INSTRUMENTS AND METHODS OF INVESTIGATION

Positron annihilation spectroscopy in materials structure studies

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<u>Abstract.</u> A relatively new method of materials structure analysis — positron annihilation spectroscopy (PAS) — is reviewed. Measurements of positron lifetimes, the determination of positron 3γ - and 2γ -annihilation probabilities, and an investigation of the effects of different external factors on the fundamental characteristics of annihilation constitute the basis for this promising method. The ways in which the positron annihilation process operates in ionic crystals, semiconductors, metals and some condensed matter systems are analyzed. The scope of PAS is described and its prospects for the study of the electronic and defect structures are discussed. The applications of positron annihilation spectroscopy in radiation physics and chemistry of various substances as well as in physics and chemistry of solutions are exemplified.

1. Introduction

During recent years extensive research has been in progress in the field of the positronics of various substances and their states [1-61]. The interest in studying positronics is not

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Received 16 March 2001, revised 10 July 2001 Uspekhi Fizicheskikh Nauk **172** (1) 67–83 (2002) Translated by E Yankovsky; edited by A Radzig accidental. On the one hand, this is related to such fundamental problems of physics as the birth and evolution of the Universe and/or universes [11], positron astrophysics [11, 20, 54], the interaction between matter and antimatter [11, 15], and the study of new modifications of Wheeler complexes in matter [14, 16, 17, 19, 21-23, 46, 52, 53, 55–58]. On the other hand, the interest in positronics is related to the search for new unique methods of investigating the electronic structure and some physicochemical characteristics of matter [1–12, 25-27, 34-68] (including solids) in addition to the already existing methods (optical, electrical, magnetic, etc.) and to the possibilities of manufacturing devices and equipment that operate on the basis of the interaction between radiation and matter.

Experimental studies have already been conducted on positron annihilation in metals, alloys, ionic type condensed media (in alkali halide crystals, hydrides and oxides of metals, and other substances of the ionic type), elementary semiconductors (Si, Ge, Se, semiconducting III–V and II–VI compounds), polymers, and so forth. It was found that the sensitivity of the positron method (the annihilation characteristics) to the electronic and defect structures of these substances is high.

Thus, positron annihilation spectroscopy (PAS) may be considered as a method for studying the electronic structure, determining the structure, nature, and concentration of point and extended defects, and investigating the disrupted surface layers and surface states in metals, alloys, semiconductors, ionic crystals, and other substances that have firmly established themselves in the physics and chemistry of solids [14– 44]. Studies involving semiconductors, ionic crystals, metals, and condensed media that have been conducted over the last few years (but have not been properly reflected in the scientific literature) have revealed some new effects in the positron annihilation spectra of these substances, such as the existence of several positron lifetimes, the fine structure of the curves representing the angular distributions of annihilation photons, the enhanced probability of three-photon annihilation, and the presence of magnetic quenching of some of the main characteristics of positron annihilation spectra (quenching orthopositronium states) and so on. Thus, one can draw the conclusion that semiconductors, ionic crystals, metals, and some condensed media exhibit a broad spectrum of positron and positronium states.

These results stimulate interest in further experimental and theoretical research and in analysis of positron states, positron processes, and positron annihilation in crystals and other condensed media with the aim of systematizing the data already gathered, classifying the positron and positronium states, describing their properties and the effect of various external factors (magnetic field, temperature, pressure, etc.), and more thoroughly establishing the possible applications of the positron method.

The present review is devoted mainly to the studies of Russian scientists in the field of applications of positron annihilation processes in various substances, not reflected in publications and conference proceedings (e.g. see Refs [7, 8] and the reviews [3-6, 9, 10, 43, 44]) and to the new measurements done by the PAS method. By way of an example we analyze the salient features of positron annihilation in metals, semiconductors, ionic crystals, and some condensed media (amorphous substances and solutions).

In addition, we discuss the peculiarities of the angular distribution spectra of annihilation photons for positron annihilation in a number of investigated metals, peculiarities related to the new annihilation mechanism (via formation in metals of Wheeler complexes of $e_2^-e^+$ composition) and to finding the electron concentration n_p in the conduction band of the metal [11], and the possibilities of using the positron annihilation method in studies covering semiconductors and ionic crystals [11, 12] (for example, in determining the effective atomic charges and the effective masses of positron polarons in ionic type media, and in investigating the structural imperfections of the crystal).

Particular emphasis is placed on the use of positron tomography in the nondestructive quality control of technologically important materials, in determining the vacancy formation enthalpy (H_{IV}) in crystals, and in developing positron microtomography of layer structures [11, 12].

What is also important is research in which positron spectroscopy is applied to studying liquid media, positronium in radiation physics and chemistry, and the properties and structure of the surface layers of liquids [12]. In this connection we discuss the new possibilities and prospects of using PAS in investigations of the electronic and defect structures of these objects, in radiation physics and chemistry of various substances, and in the physics and chemistry of solutions.

Establishing the mechanism of positronium formation in condensed dielectric media makes the PAS method a highly effective instrument for studying the primary stages of intratrack processes and for determining the physicochemical characteristics of primary radiolysis products. The employment of positron spectroscopy in studying the properties of surfaces and the structure of liquid media is only in its infancy, and we can expect remarkable results in this area of research.

2. Experimental methods of positron spectroscopy of materials

2.1 Theory of the methods

The annihilation of positrons in collisions with electrons is accompanied by the emission of one, two, or more photons (γ -quanta). Single-photon electron – positron annihilation is possible only in the presence of a third body (a nucleus or electrons) that carries away the recoil momentum. When a free positron and a free electron annihilate, at least two photons are created.

The positron annihilation cross section rapidly decreases with an increase in the number of emitted photons. When the number of created photons increases by one, the annihilation cross section is multiplied by the fine-structure constant $\alpha = 1/137$, i.e. the probability of the annihilation process decreases more than by two orders of magnitude.

The cross section of two-photon annihilation of a free positron and a free electron was calculated by P Dirac. In the nonrelativistic approximation this cross section increases with decreasing relative velocity v of the colliding particles [1, 4]:

$$\sigma_{2\gamma} = \sigma_{\rm D} = \pi r_0^2 \, \frac{c}{v} \,, \tag{1}$$

where r_0 is the classical electron radius, and c is the speed of light.

As $v \to 0$, the cross section σ_D becomes infinite. However, the positron annihilation rate λ_D tends to a finite limit:

$$\lambda_{\rm D} = \sigma_{\rm D} v \, n_{\rm e} = \pi r_0^2 c n_{\rm e} \,, \tag{2}$$

where $n_{\rm e}$ is the electron concentration.

An electron – positron annihilation is possible only if the momentum and energy conservation laws are met, which in the case of two-photon annihilation have the form

 $k_1 + k_2 = p = 2mv, (3)$

$$k_1 c + k_2 c = E = 2mc^2 \,. \tag{4}$$

Here $m = m_0/\sqrt{1 - v^2/c^2}$, where m_0 is the electron rest mass, k_1 and k_2 are the photon momenta, *E* is the energy of the electron-positron pair, and *v* is the velocity of the pair's center of mass in the laboratory frame of reference.

Equations (3) and (4) imply that if the pair's center of mass in the laboratory system of coordinates is fixed (v = 0), the two photons fly apart in opposite directions (angle θ in Fig. 1 goes to zero) with the same energy: $k_1c = k_2c = m_0c^2 =$ 0.511 MeV.

When $v \neq 0$, the angle between the directions in which the photons fly apart differs from 180° and their energy is not equal to 0.511 MeV. If the pair momentum $p \ll m_0 c$, the deviation angle θ (see Fig. 1) is defined by

$$\sin\theta \approx \frac{p_{\perp}}{m_0 c} \,, \tag{5}$$



Figure 1. Schematic of the photons' flying apart in the two-photon electron – positron annihilation.

and the change in the photon's energy (the Doppler shift) is given by the formula

$$\Delta E_{\gamma} \approx \frac{p_{\parallel}c}{2} \,. \tag{6}$$

Thus, in the case of two-photon annihilation, measuring the deviation angle θ of the photons from 180° or the Doppler shift ΔE_{γ} of the annihilation line (0.511 MeV) makes it possible, at least in principle, to determine the momentum of the electron-positron pair in the laboratory frame of reference.

In the case of three-photon annihilation, the conservation laws do not unambiguously determine the momenta and energies of the emerging photons. At v = 0, all three photons fly apart in the same plane. The deviation angles (for $v \neq 0$) from this plane is of order v/c. In contrast to two-photon annihilation, the photons that are created in three-photon annihilation have a continuous energy distribution from 0 to 0.511 MeV.

In many substances the annihilation of positrons proceeds through bound states of positrons with electrons, atoms, molecules, and various defects (see below). The simplest bound two-particle system e^+e^- became known as positronium (symbol Ps).

It was found that the binding energy of the positronium atom is twice as small and that the orbit radii are twice as large as those of the hydrogen atom:

$$E_{\rm n} = -\frac{m_0 e^4}{4\hbar^2 n^2} \,, \tag{7}$$

$$r_{\rm n} = \frac{2\hbar^2 n^2}{m_0 e^2} \,. \tag{8}$$

In the ground state of the positronium atom (n = 1), the binding energy $E_{Ps} = -E_1 = 6.77$ eV and the Bohr radius $a_{Ps} = 2a_0 = 0.106$ nm (where a_0 is the first Bohr radius of the hydrogen atom).

