Nucl. Sci. and Tech., Vol.6, No. 1 (2016), pp. 50-55

Nuclear Science and Technology

Journal homepage: https://jnst.vn/index.php/nst

Positron annihilation in mordenite zeolite

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Abstract: The theoretical study of the positron annihilation in complex material such as zeolite is greatly significant to support and increase the accuracy analysis of the material structure from the experimental data of the positron annihilation. The mordenite zeolite is a big and complicated structure consisting of channels and cavities. The analysis of the mordenite structure is studied by the PALS so depending on the selection of the positron lifetime components of the positron annihilation spectra fitting methods. Therefore, these positron life times in on TO_4, Na, Ca, K, Fe, H_2O and the rings which form the channels and cavities are sophisticatedly studied by the DFT calculation using Ab-initio. The mordenite and modified mordenite zeolite structures are precisely analyzed, and the physical behaviors of the positron in these are more understood by these theoretical results.

Keyword: *positron, DFT, PALS, zeolite, mordenite, annihilation.*

I. INTRODUCTION

Positron annihilation lifetime spectroscopy (PALS) is a traditional method of non-destructive testing, allowing to study electronic structure of materials, the defects in metals and semiconductors, as well as in the study of zeolite structures [12, 13, 14]. This experimental technique is a powerful tool for probing the microstructure of condensed matter and shows an advantage over other microprobes. But the analysis of experimental positron lifetime spectra to obtain the mean positron lifetime components in material, especially in the zeolite structures, depends on so many sensitive factors of numerical analysis of the positron annihilation spectra. A few methods are accessible, like fitting a simplified model function [1, 2] or deconvolution [3, 4]. The results depend highly on assumptions made during the analysis. Even so, the exact solution of the problem is not obtainable; however, even approximate results provide a valuable piece of information. In this work, the assumption of PALS analysis such as positron lifetime components in a perfect element structure of materials is accurately determined by the DFT calculation of the positron annihilation in the material. Then these results are used in the analysis of the positron annihilation spectra to obtain precisely the mean lifetime of the positron which is characterized to the properties of the materials.

II. THEORY AND MODELING

Overview two-component density theory

To solve the needed electron and positron densities a two-component generalization of the density functional theory (TCDFT) can be used [6].

https://doi.org/10.53747/jnst.v6i1.146
Received 07 September 2015, accepted 31 March 2016

$$E[\rho_-,\rho_+] = F[\rho_-] + F[\rho_+] + \int [\rho_-(r) - \rho_+(r)]V_{ext}(r)dr - \int\left(\int \frac{\rho_-(r)\rho_+(r')}{|r-r'|}dr'\right)dr + E_c^{e-p}[\rho_+,\rho_-] \quad (1)$$

where

$$F[\rho] = T[\rho] + \frac{1}{2}\int\left(\int \frac{\rho(r)\rho(r')}{|r-r'|}dr'\right)dr + E_{xc}[\rho] \quad (2)$$

energy function of noninteracting electrons or positrons, E_{xc} is the exchange-correlation energy and $E_c^{e-p}[\rho_+;\rho_-]$ is the positron-electron correlation-energy function.

From equation (1), the ground state electron and positron densities are solved by a generalized Kohn-Sham variation method. This requires solving one – particle Schrodinger equations for electron and positron wave functions. For positron this reads

$$-\frac{1}{2}\nabla^2\psi_i^+(r) + V_{eff}(r)\psi_i^+(r) = \varepsilon_i\psi_i^+(r) \quad (3)$$

with effective potential written as

$$V_{eff}(r) = \varphi(r) + \frac{\delta E_{xc}[\rho_+]}{\delta\rho_+(r)} + \frac{\delta E_c^{e-p}[\rho_+,\rho_-]}{\delta\rho_+(r)} \quad (4)$$

where

$$\varphi(r) = \int \frac{\rho_0(r') + \rho_+(r') - \rho_-(r')}{|r-r'|}dr' \quad (5)$$

is the total Coulomb potential and ρ_0 the charge density from which the external potential V_{ext} arises. For electron, the effective potential is the same as (4) with ρ_+ and ρ_- swapped and the sign of the Coulomb potential reversed.

