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Effective Concentration of Electrons in Metals upon Measurements via Positron Annihilation Spectroscopy

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Abstract—Calculations are performed together with the summarization of published data on the measurement of positron annihilation rates in a number of simple substances. The information potential of different methods underlying positron annihilation spectroscopy is analyzed as applied to the study of condensed matter. The features of the mechanism of positron annihilation in metals are discussed. The possibility of investigating the electronic and defect structures of metals and alloys using the method of the time distribution of annihilation photons is considered.

Keywords: positron, positronium, annihilation, positron annihilation spectroscopy, defects, conduction band, electron configuration of atoms, transition metals

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INTRODUCTION

Positron annihilation spectroscopy (PAS) is a modern method for studying the structure of substances. Its essence is that positrons arising from the β^+ decay of a radioactive source (as a rule, the nuclei of isotopes ^{22}Na, ^{64}Cu, ^{58}Co, and ^{44}Ti) are implanted into the sample under examination and, subsequently, annihilation γ-ray characteristics are recorded. In this case, a positron is interpreted as a probe whose annihilation characteristics depend on the parameters of the medium it is in.

In any substance, the positron annihilation process can proceed both as free collisions with the electrons of a medium and via the formation of bound states between positrons and electrons, atoms, molecules, and different defects so that each annihilation channel makes its own specific contribution to the experimental annihilation spectrum. It should be noted that, before annihilation, most of the positrons succeed in thermalizing and the annihilating positron–electron pair possesses an energy determined mainly by the electron energy.

In nonconducting media, positronium (Ps) atoms can be generated upon the interaction between a thermalized electron (e^+) and one of the track electrons knocked out by a positron during its ionization deceleration along the final segment of the positron track. Ps is a bound state of an electron and a positron. Like a hydrogen atom, Ps can exist in the ortho- or parastate depending on the mutual orientation of e^+ and e^- spins. The probabilities that Ps is formed in the ortho- or parastate are in the ratio 3 : 1. The parapositronium lifetime is 0.125 ns in free space (before annihilation into two γ quanta), and the lifetime of orthopositronium is 142 ns in free space, breaking down into three γ quanta. However, if orthopositronium exists in the medium, a positron can annihilate not only with its own electron but also with one of the surrounding molecular electrons, with which fast two-photon annihilation is possible. In this case, the orthopositronium lifetime decreases drastically depending on the electron density near the positron-annihilation region. When vacancy (e.g. radiation-induced) defects appear, the lifetime of the orthopositronium captured at some defect will depend on the size of the cavity where it is situated. In the case of parapositronium, a positron annihilates with its own electron, and the experimentally determined energy of the pair also depends on the size of the cavity containing the Ps. These properties are cardinal in finding nanocavity sizes and structural defects.

Naturally, the correct interpretation of PAS experimental spectra requires reliable theoretical models describing Ps generation and its interaction with defects and intermediate-radiolysis products.

At present, three basic methods of PAS are actively used in practice.

(i) Recording of the time distribution of annihilation photons (TDAP). In this case, the lifetime of each e^+ implanted into the sample (i.e., the time interval between recording initial γ quantum emitted by a

Table 1. Positron lifetimes (in picoseconds) in vacancy defects

Defect type	Positron lifetimes, ps	Vacancy radii, Å	Si volume—defectless material	Positron lifetimes, ps	Vacancy radii, Å
Fe bulk	110	–	Si bulk	219	–
Fe dislocation	165	1.3	Si dislocation	266–270	1.7
Fe monovacancy	175	1.41	Si monovacancy	318–325	2.3
Fe divacancy	197	1.6	Si tetravacancy	425 ± 30	3.4
Fe trivacancy	232	1.9	Si pentavacancy	505 ± 20	4.5
Fe tetra vacancy	262	2.2	Si sixth vacancy	>520	4.8
Fe sixth vacancy	304	2.6			

radioactive nucleus, the positron source at the instant of β decay, and one of the annihilation photons with an energy of 0.511 MeV) is measured.