In the nonrelativistic approximation, the positronium wave functions corrected for the reduced mass are the same as for the hydrogen atom. For instance, the positronium ground-state wave function assumes the form

$$\psi_1(r) = \frac{1}{\sqrt{\pi a_{\rm Ps}^3}} \exp\left(-\frac{r}{a_{\rm Ps}}\right). \tag{9}$$

Depending on the mutual orientation of the spins of e^+ and e^- , one must distinguish between two ground states of the positronium atom: the singlet state ${}^{1}S_{0}$ (parapositronium, p-Ps), when the spins of e^- and e^+ are antiparallel (total spin zero), and the triplet state ${}^{3}S_{1}$ (orthopositronium, o-Ps), when the spins of e^- and e^+ are parallel (total spin one). Orthopositronium has three substates which differ in the value of the magnetic quantum number m: +1,0,-1; for parapositronium one finds m = 0. Hence, the relative statistical weight of orthopositronium is 3/4, and that of parapositronium, 1/4.

The cross section and the nature of annihilation depend on the mutual orientation of the spins of the particles participating in the annihilation process. For instance, parapositronium undergoes two-photon annihilation, while orthopositronium undergoes three-photon annihilation. The probabilities of the spontaneous annihilation of p-Ps and o-Ps atoms are also different.

The annihilation rate λ_s^0 and the mean lifetime τ_s^0 with respect to spontaneous annihilation of the ground-state parapositronium are related as follows

$$\lambda_{\rm s}^0 = \frac{1}{\tau_{\rm s}^0} = 4\pi r_0^2 c \left| \psi_1(0) \right|^2,\tag{10}$$

where $|\psi_1(0)|^2$ is the probability of finding the electron in the vicinity of the positron. Substituting (9) into (10), we get

$$\lambda_{\rm s}^0 = 8 \times 10^9 \, {\rm s}^{-1} \,, \qquad \tau_{\rm s}^0 = 1.25 \times 10^{-10} \, {\rm s} \,.$$
 (11)

Allowing for the ratio $\sigma_{3\gamma}/\sigma_{2\gamma} = 1/372$ and the statistical weight of the triplet state, we arrive at the following value of the annihilation rate for a ground-state orthopositronium:

$$\lambda_t^0 = \frac{1}{\tau_t^0} = \frac{\lambda_s^0}{1115} = 7.14 \times 10^6 \text{ s}^{-1} , \qquad \tau_t^0 = 1.4 \times 10^{-7} \text{ s} .$$
(12)

An external magnetic field splits the energy levels of the positronium atom (the Zeeman effect) and leads to what is known as magnetic quenching [1, 4, 12].

The most commonly used experimental methods for observing the positron annihilation in matter are based on measuring the positron mean lifetime, observing the angular correlation of the annihilation photons, and determining the rate of three-photon annihilation of positrons. Other methods also exist, such as the measurement of the energy spectrum of the annihilation radiation (the Doppler shift, in particular) and a combination of measurements of the positron lifetime with that of the angular correlation of the annihilation photons (the combined method), etc. Some of the basic methods are examined below.

2.2 Measuring the positron lifetime in matter

Measuring the positron lifetime in matter involves using the ²²Na nuclide (with a half-life $T_{1/2} = 2.6$ a). The essence of the method of determining the positron lifetime amounts to measuring the delayed coincidence counting rate between the nuclear gamma quantum with an energy of 1.28 MeV (start — at the zero time) in the transition

22
Na $\rightarrow ^{22}$ Ne + e⁺ + γ (1.28 MeV)

and one of the 0.511-MeV photons emitted in the annihilation of the positron (stop signal). The positron and the nuclear photon (1.28 MeV) are emitted almost simultaneously (with a time interval no longer than 10^{-11} s). Thus, detection of the nuclear photon (1.28 MeV) serves as a signal that the positron has landed in the medium, while detection of the 0.511-MeV photon testifies that the positron has perished.



Figure 2. Schematic of the installation for measuring the positron lifetime.

The facility used in measuring the positron lifetime is depicted schematically in Fig. 2. The radioactive source I with an activity of $(1-2) \times 10^6$ Bq emits positrons which land in the substance 2 being studied and annihilate in it. The scintillation detectors 3 and 4 record the start and stop γ -quanta. Both detectors generate signals S_1 and S_2 , linked in time to the emission of the respective photons.

The time interval between events is measured by a system of nanosecond electronic units, which includes null detectors in the time channels, amplitude analysis units, and a converter 5 which transforms the time interval into the signal's amplitude. The spectrum of the time distribution of annihilation photons (TDAP) is registered by a multichannel pulse analyzer δ .

An example of a spectrum of positron lifetimes in polymethyl methacrylate, depicted in Fig. 3, shows that in polymer materials positrons live very long (up to 16 ns and even longer), while the positron lifetime in silicon is within the 0.2-0.3-ns range.



The observed spectrum is a linear combination of several spectra with different lifetimes:

$$N(t) = \int R(t, t_1) \sum_{i=1}^{n} A_i \exp\left(-\frac{t_1}{\tau_i}\right) \mathrm{d}t_1 \,. \tag{13}$$

Here, $R(t, t_1)$ is the instrument function of the installation for measuring TDAP, *n* is the number of components in the spectrum, τ_i is the positron lifetime in the substance, and A_i is the fraction of positrons with the lifetime τ_i .

For the majority of modern setups, the half-width (the width at half-height) of the instrument function in Eqn (13) is in the 0.2-0.3-ns range. Computer processing of the spectra (usually the PATFIT program is employed) makes it possible to determine the positron lifetimes in matter that lie within the 0.1-30-ns interval and the probabilities of the different positron annihilation channels: o-Ps, p-Ps, e⁺, etc.

The positron lifetime in matter depends on the number density of electrons in the positron annihilation region. In the presence of a free volume (a void) in the substance, the positron lifetime is determined by the void size [24]:

$$\tau = \frac{1}{2} \left(1 - \frac{R}{R + \Delta R} + \frac{1}{2\pi} \sin \frac{2\pi R}{R + \Delta R} \right)^{-1}, \qquad (14)$$

where *R* is the void radius, and ΔR is the thickness of the electron layer ($\Delta R = 0.166$ nm).

Equation (14) shows that the measurement of TDAP makes it possible to extract information about defects in the substance. Generally speaking, measuring the parameters of the temporal annihilation spectra (mean lifetimes τ_j and intensities I_j) allows one to estimate the nature of the positron states, the mechanism of positron annihilation in the substance, and thus the properties of the medium itself.

2.3 Methods of determining the three-photon positron annihilation probability

In the absence of positronium formation, the relative probability of three-photon positron annihilation is $P_{3\gamma}^0 = 1/372$. When positronium is formed in matter due to three-photon orthopositronium annihilation, the relative probability of three-photon annihilation of the positron increases: $P_{3\gamma} > P_{3\gamma}^0$. Hence measurements of the relative probability $P_{3\gamma}$ provide a direct indication of positronium formation in matter.

A setup used to observe three-photon positron annihilation is schematically depicted in Fig. 4. Three scintillation detectors of annihilation photons are placed in one plane at an angle of 120° to each other at equal distances from the sample with the source. Such an arrangement of the detectors permits the detection of the three photons from a single act of three-photon positron annihilation with the same energy $[(2/3)m_0c^2 = 340 \text{ keV} \text{ each}]$. Measurements of the probability $P_{3\gamma}$ are usually done with respect to aluminium, in which positronium is sure not to form; hence $P_{3\gamma}^{AI} \approx P_{3\gamma}^0 = 0.27\%$. A detailed description of the setup and the measuring technique can be found in Refs [1, 25].

In addition to direct methods, in which the probability $P_{3\gamma}$ of three-photon positron annihilation is determined from the coincidence counting rate for the three photons, there are indirect approaches. One of these amounts to measuring the energy spectrum of the annihilation radiation (only one



Figure 4. Schematic of the setup for observing three-photon positron annihilation: *1*, crystal; *2*, Pb-collimator; *3*, photoelectric multiplier; *4*, fast (10 ns) coincidence circuit; *5*, trigger; *6*, slow (1 μ s) coincidence circuit, and *7*, amplitude analyzer.

detector is used, and the output pulses from this detector are fed to the amplitude analyzer). This method was used in works [1, 25]. Finally, the relative probability of three-photon annihilation can be determined from the increase in the coincidence counting rate for two photons as the probability of three-photon annihilation decreases due to, say, magnetic quenching of positronium.

2.4 Determining the two-photon positron annihilation probability

The method of finding the probability of two-photon positron annihilation is based on measuring the angular distribution of the annihilation photons [1–6, 10]. An electron – positron annihilation requires the fulfilment of the law of conservation of charge parity. This means that in the event of two-photon annihilation of an electron – positron pair at rest the two photons fly apart in opposite directions (the angle of photons' flying apart is 180°) and carry away equal amounts of energy $m_0c^2 = 0.511$ MeV. If the pair momentum *p* is nonzero, the angles (see Fig. 5) between the directions in which the photons fly apart differ from 180° by a value of θ (in the laboratory frame of reference) and the photon energy is not 0.511 MeV anymore.

The range of possible values of the angle θ is extremely narrow (less than 1°), with the result that in the calculations we use the angle θ proper instead of sin θ . The distribution over the angles θ is called the angular distribution of annihilation photons (ADAP). If the pair momentum $p \ll m_0 c$, the angle θ is given by the formula

$$\theta = \frac{p_\perp}{m_0 c} \,. \tag{15}$$

The Doppler broadening ΔE of the annihilation line is defined by the expression

$$\Delta E_{\gamma} = \frac{p_{\parallel}c}{2} \,, \tag{16}$$

where p_{\perp} and p_{\parallel} are the transverse and longitudinal components of momentum **p**, respectively (see Fig. 1).