From the obtained wave functions, the electron and positron densities can be calculated by

$$\rho_-(r) = \sum_{\varepsilon_i \le \varepsilon_f}|\psi_i(r)|^2, \rho_+(r) = \sum_{i=1}^{N_+}|\psi_i^+(r^2)| \quad (6)$$

The summation on electron states is up to the Fermi level but usually only one positron ($N_+ = 1$) needs to be considered. The Kohn-Sham equations must be solved self-consistently using iterative scheme simultaneously for electron and positron states.

In equation (4) we still have unknown terms E_{xc} and E_c^{e-p}, which, are determined by the LDA [6] and GGA[7] approximations. The electron-positron correlation energy E_c^{e-p} is usually calculated on the limit of the vanishing positron density.

Positron life time

The positron annihilation rate is proportional to the electronic density at the positron and can be calculated from the overlap integral as

$$\lambda = \frac{1}{\tau} = \pi r_0^2 c\int \rho_+(r)\rho_-(r)g(0;\rho_+,\rho_-)dr \quad (7)$$

where r_0 is the classical electron radius, c is the speed of light, ρ_+ and ρ_- are the positron and electron densities and g(0; ρ_+; ρ_-) is the electron-positron pair correlation function evaluated at the positron [6], called the enhancement factor of the electron density at the positron, and calculated by LDA, Lantto, Boronski and Nieminen [6]; another form for enhancement given by Arponen, Pajanne and Barbiellini et al [7]; and the GGA [7] the variation in electron density.

Positron wave function

A parameterized positron wave function [8] is used in the calculation of the positron life time in mordenite zeolite

$$\psi^+(r) \approx a_0 + a_1\left(\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{r} e^{-\left(\frac{r'}{\sqrt{2}a_2}\right)^2}dr'\right)^{a_3} \quad (8)$$

where r is the distance from the center of the atomic sphere and a_i are fitted parameters i={0,…,3}. The parameters have been calculated using the LMTO-ASA method [5].

The sumary of mordenite zeolite and the modeling strategy

Mordenite is one of the most siliceous natural zeolites. It has an orthorhombic unit cell of topological space-group symmetry Cmcm (a=18.13, b= 20.5, c= 7.52 Å) with idealized chemical composition $Na_8Al_8Si_{40}O_{96}\cdot 24H_2O$ [9, 10, 11]. It is structured from the primary building unit or the basic building unit (BBU), TO_4, which is the tetrahedron whose in the center are atoms with relatively low electronegativities (Si, Al, P, Zn, etc.) and in the corners are oxygen anion. The second building unit or the composite building unit (CBU) can be formed by the linking together groups of BBUs. The simplest examples of CBUs are rings. All zeolite structure can be viewed as composing of different size of the rings. In general, a ring containing n tetradera is called an n ring.

For the MOR framework type can be considered as forming of 12 –rings along the straight large pore, and the small 8 – ring pore connecting the 12 – ring channels. It also contains the 4 – ring and 5 – ring channels. The water molecules are captured in the 12 – ring and 8 – ring channels.

To understand deeply the positron annihilation in the mordenite zeolite, the positron lifetime in the primary building and the second building units of the mordenite is studied by DFT. There are four types of T – atom, T_1, T_2, T_3, and T_4, whose are the different geometry of T –O –T linkages and T can be Si, Al, P, or Zn as shown in the figure 1. The simulations are done with these atoms TO_4 whose the geometry configurations are extracted from the single crystal – X ray study of the mordenite zeolite [9]. And these different positron lifetimes in these structures will be shown in the table 1. Then the positron annihilations in CBUs such as 4 - rings, 5 – rings, 8 – rings and 12 – rings are calculated.

The positron annihilations in the more complex unit such as channels or pores are also done. To describe the ion exchange in mordenite zeolite, the Na atoms are replaced by the Fe^{2+} and Fe^{3+}. Then the positron annihilation is studied for these ions – exchange structures.

