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Relationship between positron bulk lifetime and lattice constants—research on NaCl-type crystals*

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The positron lifetimes of some compounds with NaCl-type crystal structure are calculated with the method of atomic superposition approximation (ATSUP) based on the theories of local-density-approximation (LDA) and general-gradient-approximation (GGA). The systematical results are fitted to a curve as a function of lattice constants. The positron bulk lifetimes of some other compounds with NaCl-type crystal structure, which are deduced from the systematical results, are in agreement with the experimental results given in other literature.

Keywords: positron bulk lifetime, NaCl-type crystal structure
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1. Introduction

Some important information about microscopic structures of materials can be obtained from positron annihilation lifetime spectroscopy (PALS).[1−3] In order to gain positron lifetime, some theoretical methods of calculating positron lifetime have been built up.[4−7] However, the theoretical calculation is inconvenient and time-consuming. If the positron lifetime has a simple conjunction with a few available parameters, one perhaps can obtain positron lifetimes of materials easily. Puska *et al.* found that for some semiconductors, the positron lifetime varied linearly with the unit-cell volume.[8] Later, Siethoff fitted the graph and obtained a formula which was expressed as:[9]

$$\tau_{\rm B} = C a_0^{3/2}, \tag{1}$$

where $C = 543.8$ ps/nm$^{1.5}$. Siethoff pointed out that the formula $\tau_{\rm B} = c + d a_0$ ($c = -86.5$ ps, $d = 565$ ps/nm) fitted by Pareja and Cruz[10] was not contradictory to the above findings since a parabolic law such as Eq. (1) can be always approximated by an expression $y = c + dx$ if the data lie far enough from the origin of the coordinate system and are somewhat scattered. He also indicated that the positron lifetimes of those semiconductors which have diamond cubic zincblende or wurtzite structures had a tight connection with lattice parameters.

In the present article, the crystal structure of NaCl-type is studied. The superposed-neutral-atom model and the finite-difference method (SNA–FD) are used to calculate the positron lifetimes of some I–VII compounds (all of the I–VII compounds have the same crystal structures as NaCl, except for CsF, CsCl, CsBr, CsI). The calculated positron lifetimes are fitted as a function of lattice constants. A simple systematical formula is obtained, which is similar to Eq. (1). The formula can be used to predict positron bulk lifetimes of other compounds which have the NaCl-type structure. The positron lifetimes of some other compounds predicted by this systematical study, are compared with the experimental values given in the literature.

2. Atomic superposition approximation method

The SNA–FD method is extensively used in the positron lifetime calculation. In this method, the electron density and the crystalline Coulomb potential are constructed by atomic superposition approximation (ATSUP) method developed by Puska and Nieminen.[11,12] In the ATSUP approximation, the electron density is constructed by superimposing individual atomic charge densities as follows:

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$$n_{-}(r)=\sum_{i} n_{-}^{\mathrm{at}}(r-R_i), \tag{2}$$

where n_{-}^{at} is the free-atom electron density, and R_i is the occupied atomic site. The crystal Coulomb potential $V_{\mathrm{c}}(r)$ is expressed as

$$V_{\mathrm{c}}(r)=\sum_{i} V^{\mathrm{at}}(r-R_i), \tag{3}$$

where V^{at} is atomic Coulomb potential.

To calculate the positron density, an effective positron potential is essential, and it expressed as

$$V_{+}(r)=V_{\mathrm{C}}(r)+V_{\mathrm{corr}}(n_{-}), \tag{4}$$

where V_{corr} is the positron–electron correlation potential, and n_{-} is the electron density. Then the Schrödinger equation is solved by the numerical method and the positron density is obtained as[13]

$$n_{+}(r)=|\psi_{+}(r)|^2 . \tag{5}$$

The positron annihilation rate is given by

$$\lambda=\pi r_0^2 c\int \mathrm{d}r\cdot n_{+}(r)\cdot n_{-}(r)\cdot\gamma(r), \tag{6}$$

where r_0 is the classical electron radius, c is the speed of light in vacuum, and $\gamma(r)$ is so-called enhancement factor. Thus the positron lifetime τ is obtained as $\tau=1/\lambda$.