Thus, by measuring the coincidence counting rate for the photons in two-photon positron annihilation as a function of the angle θ (the deviation of the photons' flying apart from 180°) or the Doppler broadening ΔE_{γ} of the annihilation line (0.511 MeV) it is possible to determine the momentum of e⁺e⁻-pairs (or electrons if positron momentum is small compared to electron momentum).

An installation used to measure angular distributions of annihilation photons is depicted schematically in Fig. 5[1-6]. The positrons emitted by the radioactive source 2 land in the substance 3 under investigation and annihilate there, the process being accompanied by the emission of two photons. These photons fly apart in different directions at an angle to each other and are registered by detectors. The signals from the detectors 1 and 4 pass through the amplifier 6, the discriminator 7, and the coincidence circuit 8 and are fed to the counter 9 which registers events related to the simultaneous landing of annihilation photons into both detectors. The entrance windows of the photon detectors are slits that have angular dimensions θ_y and θ_z and are parallel both to each other and to the sample surface, being disposed bilaterally along the sample (such an experimental arrangement is called parallel-slit).



Figure 5. A schematic of the setup for observing the angular correlation of annihilation photons: *1*, moving detector; *2*, positron source; *3*, sample; *4*, stationary detector; *5*, scintillator; *6*, amplifier; *7*, discriminator; *8*, coincidence circuit, and *9*, counter.

The conditions imposed on the angular dimensions θ_y and θ_z are as follows

$$\theta_y = \frac{\Delta p_y}{m_e c} \gg 2 \frac{p_{\max}}{m_e c}, \qquad \theta_z = \frac{\Delta p_z}{m_e c} \ll \frac{p_{\max}}{m_e c}.$$
(17)

Here, Δp_y and Δp_z are the instrumental resolutions in the components p_y and p_z of the momentum, m_e is the electron mass, c is the speed of light, and p_{max} is the maximum value of the electron momentum in the substance.

The number of photons registered simultaneously by the two detectors (the selection of such cases is done by the coincidence circuit δ) is given by the expression

$$N_{\rm c}(\theta) = A \int_{p_z - \Delta p_z/2}^{p_z + \Delta p_z/2} \mathrm{d}p_z \int_{-\Delta p_y}^{+\Delta p_y} \mathrm{d}p_y \int_{-\infty}^{+\infty} \mathrm{d}p_x \, n_{\rm e}(\,p_x,\,p_y,\,p_z)\,,$$
(18)

where A is the normalization constant, and $n_e(p_x, p_y, p_z)$ is the electron momentum distribution density in the substance being studied. If we combine Eqn (18) with the conditions (17), we get

$$N_{\rm c}(\theta) = A \,\Delta p_z \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \mathrm{d}p_x \,\mathrm{d}p_y \,n_{\rm e}(\,p_x,\,p_y,\,p_z)\,. \tag{19}$$

Usually the probability $f(\theta)$ [rather than the number $N_c(\theta)$ of photon coincidences] is used as ADAP. In this case the normalization constant A in Eqns (18) and (19) is chosen such that the following normalization condition is met:

$$\int_{-\pi/2}^{+\pi/2} f(\theta) \,\mathrm{d}\theta = 1 \,. \tag{20}$$

The ADAPs of some metals are exemplified in Fig. 6.

Thus, in the parallel-slit geometry of the experiment, the number of photon coincidences is defined as the integral of the electron distribution density over the electron momentum projections parallel to the plane of the sample under investigation. This makes it possible to study the third projection of the electron momentum, which is perpendicular to the sample plane.

In the case of spherical symmetry of the electron momentum distribution, the results of experiments involving the parallel-slit geometry can be used to find the electron



Figure 6. Angular distributions of annihilation photons in the samples of magnesium, aluminium, copper, and indium. The dashed curves represent the parabolic (*I*) and Gaussian (2) components of the respective distributions; the solid curves depict the sums of the components *I* and 2, and the full dots represent experimental values.

momentum distribution density [1]:

$$n_{\rm e}(p) = \frac{A}{\theta} \frac{\partial f(\theta)}{\partial \theta} , \qquad (21)$$

where $p = \theta m_e c$ is the electron momentum.

The angular resolution of modern installations reaches 0.3 mrad with good statistics $[10^4-10^5 \text{ momenta per point at}$ the maximum of the $f(\theta)$ curve], which makes it possible to obtain the detailed structure of the correlation curves (e.g., see Refs [1, 6–8]). The angular correlation curves may contain the narrow and broad components (Fig. 7).

The narrow component usually owes its origin to lowenergy atoms of parapositronium, and the broad component to the annihilation of free positrons or the positron incorporating into orthopositronium and the electrons in the medium. When completely thermalized parapositronium atoms annihilate at room temperature, the deviation of the angle between the directions of propagation of the two annihilation photons from 180° is only $\theta \approx 0.5$ mrad for the narrow component, and $\theta \approx 10$ mrad for the broad component.

The experimental spectra are well described by a linear combination of several Gaussian functions, and in the case of metals a parabolic component is added to them. Each function describes a specific positron annihilation channel and is characterized by intensity (annihilation probability) and variance, which is uniquely related to the energy of the annihilating pair.

2.5 Doppler broadening of the annihilation line

The movement of the center of mass of the annihilating pair with respect to the laboratory frame of reference gives rise not only to the deviation angle of the photons from 180° but also to the Doppler broadening of the annihilation line



Figure 7. Angular distribution of annihilation photons: light circles correspond to pure ice at -40 °C; dark circles correspond to pure water at 20 °C, and the dashed curve represents the corrected angular distribution of Ref. [1].

(0.511 MeV). The development of the method of observing the Doppler broadening of the annihilation line was hindered by the absence of effective detectors with sufficiently high energy resolution. Thanks to the fabrication of semiconductor Ge(Li) detectors, this method is coming into use in addition to the angular correlation method (for instance, see Refs [1, 2]).

A Ge(Li) detector (usually of planar type with a volume of $2-3 \text{ cm}^3$) is used to observe the Doppler broadening of an annihilation line. The pulses from the detector are fed to a multichannel amplitude analyzer. So far the best resolution is not very high: 1.3-2.3 keV, which matches the angular resolution of installations used to observe the angular correlation of photons ($\Delta\theta = 4-9$ mrad). Nevertheless, the annihilation emission line proves to be much broader than the energy resolution curve. The results of measuring the Doppler broadening of an annihilation line in some metals and other substances are in good agreement with the data on angular correlation of annihilation photons [1, 2].

Despite the fairly low resolution, the observation of Doppler broadening has a number of advantages over the angular correlation method. The latter requires employing a complex mechanical system to fix the photons' deviation angle and a powerful source of positrons to achieve good statistics. All this is unnecessary in studying the shape of the positron annihilation line.

To illustrate the possibilities of the PAS method we will now discuss some of the results of the research conducted over the last few years.

3. Positron annihilation in metals

Positron annihilation has been intensively studied in metals [1-12, 25-27], and the reason for this is that the positron annihilation method makes it possible to determine such important characteristics of metals as the electron momen-

tum distribution, the Fermi energy $\varepsilon_{\rm F}$ (usually measured in eV), the number of free electrons $Z_{\rm c}$ per metal atom, and the concentration $n_{\rm p}$ (in cm⁻³) of such electrons in the conduction band. These characteristics, as is well known, largely determine the mechanical, electrical and magnetic properties of metals.

Not all valence electrons in the crystal lattice of a metal are bound to their atoms. Some of these electrons ($Z_c \ge 1$ per atom) are capable of moving in the bulk of the metal and form an electron gas into which the skeleton of positive ions was immersed, as it were. The electron gas, in turn, balances the forces of electrostatic repulsion between the ions and binds these ions into a solid (metallic bonding).

The number of electrons Z_c and the electron concentration n_p in a perfect metal differ, of course, from those in real (e.g. polycrystalline) metals. Hence in this review we present the results of experimental studies of positron annihilation (the ADAP) for a number of polycrystalline samples of metals, so as to establish the special features of the annihilation mechanism and to find the parameters ε_F , Z_c , and n_p and their dependences on the nature of the metals.

3.1 Method, theory, and experimental results

ADAP measurements have been carried out using an installation with a parallel-slit geometry of registering annihilation photons (see Fig. 5). The source of positrons was the radioactive isotope 22 Na with an activity of 3.7×10^9 Bq. The peak number of coincidences was approximately 2×10^4 . The samples with a volume of $10 \times 20 \times 10$ mm³ were cut out from whole slabs of the metal and did not undergo any special treatment. Mg, Al, Cu, Zn, In, Sn, Pb, and Bi were chosen as the examples of metals for the investigations.

In metals, the valence electrons are usually separated into two groups: the conduction electrons (free electrons), and the electrons belonging to the ion cores of the atoms (bound electrons). The conduction electrons possess the following momentum distribution

$$n_{\rm e}(p) = \left(\exp\frac{p^2/2m - \varepsilon_{\rm F}}{k_{\rm B}T} + 1\right)^{-1},$$
(22)

where $\varepsilon_{\rm F}$ is the Fermi energy, $k_{\rm B}$ is the Boltzmann constant, and *T* is the thermodynamic temperature.

At low temperatures, the conduction electron momentum distribution is close to rectangular. This means that the ADAP spectra of polycrystalline metals must have a parabolic component

$$f_{\rm p}(\theta) = \begin{cases} \frac{3I_{\rm p}}{4\theta_{\rm p}^3}(\theta_{\rm p}^2 - \theta^2), & |\theta| \le \theta_{\rm p}, \\ 0, & |\theta| > \theta_{\rm p}. \end{cases}$$
(23)

Indeed, component (23) clearly manifests itself for all metals even at room temperature.