(ii) Measuring the angular distribution of annihilation photons (ADAP), in which the angle of photon divergence from 180° is recorded upon 2γ annihilation.

(iii) Measuring the Doppler broadening of annihilation lines (DBAL). In this case, the difference between the annihilation-photon energy (at 2γ annihilation) and 0.511 MeV is measured. This is especially efficient if recording relies on the coincidence circuit where the trigger is the photon emitted by the radioactive nucleus immediately after positron production.

The TDAP technique provides data on the electron density at the place of positron annihilation, and the ADAP and DBAL methods provide information on the electron momentum distributions in the medium. In conducting media, defects (e.g., vacancies) commonly possess a surplus negative charge and thus attract positrons.

On account of comparison between the measured positron lifetimes in the materials under study and the known lifetimes in different types of defects, their type can be identified. Moreover, from measurements of the fraction of positrons annihilating in this defect, it is possible to acquire information on defect concentrations. Published data on positron lifetimes (in picoseconds) at vacancy defects of silicon and iron are presented in Table 1 [1–7].

Angular annihilation spectra contain information on the energy of the annihilating positron–electron pair. Since practically thermalized electrons participate in the annihilation process, the measured energy of the given pair is mainly determined by that of electrons belonging to atoms of the medium surrounding the defect. A comparison between the measured energy and tabular values of the ionization potentials enables us to obtain data on the chemical composition of the medium in the vicinity of the positron-annihilation region.

Thus, material studies based on different positron techniques, in particular, the TDAP and ADAP approaches, enables the acquisition of detailed information on a medium's electron and defect structures and its chemical composition. The positron technique applied to the atomic industry makes it possible to investigate radiation-induced defects with a size of up to 1 nm^3. As regards such defects, the PAS sensitivity threshold is approximately 10^{14} defect/cm^{-3}. Analogous investigations can hardly be implemented by means of any other defectoscopy method (e.g., transmission electron microscopy, 3D atom probing, small-angle neutron scattering, and IR oscillation spectroscopy). Such a state of affairs determines the interest in positron techniques which are widely used in many scientific centers.

Positron diagnostic techniques are finding wide application in studying the electron structure of metals and alloys. This is related to the fact that they enable us to define the important characteristics of metals, such as electron distributions over momenta, the Fermi-level energy ε_F, the number Z_{free} of free electrons per metal atom, and their concentration n_c in the conduction band. As is known, these characteristics determine in many respects mechanical, electrical, and magnetic properties of metals.

THEORY OF THE METHOD

Positron-annihilation rate λ can be expressed in terms of collisions with a medium's electrons:

$$\lambda_{exp} = \sigma_D v N_e, \quad (1)$$

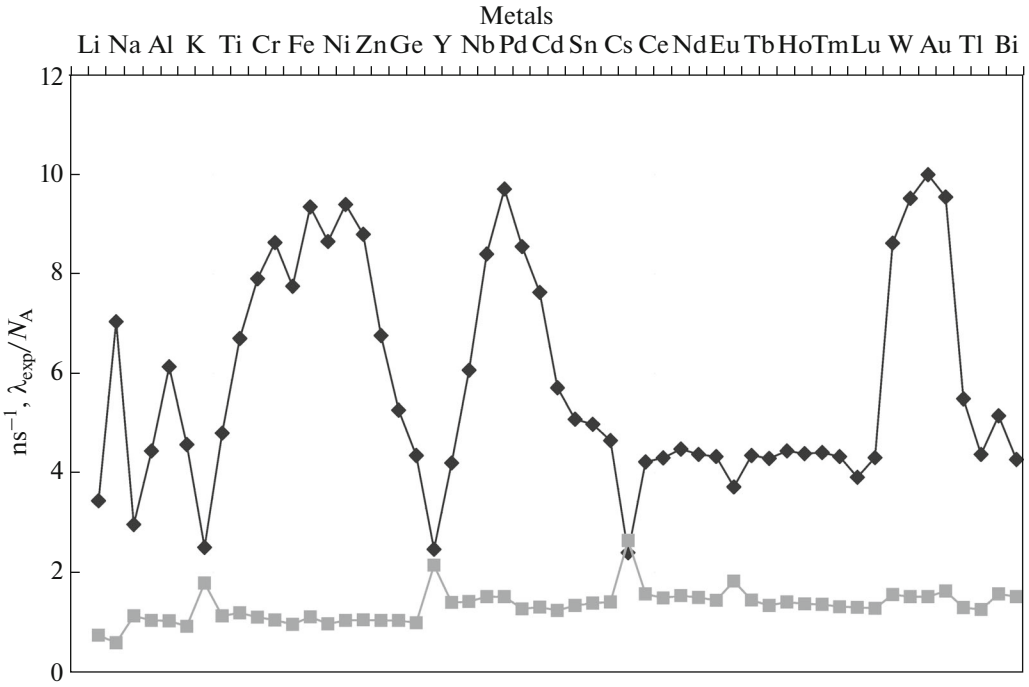
Here, $\sigma_D = \pi r_0^2 c/v$ is the Dirac cross section of two-quantum annihilation, where v is the positron velocity, $r_0 = \dfrac{e^2}{mc^2}$ is the classical electron radius, and c is the speed of light, and $N_e = N_A Z$ is the electron concentration, where N_A is the atomic concentration and Z is the number of electrons interacting with the positron.

Thus, quantity

$$Z = 1.354 \times 10^{13} \frac{\lambda_{exp}}{N_A} \quad (2)$$

Table 2. Electronic properties of metals: λ_{exp} is the positron-annihilation rate, λ_{exp}/n_a is the annihilation rate per unit atom, and n_a is the metal atom concentration

Metal	Electron shell		λ_{exp}, ns^{-1}	$\lambda_{exp}/N_A \times 10^{-13}$	$N_A \times 10^{22}$
In	$4d^{10}5s^25p^1$		5.23	1.33	3.80
Sn	$4d^{10}5s^25p^2$		5.13	1.38	3.70
Bi	$5d^{10}6s^26p^3$		4.27	1.51	2.80
Pb	$5d^{10}6s^26p^2$		4.83	1.56	3.30
Zn	$3d^{10}4s^2$		6.4	1.03	6.57
Mg	$2s^22p^63s^2$		4.46	1.03	4.30
Al	$3s^23p^1$		6.06	1.02	6.0
Sc	$3d^14s^2$		4.8	1.12	4.0
Ti	$3d^24s^2$		6.7	1.18	5.7
V	$3d^34s^2$		7.9	1.09	7.2
Cr	$3d^54s^1$		8.3	1.04	8.3
Mn	$3d^54s^2$		7.75	0.95	7.9
Fe	$3d^64s^2$		9.35	1.10	8.50
Co	$3d^74s^2$		8.65	0.96	9.09
Ni	$3d^84s^2$		9.4	1.03	9.13
Cu	$3d^{10}4s^1$		8.3	1.04	8.50
Y	$4d^15s^2$		4.2	1.39	3.03
Zr	$4d^25s^2$		6.06	1.41	4.29
Nb	$4d^45s^1$		8.4	1.51	5.56
Mo	$4d^55s^1$		9.71	1.51	6.41
Tc	$4d^55s^2$	($4d^65s^1$)	–	–	7.07
Ru	$4d^75s^1$		–	–	7.39
Rh	$4d^85s^1$		–	–	7.26
Pd	$4d^{10}$		8.55	1.26	6.80
Ag	$4d^{10}5s^1$		7.63	1.30	5.86
Yb	$4f^{14}6S^2$		3.91	1.29	2.42
La	$4f^{14}5d^16S^2$		4.31	1.27	3.39
Hf	$4f^{14}5d^26S^2$		–	–	4.49
Ta	$4f^{14}5d^36S^2$		8.62	1.55	5.55
W	$4f^{14}5d^46S^2$	($4f^{14}5d^56S^1$)	9.52	1.51	632
Re	$4f^{14}5d^56S^2$	($4f^{14}5d^66S^1$)	–	–	6.80
Os	$4f^{14}5d^66S^2$		–	–	7.15
Ir	$4f^{14}5d^76S^2$		–	–	7.07
Pt	$4f^{14}5d^96S^1$		10	1.51	6.62
Au	$4f^{14}5d^{10}6S^1$		9.55	1.62	5.90
Hg	$4f^{14}5d^{10}6S^2$		5.49	1.29	4.07