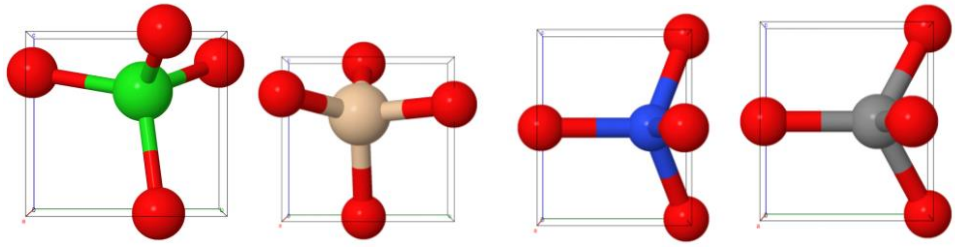
These theoretical calculations will be applied to analyze the experimental PALS to obtain the correct positron lifetime components used to survey the mordenite structures.

III. RESULTS AND DISCUSSION

The positron annihilation characteristics in the tetrahedral atoms TO4 in the mordentite structures of platy synthetic zeolite sample [9] are calculated by Mika doppler code[5] and shown in the table I. The input data are atomic coordinates of TO4 and the rings. The exchange and correlation potentials are approximated by GGA.

The mordenite structures are obtained from American mineralogist crystal structure database [9]. The positron lifetime in the four type T atoms is not so different. The average positron lifetimes in four types of SiO_4 and AlO_4 are 59.2 ps and 59.9 ps, respectively. These positron lifetimes can be considered as the shortest lifetime component of the positron in zeolite.

Because of the symmetry, the 4 – ring is constructed by two T_3 and two T_4 atoms, the 5 – ring is composed of one T_1, one T_3, one T_4 atoms and two T_2 atoms, the 8 – ring is consisted of four T_1 and four T_3 atoms, and the 12 – ring is formed by four T_1, four T_2, and four T_4 atoms.



T_1 – type T_2 – type T_3 – type T_4 – type

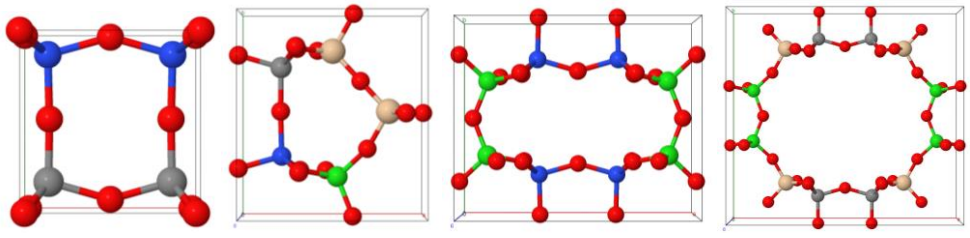
Fig.1: The geometries of four types T atom.

Table I. The positron annihilation rate, lifetime, core and valence enhancement factors, and the percentage of the core annihilation in TO4 (T: T1, T2, T3, T4 types) of mordenite are calculated by Mika doppler code.

TO_4		λ ($10^9 s^{-1}$)	τ (ps)	g_{core}	g_{val}	% λ core
T1	SiO_4	16.128	62.00	2.1265	2.517	83.78
	AlO_4	14.916	67.04	2.2176	2.716	73.85
T2	SiO_4	20.771	48.14	2.0243	2.429	72.96
	AlO_4	21.896	45.67	1.9579	2.178	89.40
T3	SiO_4	16.833	59.41	2.2772	2.344	82.81
	AlO_4	16.749	59.71	2.2806	2.3495	83.35
T4	SiO_4	14.861	67.29	2.4968	2.6411	74.73
	AlO_4	14.881	67.20	2.4422	2.6324	76.53