Figure 6 depicts the ADAP spectra for a number of polycrystalline metals, obtained in our experiments. By subtracting the parabolic component from the total spectrum, we arrive at the following dependence for the remainder $f_{\rm g}(\theta)$ which is well described by a Gaussian curve:

$$f_{\rm g}(\theta) = \frac{I_{\rm g}}{\sqrt{2\pi} \,\theta_{\rm g}} \exp\left(-\frac{\theta^2}{2\theta_{\rm g}^2}\right). \tag{24}$$

The intensities I_p and I_g of the parabolic and Gaussian components are equal numerically to the relative area of each component in the ADAP spectrum, with $I_p + I_g = 1$; here, θ_g is the variance of the Gaussian curve, and θ_p is the angle at which the parabolic curve intersects the horizontal θ -axis.

Furthermore, using the parameter θ_p (the angle of cutoff of the θ -axis by the parabola; see Fig. 6), which can be found from the experiment, we can estimate the Fermi momentum p_F and the Fermi energy ε_F of the metal under investigation:

$$p_{\rm F} = \theta_{\rm p} mc \,, \tag{25}$$

$$\varepsilon_{\rm F} = \theta_{\rm p}^2 \, \frac{mc^2}{2} \,. \tag{26}$$

Within the model of a free electron gas, the parameter θ_p determines the number Z_c of free electrons (the number of conduction electrons) per metal atom and the concentration $n_p(\theta)$ of such electrons:

$$Z_{\rm c} = \frac{8\pi}{3} \left(\frac{mc^2}{h}\right)^3 \frac{A}{\rho N_{\rm A}} \theta_{\rm p}^3 \,, \tag{27}$$

$$n_{\rm p}(\theta) = Z_{\rm c} n_{\rm A} = \frac{8\pi}{3} \left(\frac{mc^2}{h}\right)^3 \theta_{\rm p}^3, \qquad (28)$$

and the energy for the ion core electrons (i.e. the electrons for which the ADAP spectra have a Gaussian distribution):

$$\varepsilon_{\rm g} = \frac{3}{2} \frac{mc^2}{2} \theta_{\rm g}^2 \,, \tag{29}$$

where N_A is the Avogadro constant, *h* is the Planck constant, *A* is the atomic mass of the metal, and ρ is the metal's density.

It is common practice to compare the experimental values of the parameters Z_c , ε_F , and n_p with those for a perfect metal. We call a metal perfect if all its valence electrons are in the conduction band. In this case the number of conduction electrons Z_c per metal atom is determined by the number of the group in the Periodic Table. Then within the model of a free electron gas, the Fermi energy ε_F and the conduction electron concentration n_p are its constants:

$$\varepsilon_{\rm F} = \frac{h^2}{8m} \left(\frac{3}{\pi} n_{\rm A} Z_{\rm c}\right)^{2/3},\tag{30}$$

$$n_{\rm p} = Z_{\rm c} n_{\rm A} = \frac{N_{\rm A} \rho}{A} Z_{\rm c} \,, \tag{31}$$

where n_A is the number of atoms per unit volume of the metal [28].

3.2 ADAP spectra of the metals under investigation

The ADAP spectra measured in magnesium, aluminium, copper, and indium and the results of their resolution into the parabolic and Gaussian components (the dashed curves) are depicted in Fig. 6. The solid curve in each case is the sum of these two components and provides a good description of the experiment. The ADAP resolution parameters of the metals in question and those of aluminium and copper [37] are listed in Table 1 (the values of the intensity I_g are not given, since $I_g = 1 - I_p$).

Table 1 shows that the magnitudes of the intensities of the Gaussian (I_g) and parabolic (I_p) components are comparable, i.e. it is highly probable that the positrons interact both with valence electrons belonging to ion cores and with

Table 1. Basic characteristics of metals and the positron annihilation parameters.

Characteristic	Mg	Al	Cu	Zn	In	Sn	Pb	Bi	
Zc	2.00	3.00	1.00	2.00	3.00	4.00	4.00	5.00	
$n_{\rm A}, 10^{22} {\rm cm}^{-3}$	4.30	6.00	8.40	6.50	3.80	3.60	3.30	2.80	
$\lambda_{\rm exp},{\rm ns}^{-1}$	4.44	6.13	8.80	6.76	5.08	4.98	5.15	4.27	
$\theta_{\rm p}^{\rm expt}$, mrad	5.41	6.83	5.50	5.85	5.77	6.15	5.62	6.01	
			5.57						
θ_{g}^{expt} , mrad	4.63	4.46	4.84	4.85	4.43	5.02	4.63	4.72	
5		6.40 [37]	6.31 [37]						
$\theta_{g}^{\text{theor}}, \text{mrad} (32)$	3.50	4.30	2.80	3.50	4.00	4.70	3.80	4.30	
I _p	0.72	0.69	0.38	0.45	0.56	0.64	0.41	0.55	
$n_{\rm p}(\tau), 10^{22} {\rm ~cm^{-3}}$ (38)	43.10	57.20	45.90	41.10	38.50	43.40	28.60	31.50	
$n_{\rm p}(\theta), 10^{22} {\rm cm}^{-3}$ (33)	9.40	18.80	10.30	11.90	11.40	13.80	10.50	12.90	
$n_{\rm p}, 10^{22} {\rm cm}^{-3}$ (31)	8.60	18.10	8.45	13.10	11.50	14.50	13.20	14.10	
φ	2.15	2.85	2.30	2.05	1.93	2.17	1.40	1.50	
f	4.60	3.10	4.50	3.50	3.40	3.20	2.70	2.50	
$\varepsilon_{\rm F}^{\rm expt}$, eV (26)	7.50	11.60	8.00	8.70	8.50	9.60	8.00	9.20	
ε_{g}^{expt} , eV (29)	8.20	7.60	8.90	9.00	7.50	9.60	8.20	8.40	
c .		15.60	15.2						
$\varepsilon_{\rm F},{\rm eV}$ (30)	7.10	11.60	7.00	9.40	8.60	10.00	9.40	9.90	
<i>Note</i> : the errors in determining θ_p , θ_g and I_p , I_g do not exceed 0.5 and 5%, respectively.									

conduction-band electrons. The high value of I_p is, probably, caused by the fact that a positron in a metal is surrounded by a peculiar electron 'coat' (due to the Coulomb attraction of conduction electrons by a positron), which leads to screening of the positron. According to Ferrante [29], even the three-particle leptonic system predicted by Wheeler [30] (with the composition $e^-e^+e^-$), the positronium ion, may form in metals.

Generally, it can be assumed that in a metal a negatively charged Wheeler type complex $Ps^{-\eta}$ forms, whose effective charge η (*-e*) depends on the nature of the metal. Here η (*-e*) is the effective ion charge in fractions of the electron charge. A complex of this kind may interact rather strongly with the valence electrons of the ion cores, a process accompanied by the formation of relaxing metastable quasi-atomic systems $Ps^{-\eta}$ and incorporating the valence electrons near an ion core and the ion core proper, by analogy with the formation of positron – anion quasi-atomic systems in ionic crystals, which ensures the high values of the Gaussian component I_g (see Table 1).

Near the ion cores the electron wave functions of the complex $Ps^{-\eta}$ are transformed into the atomic electron wave functions of the outer valence electrons, while the positron wave function of the loosely bound positron (if we exclude the possibility of the positron positioning itself on the nucleus of the metal ion) can be chosen in the form of the wave function of a loosely bound optical positron [13].

In the Slater orbital approximation for the electron wave functions [13] and a positron wave function of this type, the half-width Γ_g at a half-height of the ADAP curves (see Fig. 6) can be calculated using the following expression [13]:

$$\Gamma_{\rm g} = \frac{1}{2} C_{n(s,p,d)} \beta_{n(s,p,d)} , \qquad (32)$$

where the $C_{n(s, p, d)}$ are the conversion factors

$$\begin{split} C_{2(s,p)} &= 3.52 , \qquad C_{3(s,p)} = 2.86 , \qquad C_{4(s,p)} = 2.52 \\ C_{5(s,p)} &= 2.48 , \qquad C_{6(s,p)} \approx 2 , \end{split}$$

and the $\beta_{n(s,p,d)}$ are the Slater parameters of the electron n(s, p, d)-orbitals of the atoms. The width θ_g (which corresponds to the variance of the Gaussian curve) is given by the formula

$$\theta_{\rm g} = \frac{\Gamma_{\rm g}}{\sqrt{2\ln 2}} = 0.85\Gamma_{\rm g} \,.$$

Table 1 lists the values of $\theta_g(n(s, p))$ calculated using formula (32) and taken from the experiment for the metals in question. The agreement between the calculated and experimental values of θ_g is quite satisfactory, which points to the meaningfulness of the chosen mechanism of positron annihilation in metals.

3.3 Determining the electron concentration n_p in the metal conduction band

As indicated above, the conduction electron concentration n_p is the basic characteristic of the metallic state. Various methods are used to determine n_p : electrical, optical, galvanomagnetic (for instance, the Hall effect), and measuring the electronic part of the metal's heat capacity and the surface impedance at radio frequencies. Knowing the temperature dependences of n_p , one can determine the values of p_F and ε_F as well as the concentration of the free electron gas ($n_p = N/V$, where N is total number of electrons, and V is the volume).