Comparison between (squares) the positron-annihilation rates λ_{exp} in metals and (rhombs) the ratio of the annihilation rate to the metal-atom concentration N_A. The positron-annihilation rates (in ns^{-1}) are plotted on the ordinate axis. The λ_{exp}/N_A ratio is practically constant.

characterizes the effective number of atomic electrons annihilating with the positron.

RESULTS AND DISCUSSION

In this work, data (Table 2, figure) on measuring the positron-annihilation rate in a number of simple (Mg, Al, Cu, Zn, In, Sn, Pb, and Bi) and transition metals, which were previously obtained by our group and known from publications [1–25], are presented.

The experimentally measured positron-annihilation rates in metals vary in a rather wide range (from 2.5 ns^{-1} (K) to 10 ns^{-1} (Pt)). However, it was revealed that the λ_{exp}/N_A ratio, i.e., the annihilation rate per unit atom, changes only slightly. For example, in the case of metals from the third period, this ratio varies from 1.1 (Na) to 1.0 (Al). For the majority of metals belonging to the fourth period, the ratio is unity except for Sc (1.1), Ti (1.2), and K (1.78). In the case of metals in the fifth period, the average value of the given parameter is 1.3. For the sixth period, many available experimental data indicate that its value decreases steadily from 1.56 (La) to 1.27 (Lu). Moreover, it is seen from data summarized in Table 2 that, for transition metals, the positron annihilation rate per unit atom is actually independent of the *d*-shell population.

Questions arise as to which electrons participate in positron annihilation and whether information on the electron configuration of atoms can be acquired only from TDAP experimental results.

The figure and Table 2 present theoretical and experimental data obtained by different authors with the help of TDAP measurement setups [1–25]. The experimental results were processed under the assumption that, in perfect metals, positron annihilation is described by a single exponent with a characteristic rate of λ_{exp}. In this case, λ_{exp} is the average rate of annihilation at valence, core, and *d*-shell electrons. In reality, the rates of annihilation at these electrons are different [19, 20], but their experimental separation is impracticable.

As is evident from data in Table 1, the λ_{exp}/N_A ratio is practically constant. For some atoms, the deviation from a constant value is apparently explained by the different degrees of substance polarization, i.e., a local increase in electron concentration near the positron position, which is more pronounced for alkali metals. Moreover, the *d*-electrons of alkali metals do not contribute to the total annihilation rate. The rate of positron annihilation with valence electrons is smaller than that with *d*-electrons [19].

The observed significant differences in the positron annihilation rates of perfect metals are associated with different atomic concentrations (densities).

CONCLUSIONS

Data obtained by our group and known from publications, namely, the positron-annihilation rates in several simple (Mg, Al, Cu, Zn, In, Sn, Pb, and Bi)

and transition metals, which were measured via the technique of the time distribution of annihilation photons, are analyzed. It is demonstrated that the observed significant differences in the positron annihilation rates of perfect metals is caused only by different atomic concentrations (densities). In the case of transition metals, the positron-annihilation rate per unit atom is hardly dependent on the *d*-shell population. As applied to transition metals, the TDAP technique provides no information on the electron configuration of atoms. At the same time, this technique enables us to investigate vacancy, including radiation-induced, defects of metals, namely, to determine their type, size, and topology.

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