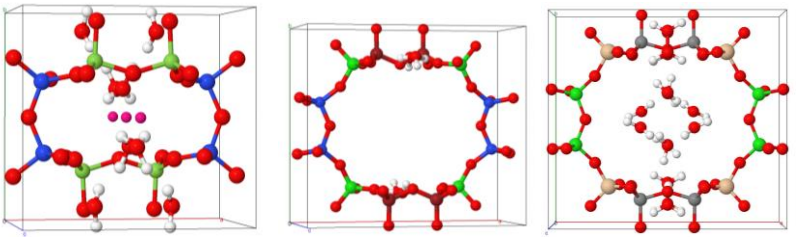
The geometry configurations of these rings are shown in the figure 2. The water molecule are captured in the 8 – ring and 12-ring as shown in the figure 6. The three Na atoms are also contained in the 8 – ring as shown in the figure 3.

The average positron lifetimes in these rings are determined as given in the table II. The theoretical results indicate that the positron lifetime is increased as the size of ring is increased. The positron lifetime is significantly different from the 8 – ring with Na atoms to without Na atoms. The difference of positron lifetime is also happened to the 8 – ring with Fe^{2+} and Fe^{3+}, 12 – ring with H_2O molecule and without H_2O molecule.



4 – ring 5 – ring 8 – ring 12 – ring

Fig. 2: The geometry configuration of 4 –ring, 5 – ring, 8 – ring and 12 - ring.



$8^*_{1,2,3}$ – ring 12_1^* – ring 12_2^* – ring

Figure 3: The geometry configuration of 8_1^* – ring, 8_2^* – ring, 8_3^* – ring, 12_1^* - ring and 12_2^* – ring.

Table II. Positron annihilation rate, lifetime, core and valence enhancement factors, and the percentage of the core annihilation in the channels of mordenite are calculated by Mika doppler code.

Channels	λ ($10^9 s^{-1}$)	τ (ps)	g_{core}	g_{val}	% λ_{core}
4 – rings channels	6.203	161.22	2.5616	3.5824	57.01
5 – rings channels	2.721	367.51	2.8774	5.3823	64.68
8 – rings channels	1.828	547.08	3.1877	6.8354	59.47
8_1^*– rings channels	2.038	490.56	5.9427	11.3836	78.42
8_2^*– rings channels	2.765	361.62	3.057	5.379	71.29
8_3^*– rings channels	2.556	391.13	3.024	5.577	65.75
12 – rings channels	1.327	753.50	2.942	6.183	48.65
12_1^* - rings channels	1.407	710.79	3.058	6.0483	51.00
12_2^* - rings channels	2.849	350.99	3.058	6.0483	51.00

where 8_1^* - ring is 8 – ring channel which is contained three Na atoms and eight H_2O molecular, 8_2^* - ring is 8_1^* – ring channel which is replaced three Na atoms by three Fe^{2+}, 8_3^* - ring is 8_1^* – ring channel which is replaced three Na atoms by three Fe^{3+}, 12_1^* - ring is 12 – ring channel which is contained four H_2O molecular, and 12_2^* - ring is 12 – ring channel which is contained sixteen H_2O molecular.

The calculation results of the positron lifetime components are good in the range of the experimental results which are from 105 ps to 650 ps for short and medium lifetime components [13, 14]. These results pointed out that the positron lifetimes in the 8 – rings and 12 – rings are changed by the number of the water molecule captured. The Fe ion – exchange in the 8 – ring can be also determined by the positron lifetime as shown in the table II.

From these calculations, the number of the positron lifetime component in analysis of PALS can be extended from four components to six or eight components.

IV. CONCLUSIONS

The positron lifetime components in the mordenite zeolite are determined by DFT. These results are good agreement in the range of the experimental analysis of PALS. The

mordenite structures and Fe ion – exchange of mordenite can be accurately analyzed by the combination of these calculations and the analysis of the positron annihilation lifetime spectroscopy. The increasing of the number of lifetime components in the analysis of PALS of the mordenite and ion – exchange mordenite can be well carried out by these theoretical results.

ACKNOWLEDGMENTS

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under Grant number “103.04-2013.11”.

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