The positron annihilation method is the one in which the electron concentration n_p in metals is measured directly. Bearing in mind that all the positrons in metals annihilate in free collisions, we can write down the expression for determining $n_p(\theta)$ from the ADAP spectra (see Table 1 and Fig. 6):

$$n_{\rm p}(\theta) = 5.942 \times 10^{20} \, \theta_{\rm p}^{3} \, \left[{\rm cm}^{-3} \right].$$
 (33)

The electron concentration in the conduction band can be found by measuring the rate at which positrons annihilate in the metal. Indeed, in this case positronium is not formed, and the positron annihilation rate is determined by the concentration of the electrons with which the positrons collide:

$$\lambda_{\rm d} = \sigma_{\rm d} v n_{\rm e} \,. \tag{34}$$

Here, $\sigma_d = \pi r_0^2 / \beta = (\pi r_0^2 / v)c$ is the Dirac cross section of two-photon annihilation, v is the positron velocity, and r_0 is the classical electron radius.

If we assume that n_e is the sum of the concentrations of the conduction electrons (n_p) and the ion core electrons (n_g) , we can write expression (34) as follows

$$\lambda_{\rm d} = \lambda_{\rm p} + \lambda_{\rm g} \,, \tag{35}$$

where λ_p and λ_g are the rates of positron annihilations on the conduction and core electrons, respectively. Then the annihilation probabilities in each of the above-mentioned channels are

$$I_{\rm p} = \frac{\lambda_{\rm p}}{\lambda_{\rm p} + \lambda_{\rm g}} \,, \tag{36}$$

$$I_{\rm g} = \frac{\lambda_{\rm g}}{\lambda_{\rm p} + \lambda_{\rm g}} \,. \tag{37}$$

Equations (33), (36), and (37) make it possible to establish the relationship between the measured rate of positron annihilation in the metal, $\lambda_{\text{meas}} = \lambda_{\text{d}}$, the concentrations n_{p} and n_{g} of the conduction electrons and the core electrons, and the corresponding annihilation probabilities I_{p} and I_{g} found in angular experiments:

$$n_{\rm p}(\tau) = \frac{\lambda_{\rm meas} I_{\rm p}}{\pi r_0^2 c} = 1.354 \times 10^{23} \lambda_{\rm meas} I_{\rm p} \, \left[{\rm cm}^{-3} \right], \tag{38}$$

$$n_{\rm g}(\tau) = \frac{\lambda_{\rm meas} I_{\rm g}}{\pi r_0^2 c} = 1.354 \times 10^{23} \lambda_{\rm meas} I_{\rm g} \, \left[{\rm cm}^{-3} \right]. \tag{39}$$

Here, $\lambda_{\text{meas}} = 1/\tau_{\text{meas}}$ is the total positron annihilation rate, τ_{meas} is the measured lifetime, and I_p and I_g are the relative areas under the parabola and Gaussian curves in the ADAP spectra (see Fig. 6).

Note that in expressions (33), (38), and (39) the parameters θ_p and θ_g are measured in mrad, and λ_{meas} in ns⁻¹. Thus, equations (33) and (38) as well as (31) allow one to estimate the conduction electron concentration n_p ; such estimates, however, make use of the results of measuring the positron annihilation parameters.

Table 1 lists the values of the conduction electron concentrations determined from ADAP spectra and formula (33) as well as from measurements of the positron annihilation rates and formula (38) and the appropriate concentrations (31) for perfect metals: $n_p(\theta)$, $n_p(\tau)$, and n_p . Comparison of these concentrations points to the fact that the values of $n_p(\theta)$ and n_p are close but differ substantially from those of $n_p(\tau)$. In view of this we believe that the factor

$$f = \frac{n_{\rm p}(\tau)}{n_{\rm p}(\theta)} = \frac{Z_{\rm c}(\tau)}{Z_{\rm c}(\theta_{\rm p})} \tag{40}$$

characterizes the rise in the electron number density in the region where the positron exists as compared to the electron number density of the free electron gas. As Table 1 shows, the values of the parameter f relating to the metals investigated lie in the interval from 2.5 to 4.6.

Thus, the interaction of positrons with the electron gas leads to a local increase in electron concentration and, as a consequence, to an increase in the positron annihilation rate. At the same time, this increase in the electron number density, apparently, has no appreciable effect on the values of the momenta and energies (and hence on θ_p) of the electrons that belong to a Ps⁻ⁿ complex, since the ADAP spectrum describing the annihilation of positrons from this complex is well approximated by a parabola, and the value of the Fermi energy determined from experiments is in good agreement with the theoretical value. Hence we can assume that the electron concentrations determined through formula (33) that are combined solely with the ADAP data most truly reflect the values of the concentration n_p of the free electron gas. This is indeed the case (see Table 1).

The effective charge η of a Wheeler complex $Ps^{-\eta}$ can be estimated by comparing the concentration $n_p(\tau)$ of electrons in the region containing a positron with the concentration

$$n(\text{Ps}) = \frac{3}{4\pi} r_{\text{Ps}}^{-3} = 2 \times 10^{23} \text{ cm}^{-3}$$
(41)

in a free positronium atom $(r_{\rm Ps} = 1.06 \times 10^{-8} \text{ cm} \text{ is the} \text{ positronium Bohr radius})$. The values of the ratio of these two concentrations, $\varphi = n_{\rm p}(\tau)/n(\text{Ps})$, are listed in Table 1. It occurred that the value of the parameter φ averaged over all the metals in question was 2.04. Obviously, the effective charge η is connected to the parameter φ through the formal relationship $\eta = \varphi - 1$, i.e. $\eta \approx 1$, as it should be in a Wheeler complex.

Thus, the positron annihilation mechanism in metals that involves the formation of Wheeler complexes has apparently been confirmed by experimental studies.

In conclusion of this section we notice that the ADAP method makes it possible to determine the parameters $(n_p, \varepsilon_F,$ and $Z_c)$ of the electron gas in metals, which are in fairly good agreement with similar parameters found in the theory of a free Fermi gas. At the same time, combining the methods of angular and time distributions of annihilation photons allows one to obtain information about the increase in electron number density at the point occupied by a positron.

4. The positron annihilation method in semiconductor and ionic crystal studies. The effective charges and masses of positron polarons

The application of the positron annihilation method in studies of the electronic and defect structures of semiconductors and ionic crystals has become possible due to the theoretical and experimental investigations into the process of positron annihilation in these materials, investigations that have allowed researchers to establish the nature of positron states and their subsequent annihilation decay.

Indeed, in the course of the theoretical analysis of positron-assisted processes and states in semiconductors and ionic crystals done in Ref. [11] it was established that there is a relationship between the main characteristics of annihilation spectra (the shape and half-width of the ADAP curves, the time annihilation spectra, and the relative three-photon coincidence counting rate) and the rate constants of formation and decay of these states, which made it possible to extract useful information about the properties of the samples under investigation (both a single-crystal and polycrystalline).

In the course of these studies it was established that the most important problems that have been solved so far and may be solved in the future with the positron annihilation method, which is a nondestructive testing technique, are as follows: the study of the electron number density anisotropy in single crystals of semiconductors and ionic crystals for different crystallographic orientations; determining the charge states of atoms in semiconductor compounds and ionic crystals; the study of semimetals and metal – semiconductor phase transitions; determining the mobility of positrons in semiconductors; the study of the nature and density of dislocations in semiconductors; the study of amorphous semiconductors and glasses as well as ion systems with a welldeveloped surface; the exposure of radiation-induced and other defects in semiconductors and ionic crystals; the study of semiconductors and ionic crystals irradiated with light or X-rays or charged particles or neutrons, and the analysis of the state of the surface and near-surface layers of semiconductors and ionic crystals.

In addition to the above applications, other ways of using the position annihilation method are possible. Most important here is the method of positron emission tomography. Below we discuss in detail the possible probing of the nature of the chemical bond in ionic type semiconductor compounds and ionic crystals as well as their defect structure using the positron annihilation technique.

In ionic type media, the positron annihilation process largely depends on the nature of the chemical bond characterized by the effective charges of the anions. For this reason, the PAS method is being successfully used to determine the effective charges η (-e) of anions in ionic type substances.

The results of measurements of Γ both in single crystals and in polycrystals and aqueous solutions of halides (e.g. NaF, NaCl, NaBr or NaI) can be found in Refs [34, 35]. The researchers used the experimental data to estimate the effective charges of the anions F⁻, Cl⁻, Br⁻, and I⁻ in the media investigated. In the series single crystal-polycrystalaqueous solution the values of Γ and η proved to be close. The fact that the values of Γ were close made it possible to draw the conclusion that the positron annihilation mechanism is the same for these media, i.e. positron annihilation involves the formation of bound states of a positron and anions $X^{-\eta}$ of the halogen (the complex $X^{-\eta}e^+ \leftrightarrow X^{-\eta+1}Ps$). So far the PAS method has been employed to find the effective charges η of anions in more than 100 ionic type compounds, and the results are in satisfactory agreement with the values from the scientific literature found by other methods.

To describe the motion of a positron in positron-anion quasi-atomic systems, a modified model of the optical positron, based on the Landau-Lifshitz potential, was proposed in Ref. [11]. The positron wave function for this case has the form

$$\Psi_{+} = \frac{1}{\sqrt{4\pi}} Ar \exp(-\alpha r) = \frac{1}{\sqrt{4\pi}} \left(\frac{4\alpha^{5}}{3}\right)^{1/2} r \exp(-\alpha r), \quad (42)$$

where α is the model parameter. The electron wave functions of positron–anion quasi-atomic systems were chosen in the form of Slater exponentials [11, 34].