Both $V_{\mathrm{corr}}(n_{-})$ and $\gamma(r)$ mentioned above can be calculated in two schemes:

(a) local-density-approximation (LDA) scheme, in which the expression of $V_{\mathrm{corr}}(n_{-})$ can be found in Ref. [14]. The widely used form of the enhancement factor is

$$\begin{aligned}\gamma_{\mathrm{BN}}(r_{\mathrm{s}}) &= 1+1.23r_{\mathrm{s}}+0.8295r_{\mathrm{s}}^{3/2}-1.26r_{\mathrm{s}}^2\\ &\quad+0.3286r_{\mathrm{s}}^{5/2}+\frac{1}{6}\left(1-\frac{1}{\varepsilon_\infty}\right)r_{\mathrm{s}}^3,\end{aligned} \tag{7}$$

where ε_∞ is the high-frequency dielectric constant of material and $r_{\mathrm{s}}=(3/4\pi n_{-}(r))^{1/3}$.

Here, we should indicate that in the LDA scheme, it is not necessary to divide the total electron density into core electrons, valence electrons and d electrons in the case of transition metals.[1,15,16]

(b) general-gradient-approximation (GGA) scheme, in which we use $\gamma(r)$ and $V_{\mathrm{corr}}(n_{-})$ as the following expression:[17]

$$\gamma_{\mathrm{GGA}}=1+(\gamma_{\mathrm{LDA}}-1)\exp(-\alpha\cdot\varepsilon), \tag{8}$$

where $\gamma_{\mathrm{LDA}}=1+1.23r_{\mathrm{s}}-0.0742r_{\mathrm{s}}^2+\frac{1}{6}r_{\mathrm{s}}^3$, and

$$V_{\mathrm{corr}}^{\mathrm{GGA}}(n_{-})=V_{\mathrm{corr}}(n_{-})\cdot\exp(-\alpha\varepsilon/3), \tag{9}$$

where α=0.22 for this calculation, $\varepsilon=|\nabla n|^2/(nq_{\mathrm{TF}})^2$ with $(q_{\mathrm{TF}})^{-1}$ being the local Thomas–Fermi screening length. It is obvious that in the GGA scheme, the high-frequency dielectric ε_∞ is not required for calculating enhancement factor. The $V_{\mathrm{corr}}(n_{-})$ in formula (2) is the same as the positron–electron correlation potential mentioned in the LDA scheme.

3. NaCl-type crystal structure

As is known, there are mainly three types of the crystal structures of AB-type ionic crystalloid—NaCl-type, CsCl-type, ZnS-type. Here we study only the crystalloid of NaCl-type whose crystal structure is given in Fig. 1.

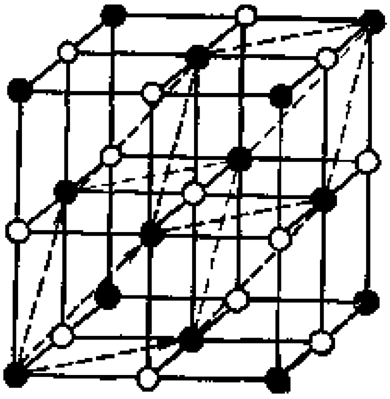

Fig. 1. Unit cell of NaCl-type structure.

Some parameters of the ionic compounds under study here are given in Table 1, where a_0 is lattice constant.

