magnesium oxide.

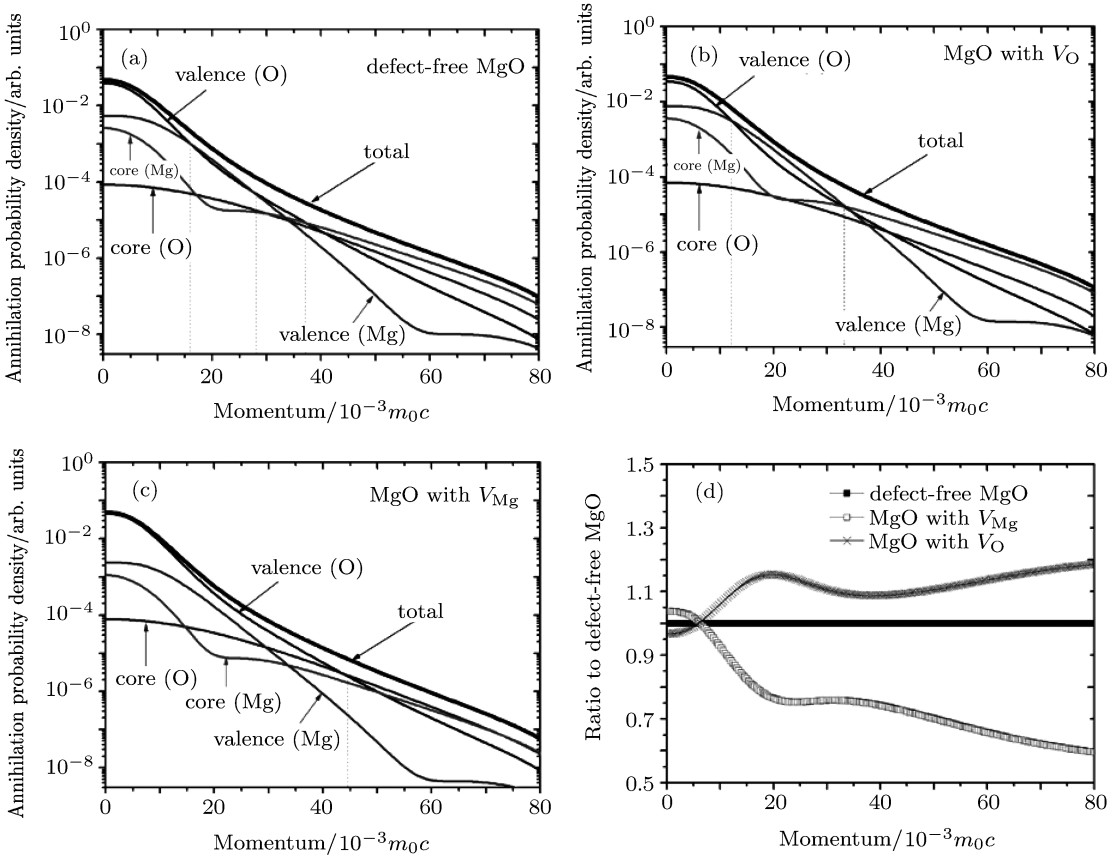


Fig. 2. Calculated positron annihilation density spectrum with momentum distributions: (a) in defect-free MgO; (b) in MgO with $V_{\rm O}$; (c) in MgO with $V_{\rm Mg}$ and (d) ratio to defect-free curves.

4. Conclusion

In this paper both the atomic superposition approximation (ATSUP) and first-principles pseudopotential plane-wave methods have been used to calculate the positron annihilation lifetime of bulk MgO with/without $V_{\rm Mg}$ or $V_{\rm O}$. And both of Arponen–Pajamme and Boroński–Nieminen positron-annihilation-rate interpolation formula are employed in these analyses. The calculated values are in good agreement with experimental values and the first-principles method gives more convincing results. The results show that the positron lifetime of bulk MgO is about 134 ps and the positron lifetime of Mg monovacancy is about 186 ps. The positron annihilation density spectra analysis reveals that positrons mainly annihilate with valence electrons of oxygen atoms when the magnesium-vacancy appears within the magnesium oxide.

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References

[1] Tang X and Dong J 2010 *PNAS* **107** 539

[2] Stackhouse S, Stixrude L and Karki B B 2010 *Phys. Rev. Lett.* **104** 208501

[3] Skvortsova V, Mironova-Ulmane N and Ulmanis U 2007 *Nucl. Instr. Meth. Phys. Res.* A **580** 434

[4] Wang F, Pang Z, Lin L, Fang S, Dai Y and Han S 2009 *Phys. Rev.* B **80** 144424

[5] Ita J and Cohen R E 1997 *Phys. Rev. Lett.* **79** 3198

[6] Xu H X, Hao Y P, Han R D, Weng H M, Du H J and Ye B J 2011 *Acta Phys. Sin.* 067803 (in Chinese)

[7] Hao Y P, Chen X L, Cheng B, Kong W, Xu H X, Du H J and Ye B J 2010 *Acta Phys. Sin.* **59** 2789 (in Chinese)

[8] Tanaka I, Mizoguchi T, Matsui M, Yoshioka S, Adachi H, Yamamoto T, Okajima T, Umesaki M, Ching W Y, Inoue Y, Mizuno M, Araki H and Shirai Y 2003 *Nature Materials* **2** 541

[9] Nitesh K, Sanyal D and Sundaresan A 2009 *Chem. Phys. Lett.* **477** 360

[10] Zhang J, Liu J D, Chen X L and Ye B J 2010 *Chin. Phys.* B **19** 117802

[11] Puska M J, Sob M, Brauer G and Korhonen T 1994 *Phys. Rev.* B **49** 10947

[12] Arponen J and Pajanne E 1979 *Annals of Physics* **121** 343

[13] Barbiellini B, Puska M J, Torsti T and Nieminen R M 1995 *Phys. Rev.* B **51** 7341

[14] Boroński E and Nieminen R M 1986 *Phys. Rev.* B **34** 3820

[15] Benosman N, Amrane N, Mecabih S and Aourag H 2000 *J. Phys. Chem. Solids* **61** 1727

[16] Surko C M and Gianturco F A 2001 *New Directions in Antimatter Chemistry and Physics* (Netherlands: Kluwer Academic Publishers) p. 130

[17] Schmahl N G, Barthel J and Eikerling G F 1964 *Z. Anorg. Allg. Chem.* **332** 230

[18] Monkhorst, Hendrik J and Pack James D 1976 *Phys. Rev.* B **13** 5188

[19] Masataka M, Yoshiyuki I and Kazuki S 2004 *Materials Science Forum* **445–446** 153

[20] Čížek J, Melikhova O, Procházka I, Kuriplach J, Kužel R, Brauer G, Anwand W, Konstantinova T E and Danilenko I A 2010 *Phys. Rev.* B **81** 024116

[21] Sharma S K, Pujari P K, Sudarshan K, Dutta D, Mahapatra M, Godbole S V, Jayakumar O D and Tyagi A K 2009 *Solid State Commun.* **149** 550