The lifetimes calculated with the positron wave functions of the type (42) and the Slater type electron wave function as related to two-photon annihilation on outer *ns*- and *np*-electrons are depicted in Fig. 8, while the calculated values of the parameters of the ADAP curves (total width of the curves at half-height) are illustrated in Fig. 9.

The theoretical formulas giving the effective charges η for a number of quasi-atomic positron – negative ion systems are



Figure 8. Dependence of the lifetimes $\tau_{ns, np}$ on the parameter α .



Figure 9. Dependence of the half- widths $\Gamma_{ns, np}$ of the ADAP curves on the parameter α .

listed in Table 2, while in Table 3 we compile the effective charges of the anions in several ionic type substances, calculated using these formulas. For the sake of comparison we also list in the tables the effective charges η of the anions in

 Table 2. Basic parameters of quasi-atomic positron – negative ion systems and the theoretical formulas used in calculating the effective ion charges.

System	п	<i>n</i> *	$\beta_{ns, p}$	Formula for calculating η
e^+B^-	2	2	1.125	$\eta(\mathbf{B}) = 0.189\Gamma - 0.75$
e^+C^-	2	2	1.45	$\eta(C) = 0.189\Gamma - 0.967$
e^+N^-	2	2	1.775	$\eta(N) = 0.189\Gamma - 0.183$
e^+O^{2-}	2	2	1.925	$\eta(O) = 0.189\Gamma - 1.283$
e^+F^-	2	2	2.425	$\eta(F) = 0.189\Gamma - 1.617$
e+Si-	3	3	1.267	$\eta({ m Si}) = 0.233\Gamma - 0.845$
e^+P^-	3	3	1.483	$\eta(\mathbf{P}) = 0.233\Gamma - 0.989$
e^+S^{2-}	3	3	1.583	$\eta(S) = 0.233\Gamma - 1.056$
e+Cl-	3	3	1.917	$\eta(\text{Cl}) = 0.233\Gamma - 1.278$
e+Ge-	4	3.7	1.027	$\eta(\text{Ge}) = 0.257\Gamma - 0.685$
e+As-	4	3.7	1.203	$\eta(As) = 0.257\Gamma - 0.802$
e^+Se^{2-}	4	3.7	1.284	$\eta(\text{Se}) = 0.257\Gamma - 0.856$
e^+Br^-	4	3.7	1.554	$\eta({ m Br}) = 0.257 \Gamma - 1.036$
e^+Sn^-	5	4	0.95	$\eta({ m Sn}) = 0.269 \Gamma - 0.633$
e^+Sb^-	5	4	1.113	$\eta({\rm Sb}) = 0.269\Gamma - 0.742$
$e^+ T e^{2-}$	5	4	1.188	$\eta(\text{Te}) = 0.269\Gamma - 0.792$
e^+I^-	5	4	1.438	$\eta(I) = 0.269\Gamma - 0.959$

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Anion	Substance	Half-width of	Effective anion charge η , $-e$			
		ADAP curve Γ , mrad	Positron method	Other methods [25]		
N^{-}	AlN	11.1	0.915	1.20 - 1.32		
O ²⁻	MgO CaO SrO BaO	12.8 14.4 14.2 12.0	1.136 1.439 1.401 0.995	$\begin{array}{rrr} 1.0 & -1.76 \\ 1.18 - 1.62 \\ 1.16 - 1.60 \\ 0.91 - 1.44 \end{array}$		
F ⁻	LiF NaF	12.0 10.5	0.65 0.368	$\begin{array}{c} 0.67\!-\!0.87\\ 0.58\!-\!0.94\end{array}$		
P -	GaP InP	10.2 9.4	1.388 1.201	0.45 0.49		
S ²⁻	Na ₂ S FeS CdS	8.3 10.3 10.4	0.879 1.344 1.367	$\begin{array}{c} 0.96 \\ 0.71 - 0.96 \\ 0.73 - 0.90 \end{array}$		
Cl-	LiCl NaCl KCl RbCl CsCl	9.2 8.6 8.3 8,6 8.9	0.866 0.726 0.656 0.726 0.796	0.67 - 0.72 0.64 - 0.92 0.79 - 0.83 0.83 - 0.87 0.84 - 0.87		
As ⁻	GaAs InAs	9.8 9.0	1.521 1.331	0.46 0.49		
Se ²⁻	ZnSe CdSe	9.9 9.9	1.688 1.688	$0.70 \\ 0.56 - 0.68$		
Br -	NaBr	7.4	0.866	$0.60\!-\!0.86$		
Sb ⁻	InSb	8.4	1.518	0.49		
Te ²⁻	CdTe	8.8	1.575	0.70		
Ι-	NaI KI	6.8 7.1	0.870 0.951	$\begin{array}{c} 0.54\!-\!0.71 \\ 0.69\!-\!0.90 \end{array}$		

the same substances, but calculated using other (nonpositron) methods [25].

The data given in Table 3 imply that the values of the positron effective charges η are close to the similar values determined by nonpositron methods. The observed discrepancies in the values of η are most probably due to the contribution of the covalent components of the chemical bond in some semiconductor compounds.

Ramasamy and Nagaragian [39] arrived at interesting results concerning the effective charges η and effective masses m_p of polarons within the scope of the optical model [11] in single crystals of metal halides (KCl and KBr) and ammonium halides (NH₄Cl, NH₄Br, and NH₄I). Their data on η and m_p in the samples of NaCl, KCl, and KBr for different crystallographic orientations of the single crystals and in the samples of NH₄Cl, NH₄Br, and NH₄I are shown in Table 4. Obviously, the values of η and m_p depend both on the nature of the crystals and on the crystallographic orientations, which agrees with the data of nonpositron methods [25].

Thus, the positron annihilation method is a new independent method capable of finding the effective charges of anions in ionic type media. The method has been theoretically substantiated within the above-mentioned modified optical model of a positron.

5. Using the positron annihilation method to study the crystal structure defects

We believe that the most important problems that can be solved by the positron annihilation method are investigations into the mechanisms and dynamics of formation, transformation, and annihilation of defects in semiconductor materials at different stages of their fabrication.

As noted earlier, annihilation experiments involve using radioactive β^+ -isotopes (²²Na, ⁶⁴Cu, etc.) which emit positrons in the 0–700-keV energy range, with the result that the mean ranges of the positrons in different materials do not usually exceed 150 µm. This means that the majority of the positrons annihilate in the near-surface layers of the materials under investigation [11].

Let us assume, for the sake of simplicity, that the main types of positron states are thermalized positrons in the bulk of the substance and positrons trapped by point and extensive defects, with the latter carrying mostly negative charges (we call such defects positron-sensitive).

An elementary examination of the kinetics of the annihilation process results in formulas for determining the mean values of the concentrations of positron-sensitive defects and the sizes of these defects from the main characteristics of the annihilation spectra:

$$I_{\rm N} = \frac{k_{\rm d}}{\lambda_1 + k_{\rm d}}, \quad 1 - I_{\rm N} = \frac{\lambda_1}{\lambda_1 + k_{\rm d}}, \quad \lambda_1 = \frac{1}{\tau_1}, \quad (43)$$

where I_N is the intensity of the narrow component in ADAP curves, k_d is the rate constant of positron trapping by defects, and τ_1 is the positron lifetime in the crystal's bulk (the reciprocal of the annihilation rate λ_1).

Table 4. Anion effective charges η and effective masses m_p of positron polarons in ionic media.

	6 1	PII			
Substance	Effective penetrability	Orientation	Γ , mrad	$\eta, -e$	$m_{\mathrm{p}}, m_{\mathrm{p}}^{*}/m$
NaCl	0.257	100	8.78 ± 0.07	0.766 ± 0.016	2.979 ± 0.062
		110	8.92 ± 0.07	0.798 ± 0.014	3.107 ± 0.066
		111	9.06 ± 0.09	0.831 ± 0.014	3.234 ± 0.054
		Polycrystal	9.06 ± 0.09	0.831 ± 0.014	3.234 ± 0.034
KCl	0.251	100	8.08 ± 0.05	0.603 ± 0.011	3.401 ± 0.44
		110	8.44 ± 0.07	0.687 ± 0.016	2.735 ± 0.064
		111	8.92 ± 0.08	0.798 ± 0.017	3.181 ± 0.068
		120	8.65 ± 0.07	0.735 ± 0.017	2.928 ± 0.068
		Polycrystal	8.50 ± 0.06	0.701 ± 0.013	2.791 ± 0.052
KBr	0.217	100	8.09 ± 0.08	0.742 ± 0.021	3.421 ± 0.084
NH4Cl			9.48	0.939	_
NH ₄ Br			8.92	0.998	_
NH ₄ I			7.25	0.758	_

From formulas (43) we get

$$k_{\rm d} = \frac{I_{\rm N}}{1 - I_{\rm N}} \,\lambda_1 \,. \tag{44}$$

In turn, if we consider only a single center of positron trapping, we can write down the following expression for the rate constant of positron trapping by defects:

$$k_{\rm d} = \sigma_+ v \overline{N}_{\rm d} = 4\pi D_+ \overline{R}_{\rm d} \overline{N}_{\rm d} \,. \tag{45}$$

Here, σ_+ is the positron trapping cross section, v is the velocity of thermalized positrons, \overline{N}_d and \overline{R}_d are the mean concentrations and defect radii within the region of the crystal wherethrough the positrons penetrate, and D_+ is the positron diffusion coefficient. Thus, using equations (43)–(45), we can determine the values of k_d , \overline{N}_d , and \overline{R}_d , provided that we know the values of such parameters as λ_1 , σ_+ , v, and D_+ .