Table 1. Lattice constants and high-frequency dielectric constants of some ionic compounds (1 Å=0.1 nm).

compounds	a_0/Å	ε_∞	compound	a_0/Å	ε_∞
NaF	4.62[3]	1.75[18]	LiCl	5.14[3]	2.79[18]
NaCl	5.62[3]	2.35[18]	LiBr	5.50[3]	3.22[18]
NaBr	5.96[3]	2.64[18]	LiI	6.00[3]	3.89[18]
NaI	6.46[3]	3.08[18]	MgO	4.207[8]	3.00[8]
KF	5.28[3]	1.86[18]	MnO	4.446[19]	
KCl	6.28[3]	2.20[18]	FeO	4.304[19]	
KBr	6.62[3]	2.39[18]	CoO	4.258[19]	
KI	7.12[3]	2.68[18]	NiO	4.177[19]	
RbF	5.54[3]	1.94[18]	BaO	5.520[23]	
RbCl	6.54[3]	2.20[18]	MgS	5.20	
RbBr	6.88[3]	2.36[18]	MnS	5.233[19]	
RbI	7.38[3]	2.61[18]	SrTe	6.660[21]	
LiF	4.02[3]	1.93[18]	BaTe	7.000[20]	
BaS	6.374[20]		TiC	4.328[24]	
SrS	6.024[21]		TiN	4.242[24]	
CaS	5.697		ScN	4.450[24]	
SrSe	6.236[21]		AgCl	5.54[3]	3.92
BaSe	6.600[20]		AgBr	5.78[3]	4.62
CaSe	5.917[22]		CaTe	6.350[22]	

4. Results and discussion

The positron bulk lifetimes of perfect single crystals are calculated within LDA and GGA schemes and the results are listed in Table 2.

Table 2. Calculated positron bulk lifetimes of some perfect single crystals with NaCl -type structure.

compounds	τ_B–LDA/ps	τ_B–GGA/ps
NaF	194	216
NaCl	268	269
NaBr	285	285
NaI	310	302
KF	232	251
KCl	319	311
KBr	341	327
KI	365	345
RbF	238	251
RbCl	331	316
RbBr	351	331
RbI	379	356

We depict τ_B as a function of a_0 and express it as $\tau_B \approx a_0^{3/2}$, which is similar to that in Ref. [9]. We find that the τ_B data can also be plotted linearly. To confirm this point of view, we fit the data to lines with computer and obtain four formulas:

(a) in LDA scheme

$$\tau_B = (19.419 \pm 0.162) \cdot a_0^{3/2}, \tag{10}$$

$$\tau_B = \text{-}\ 137.547 + (70.842 \pm 0.390) \cdot a_0; \tag{11}$$

(b) in GGA scheme

$$\tau_B = 77.075 + (14.168 \pm 0.114) \cdot a_0^{3/2}, \tag{12}$$

$$\tau_B = -26.763 + (52.236 \pm 0.276) \cdot a_0. \tag{13}$$

Parameters a_0 and τ_B are in the units of Å and ps respectively. The fitting scenarios are shown in Figs. 2 and 3. In the figures the fitting lines which pass through the solid circles are corresponding to Eqs. (10) and (11) respectively; the fitting lines which pass through the solid triangles are corresponding to Eqs. (12) and (13) respectively.

From Figs. 2 and 3 we can see that the theoretical result calculated in the LDA scheme is not always smaller than that calculated in the GGA scheme. It is not the same as the result obtained in metals or semiconductors.[9,22] When a_0 is smaller than 6 Å, the result from the LDA scheme is smaller than that from the GGA scheme. When a_0 is larger than 6 Å, the result from the LDA scheme is larger than that from the GGA scheme.

The positron bulk lifetimes of those ionic compounds which have NaCl-type crystal structure, are predicted from Eqs. (10) and (12). These compounds, predicted τ_B and some experimental results cited from the literature are shown in Table 3.