The results of the studies on the positron annihilation in single crystals of silicon [12], semiconductor III–V and II–VI compounds, chalcogenide semiconductors, alkali-halide crystals and oxides and also in epitaxial structures of different nature have shown that the positron annihilation method is highly sensitive to the electronic and defect structures of these materials, to the presence of dislocations, and to the state of the near-surface layers. The detected effect of 'attraction' of the positron to deep acceptor atoms of transition elements in gallium arsenide and gallium phosphide [11] has made it possible to use the positron annihilation method in studies of the nature, composition, and charge states of these deep acceptors.

By isolating the narrow component I_N from the ADAP curves and using formulas (44) and (45) we can estimate the sensitivity of the PAS method to the concentration of positron-sensitive defects ($N_d \ge 10^{15}$ cm⁻³). For instance, the average concentration of positron-sensitive defects in autoepitaxial structures of *n*- and *p*-type silicon proved to be of order 10^{16} cm⁻³, and the size of such defects was about 1 nm.

6. Positron tomography as a nondestructive method of materials quality control

6.1 Positron microtomography of layer structures

As noted earlier, layer (sandwich type) structures play a special role in microelectronics. The PAS method turned out to be highly informative in studies of the properties of such structures. Beams of low-energy monochromatic positrons proved to be most effective in such studies. This is due to the short range of positrons (which have an energy of several kiloelectron-volts) in matter and to the simple way in which the length of the range can be controlled by varying the positron energy. Research that will lead to the building of a facility for producing such beams is being conducted at JINR (Dubna).

Until fairly recently the application of traditional methods (ADAP and TDAP) in studying the thin near-surface layers of solids was hindered by the complexity of interpreting the experimental results. Intensive research in this field became possible after what is known as the additive model of positron annihilation in layer structures came into being [36–38] and was used to analyze ADAP. According to this model, the ADAP of a layer structure, $f(\theta)$, can be defined in the form of a sum of the ADAPs of separate layers, $f_i(\theta)$:

$$f(\theta) = \sum_{i=1}^{m} \beta_i f_i(\theta) , \qquad (46)$$

where β_i is the probability of positron annihilation in the *i*th layer, and *m* is the number of layers. Here the following normalization condition must hold:

$$\int f_i(\theta) \, \mathrm{d}\theta = 1 \,, \qquad \sum_{i=1}^m \beta_i = 1 \,.$$

Experimental verification of the model was carried out using a double layer medium consisting of copper films (6and 2-µm thick) on a single crystal of silicon acting as substrate. In Ref. [38] it was shown that the use of the additive model makes it possible to extract, with a good accuracy, the individual spectra characterizing positron annihilation in copper and silicon from the total ADAP spectra of layer structures, i.e. to get information about the properties of each layer. For copper, the researchers found the following values of the mass absorption factor μ of 0.54-MeV positrons, the absorption length *l*, and the diffusion length $L: \mu = 42.4 \pm 1.3 \text{ cm}^2 \text{ g}^{-1}$, $l = 26.5 \pm 0.8 \,\mu\text{m}$, and $L = 0.084 \pm 0.017 \,\mu\text{m}$.

A group of researchers (see Ref. [12]) studied the problem of positron microtomography of layer structures and the ways in which it differs from positron tomography used in medical research. They found that the ADAP measurement technique can be used to determine the structure and properties of the material from which the layers were fabricated and the thickness of the layers with a resolution of 0.1 μ m, and discussed the possibility of building a three-dimensional positron microtomograph for uses in microelectronics.

Thus, the positron annihilation method is a promising nondestructive method of quality control of technologically important materials employed in various fields of science and technology. Further improvements will make it possible to identify possible correlations, for instance, between the main characteristics of annihilation spectra, electrophysical parameters, and the details of growing single crystals and epitaxial structures.

The positron annihilation method may play a key role in studies of the coherent behavior of complex systems. Positrons can be used to probe atoms, molecules, and imperfections in the atmosphere of defects in solids, when the defect concentrations undergo various nonequilibrium phase transitions in the process of exchanging the fluxes of energy, matter, and information with the surrounding medium.

6.2 Determining the vacancy formation enthalpy in technologically vital materials

In Ref. [11], the idea of a new method — positron tomography — of studying the defects of technologically important materials was put forward. Positrons born in the process of β^+ -decay slow down in the bulk of the material to thermal velocities in the course of roughly 10^{-12} s. Such thermalized positrons may, first, annihilate in a two-quantum manner on the valence electrons of the crystal (material) and, second, be trapped by negatively charged point and extensive defects (on which the quality of the material depends) and then annihilate from the bound states with the emission of two annihilation photons in each annihilation event. The researchers analyzed the possibilities of using positron tomography to study the main parameters (vacancy formation enthalpies H_{IV}) of the point defects in the material that serve as positron traps [11].

As a result, the values of vacancy formation enthalpies for different materials were established. In the simplest model, where $F_{\rm f} = \text{const}$, it was found that $H_{\rm IV} = 0.51$ eV as the temperature grew from 320 to 593 K; for lead, where $F_{\rm f} = F_{\rm f}(T)$, with $F_{\rm f}$ the Doppler broadening of the annihilation spectrum, $H_{\rm IV} = 0.60$ eV in the temperature interval above 150 K. The influence of the formation of divacancies and positron metastable bound states on the monovacancy formation enthalpy has been accounted for by many researchers (for instance, see Ref. [11]). They found that in lead $H_{\rm IV} = 0.56$ eV. To our knowledge, so far no rigorous calculations of $H_{\rm IV}$ for semiconductors with allowance made for the formation of metastable bound states have ever been conducted.

As an example of the areas in which the positron tomography method could be employed we would like to mention the investigation of defects of structural materials used in industry (metals, alloys, polymers, etc.), materials used in nuclear and thermonuclear engineering, space technology, electronic engineering, and so forth.

An advantage of the positron tomography is the possibility of monitoring the quality of the most important structural units of modern technology (including electronic engineering) for a long time, since the half-life of, say, ²²Na isotope is 2.60 a, and annihilation tomograms can be taken in the course of operation of the units of various technical devices and during the repair period for such devices.

7. Applying positron spectroscopy in liquid medium studies

7.1 Positronium in the radiation chemistry of liquids

A positron in a liquid medium acts as an acceptor for a quasifree ('dry') electron, and the product of acceptance is a positronium atom. Just as a solvated electron, positronium serves as an electron donor with respect to many substances dissolved in liquids.

These features of the positron and positronium behavior make it possible to study the reactions of 'dry' and solvated electrons — two important problems in radiation chemistry.

General nature of the mechanisms of forming radiolytic hydrogen and positronium in water. When charged particles (including positrons) penetrate into condensed media, a sequence of microregions with a high concentration of the primary radiolysis products emerges along the tracks left by the particles. In water these are primarily cation radicals ('holes') H₂O⁺ and 'nonionizing' electrons with an initial energy lower than 8 eV. Such products are highly unstable and in the course of a fraction of a picosecond transform into much more long-lived OH radicals, hydroxonium ions, and solvated (hydrated) electrons $e_s^-(e_{aq}^-)$ localized in 'bubbles' [69]:

$$H_2O^+ + H_2O \to H_3O^+ + OH$$
, (47)

$$e^- \to e_{aq}$$
 (48)

It is commonly supposed that it takes about 10 ns for the recombination reaction of these particles to form the final

radiolysis products
$$H_2$$
 and H_2O_2 [70]:

$$\mathbf{e}_{\mathrm{aq}} + \mathbf{e}_{\mathrm{aq}} \to \mathbf{H}_2 + 2\mathbf{OH} \,, \tag{49}$$

$$OH + OH \to H_2O_2 \,. \tag{50}$$

Experimental examination of the intratrack processes is extremely complex. Until recently all data on such processes were gathered only by using not numerous nano- and picosecond pulse radiolysis facilities. But roughly a quarter of a century ago, Mogensen [71] and Byakov et al. [72, 73] proposed using the positron spectroscopy to explain the mechanism of radiolytic hydrogen formation.

The approach developed at the Institute of Theoretical and Experimental Physics (Moscow) was based on a new mechanism of positronium formation in a condensed medium. The basic idea here is that positronium forms within the final section of a positron track due to the recombination of the positron with one of the thermalized electrons of the positron track:

$$e^+ + e^- \to \mathrm{Ps}\,.\tag{51}$$

This reaction competes against ion – electron recombination (the latter leads to hydrogen formation) and against reactions of electrons and holes with the dissolved substance (S):

$$H_2O^+ + e^- \to H_2, H, H_2O,$$
 (52)

$$e^- + S \to S^-, \tag{53}$$

$$H_2O^+ + S \rightarrow reaction \ products$$
. (54)

From the scheme reported we see that the reactions of radiolytic hydrogen and positronium formation are very similar. Indeed, the trapping of electrons (53) by the dissolved substance and the electron solvation (48) must inhibit the reactions (52) and (51) of H₂ and Ps formation. But there are also differences. Namely, the addition of substances that act as hole acceptors (glycine or acetone) must diminish the H₂ yield but increase the Ps yield. These qualitative corollaries have been observed in experiments.

Usually the data on the mechanism of the proceeding reactions are extracted from the dependence of the yields of the radiolytic products on the concentration of the dissolved substances. In the case of employing electron acceptors, the measure of their reactivity with respect to inhibition of the hydrogen yield $G_{\rm H_2}$ (the number of formed H₂ molecules per 100 eV of absorbed energy) and the positronium yield $P_{\rm Ps}$ (the fraction of positrons forming Ps) is the concentration of acceptors at which the observed yields reduce by a factor of 2. This quantity is known as the inhibition constant.

In Fig. 10 we compare the inhibition constants of radiolytic hydrogen (K_{H_2}) and positronium (K_{Ps}) . Clearly, with rare exceptions which have a natural explanation, these constants are almost equal [74, 75], which reflects the fact that the mechanisms of Ps and H₂ formation are roughly the same.

A detailed analysis of these and other experiments has shown that the formation of positronium (as well as of radiolytic hydrogen) occurs through recombination in which a quasi-free electron takes part prior to its hydration $H_2O^+ + e^- \rightarrow H_2 + 2OH$ at each spur of the track of the ionizing particle, and $e^+ + e^- \rightarrow Ps$ in the final section of the positron track [76].

At present there exists a large body of experimental data on the effect of dissolved substances with different reactivities with respect to electrons (quasi-free and solvated) and holes



Figure 10. Comparison of the inhibition constants of hydrogen (K_{H_2}) and positronium (K_{Ps}) by substances dissolved in water. The inhibition constants of Tl⁺, Zn²⁺, and H⁺ by lanthanides, SO₄²⁻ and Cl⁻ are located inside the square.

on the yields of the main radiolysis products and positronium in water.

Experiments have revealed the presence of different types of regularities linking the yields of the main products of radiolysis of water to the concentration of the dissolved substances. For instance, the solvated electron yield always decreases exponentially with increasing the concentration C_S of the dissolved substance, while the H₂ yield may behave in two ways as $C_S \rightarrow \infty$: either $G_{H_2} \rightarrow 0$ or $G_{H_2} \rightarrow \text{const} > 0$, i.e. total or partial inhibition is observed.

Five concentration dependences $P_{Ps} = f(C_S)$ have been discovered so far, with two similar to the dependences for H₂, and three attributable only to Ps (the Ps yield may increase, decrease, or pass through a minimum with increasing C_S) [77]. Comparison of the effect of the dissolved substances on the yields of positronium and radiolytic products makes it possible to extract information about the reactivity of these substances and the mechanisms of the reactions in which they participate.

A quantitative model for the formation of positronium and radiolytic hydrogen in water. The goal of the theory is to pose a quantitative model that would explain in a unified manner the formation of radiolysis products and positronium. Such a model was built by Byakov and Nichiporov [70] and became known as the recombination – diffusion model. In the framework of this approach the intratrack processes are described by a system of equations that take into account the chemical kinetics and the diffusion of the reacting particles.

Byakov [78] posed a modernized model, which made it possible to reproduce all the above-mentioned concentration dependence types. The modernization amounted to refining the pattern of intratrack processes, which became possible thanks to the comparison of radiation-chemistry and positron data.

In the improved model all intratrack electrons participating in the chemical reaction are divided into two energy groups. The first group consists of nonionizing electrons e^{-*} with energies exceeding the energy E^* of the lower resonance trapping level; these electrons react only with the dissolved substance: $e^{-*} + S \rightarrow S^-$. The second group consists of epithermal and thermal electrons which participate both in reactions with the dissolved substance and in reactions with a positron and 'holes', which leads to Ps and H₂ formation, respectively. The electrons that escape recombination become solvated.

The quantitative relations derived from the model describe all the above-cited types of concentration dependences of the H_2 , Ps, and solvated electron yields and give physical meaning to the empirical coefficients in the formulas, coefficients that are expressed in terms of the reaction rate constants for the thermalized electrons and 'holes', the nonionizing electron trapping cross sections, and the geometric parameters in the primary particle track.

Knowing the model of Ps formation makes positron spectroscopy a useful and effective instrument for determining the physicochemical characteristics of the primary radiolysis products and studying processes in which such products participate. To illustrate this point, below we give some of the results obtained on this field of research [79–83].

Positronium formation time. Byakov et al. [76] have established through experiments the time τ_{Ps} of Ps formation in polar media. It was found to be of the same order as the electron solvation time in these media, viz. 10^{-12} s. Knowing the value of the Ps formation time makes it possible to use it as a time reference mark. It can be concluded that all intratrack processes that compete against Ps formation and change the Ps yield have a characteristic time comparable with the Ps formation time. In particular, the ion-molecular proton transfer reaction $RH^+ + RH \rightarrow RH_2^+ + R$ takes about 10^{-12} s rather than 10^{-14} s, as reported by some researchers.

The mechanism of electron solvation. The mechanism of electron solvation has been established via the example of hydrocarbon-alcohol mixtures [81-83]:

not only individual alcohol molecules but also alcohol polymers (associates consisting of several alcohol molecules) serve as solvating traps;

effective solvation begins only when the alcohol concentration exceeds a certain critical value characterized by the minimum Kirkwood correlation parameter, i.e. the maximum possible balance of the dipole moments of the molecules forming the polymer;

the bimolecular reaction rate constant of the electron solvation exceeds $10^{13}\,M^{-1}\,s^{-1}.$

The structure of the final section of a positron (electron) track. Positronium formation takes place in the relatively long final section of the positron track, where the positron motion becomes diffusive in nature. What this means is that within the given section the mean distance l_i between ionization acts is much larger than the transport electron scattering length λ_t : $l_i \ge \lambda_t$. This condition begins to be met when the positron energy is still fairly high, viz. 100-500 eV.

In liquids such as hexane and cyclohexane, where the electron thermalization length l_{th} is short compared to l_i , the final section of a positron (electron) track constitutes a set of isolated ion–electron pairs whose size is much smaller than the distance between them. In these liquids pair recombination occurs earlier than positronium formation. In liquids such as isooctane and tetramethylsilane, where the positron thermalization length l_{th} is large compared to l_i , the ions and electrons belonging to different pairs are mixed [79].

The features discovered imply that the use of such terms as blobs and short tracks in characterizing the structure of electron tracks is justified only in the case of liquids with a large thermalization length $l_{\rm th} > l_{\rm i}$.

7.2 Study of the properties and structure of surface layers of a liquid

The study of the properties and structure of the surface layers of liquids continues to be one of the fundamental lines of research in physical chemistry. The positron spectroscopy investigations conducted at the Institute of Theoretical and Experimental Physics (Moscow) were the first to extract quantitative information about the thickness of the surface layer of liquid and the orientation of molecules in this layer and to substantiate the theoretically predicted dependence of the surface tension of a liquid on the curvature radius of the interphase boundary.

Dependence of the surface tension of a liquid on the curvature radius of the interphase boundary. Thickness of the surface layer. The problem related to the phenomena of the formation of bubbles, drops, and microcrystals (such phenomena play a key role in the theories of boiling, condensation, and crystallization) was first formulated by J W Gibbs. The theoretically predicted dependence of the surface tension σ on the surface curvature radius *R* assumes the following form [84]:

$$\sigma(R) = \frac{\sigma_{\infty}}{1 + d/R} \,. \tag{55}$$

The fact that the thickness d of the surface layer (ranging from fractions of a nanometer to several nanometers) is small compared to the surface curvature radius R, which is typical of common methods, makes the experimental study of the radius dependence of the surface tension, $\sigma(R)$, extremely complicated.

An entirely new approach to the problem of determining $\sigma(R)$ through experiments was proposed by Byakov et al. [85]. The basic idea was to rely on the positronium atom annihilation. This hydrophobic particle is the best candidate for determining $\sigma(R)$. The thing is that once inside the liquid, a positronium atom forms a nanobubble such that the equilibrium radius calculated from the conditions of equality between the mechanical pressure with which the Ps atom acts on the phase interface and the capillary pressure $2\sigma/R$ that tends to shrink the bubble proves to be quite comparable with the expected value of the thickness *d* of the surface layer.

The researchers developed a method for determining the real radius of the positronium bubble from measurements of the lifetime of o-Ps and the ADAP [85]. Experiments with many liquids for which the annihilation characteristics of positrons were measured revealed that for each liquid the theoretical radius of the positronium bubble coincides with the experimental value only if the surface tension is described by formula (55), which takes into account the bubble radius. Here the thickness d of the surface layer for a given liquid must be assumed equal to the corresponding radius of the Wigner–Seitz cell.

Establishing the structure of liquid mixtures. To what extent does a mixture of liquids represent a true solution rather than a microheterogeneous structure? This question, often unresolved in modern chemistry, can be solved by the PAS method. The nanoclusters of the component with the greater polarity act as traps for the quasi-free electrons that form in the positron track and inhibit positronium production. The possibility of such interception is related to the deeper position of the bottom of the conduction band for quasi-free electrons in the polar microphase. The formation of a microheterogeneous structure can be observed when water is added to dioxane and manifests itself in a sharp drop in the Ps yield [86].

8. Conclusions

Thus, the positron annihilation method is a promising nondestructive method of structure testing for technologically important materials used in various fields of science and engineering. Further improvements will make it possible to identify possible correlations, for instance, between the main characteristics of positron annihilation spectra, electrophysical parameters, and the details of growing single crystals and epitaxial structures.

The positron annihilation method may play a key role in studies of the coherent behavior of complex systems [61-68]. Positrons can be used to probe atoms, molecules, and imperfections in the atmosphere of defects in solids, when the defect concentrations undergo various nonequilibrium phase transitions in the process of exchanging energy, matter, and information with the surrounding medium.

Establishing the mechanism of positronium formation in condensed dielectric media makes the positron annihilation spectroscopy a highly effective instrument for studying the primary stages of intratrack processes and for determining the physicochemical characteristics of primary radiolysis products.

The use of positron spectroscopy in investigating the properties of surfaces and the structure of liquid media is only in its infancy, and we can expect obtaining remarkable results in this area of research.

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