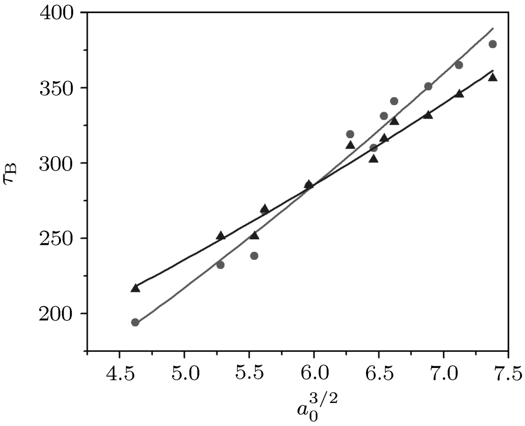

Fig. 2. Curves for τ_B versus $a_0^{3/2}$, where solid circles denote the data calculated in LDA scheme, and the line passing through these solid circles is the fitting curve, with Eq. (10) taken as the fitting formula, and solid triangles represent the data calculated in GGA scheme, the line going through the solid triangles is the fitting curve, with Eq. (12) used as the fitting formula.

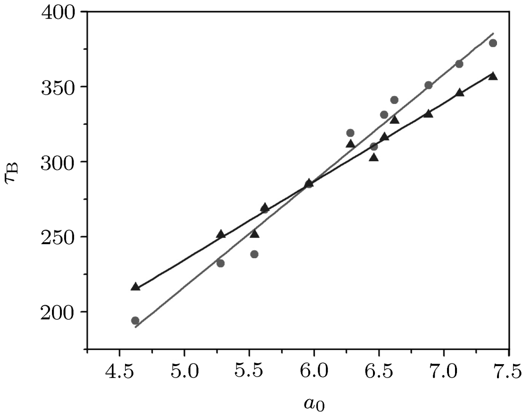

Fig. 3. Curves for τ_B versus a_0, where solid circles denote the data calculated in in LDA scheme, the line passing through these solid circles is the fitting curve, with Eq. (11) taken as the fitting formula, and solid triangles represent the data calculated in GGA scheme, the line going through the solid triangles is the fitting curve, with Eq. (13) used as the fitting formula.

Most of the relevant publications do not give the positron bulk lifetime directly, they present τ_1 and τ_2 and we can obtain the positron bulk lifetime τ_B from the formula:[29]

$$\tau_B = \frac{\tau_1 \tau_2 (I_1 + I_2)}{\tau_1 I_2 + \tau_2 I_1}. \tag{14}$$

From these data we can see that our predicted lifetimes are consistent with the experimental ones. The positron lifetime of NaCl-type crystal structure is tightly related to lattice constants and the volume of the unit cell as mentioned above.

Table 3. Predicted positron bulk lifetimes from Eqs. (10) and (12), experimental values of positron lifetimes cited from the literature (lifetime is in units of ps).

compound	predicted τ_B with Eq. (10)	predicted τ_B with Eq. (12)	experiment
LiF	157	191	
LiCl	226	242	
LiBr	250	260	
LiI	285	285	
MnO	182	210	
MgO	167	199	166[8]
FeO	173	204	
CoO	171	202	
NiO	166	198	188±20[26]
BaO	252	261	
MgS	230	245	
MnS	232	247	
BaS	312	305	315±17[26]
SrS	287	287	272±20[26]
CaS	264	270	279±23[26]
SrSe	302	298	282±23[26]
BaSe	329	317	307±26[26]
CaSe	279	281	269±29[26]
CaTe	311	304	
SrTe	334	321	307±26[26]
BaTe	360	339	339±38[26]
TiC	175	205	155[27]
TiN	170	201	
ScN	182	210	
AgCl	253	262	241±31[28]
AgBr	270	274	262±38[28]

The error of positron lifetime cited from the literature above is obtained from the error propagation formula.

5. Conclusion

First, the theoretical calculations of the positron lifetimes for the bulk state of some NaCl-type crystals are performed with the ATSUP method. The results calculated by the LDA method are not always smaller than the results calculated by the GGA method, at least for the calculations of NaCl-type crystal. Secondly, not only in diamond, cubic zincblende and wurtzite structures, but also in NaCl-type crystalline, the positron bulk lifetimes have rather simple relationships with lattice constants and the volume of the unit cell. In addition, we guess that the positron bulk lifetimes of those compounds which have the same crystal structures maybe have a certain simple relation to lattice constants or the volume of unit cell It is obviously that more calculations and experimental data are needed to confirm this view.

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