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POSITRON ANNIHILATION SPECTROSCOPY IN MATERIAL STUDIES

P. HORODEK[a,b,†], L. H. KHIEM[c], K. SIEMEK[a,b], L. A. TUYEN[a,d] AND A. G. KOBETS[a,e]

[a]*Joint Institute for Nuclear Research, Joliot-Curie 6, 141980 Dubna, Moscow region, Russia*
[b]*Institute of Nuclear Physics PAN, Radzikowskiego 152, 31-342 Kraków, Poland*
[c]*Institute of Physics, VAST, 18B Hoang Quoc Viet Street, Cau Giay District, Hanoi, Vietnam*
[d]*Center for Nuclear Techniques, Vietnam Atomic Energy Institute, 217 Nguyen Trai, D.1, Ho Chi Minh City, Vietnam*
[e]*Institute of Electrophysics and Radiation Technologies NAS of Ukraine, 28 Chernyshevsky Str., 61002 Kharkov, Ukraine*

[†]*E-mail:* pawel.horodek@ifj.edu.pl

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Abstract. *Positron annihilation spectroscopy (PAS) is a method dedicated to detection of open-volume type of defects. Nowadays, this technique is of a great interest due to the practical character of obtained results. New devices using monoenergetic positron beams are built. The paper presents the basics of PAS, a description of common experimental techniques and two examples of applications.*

Keywords: slow positron beam, positron annihilation, Doppler broadening of annihilation line, positron lifetime.

Classification numbers: 71.60.+z; 78.70.Bj.

I. INTRODUCTION

One direction of material technology development is the study of nature of defects created in the materials. Theoretically, a perfect structure in real world is never free from many kinds of imperfections which influence the material properties. Usually, depending on size, these defects are divided into points, linears and planars. Linear defects (dislocations) and planar (grain boundaries) can be relatively easy to observe by means of electron microscopy.

The method sensitive to the presence of point defects is positron annihilation spectroscopy (PAS). It allows to get information about the presence of structural defects, their concentration and type in wide range of depths. In this paper the basics of PAS, description of experimental techniques, presentation of facility at Joint Institute for Nuclear Research in Dubna as well as examples of application are shown.

II. POSITRON IN THE MATTER

The meeting of an electron (e^-) and its antiparticle positron (e^+) leads to the annihilation process while the mass of a pair e^+e^- is converted into the energy of electromagnetic field and gamma quanta are emitted. The annihilation process does not take place immediately and positron is present for a certain time in the matter after implantation. It occurs in a few stages (Fig. 1).

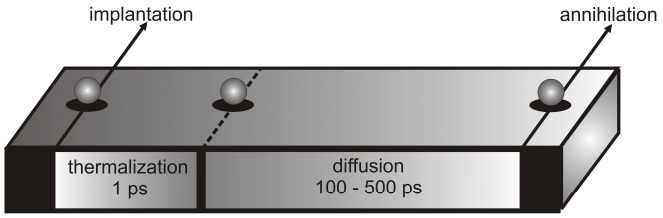

Fig. 1. Stages of positrons penetration in the matter.

At the beginning positron is implanted into the sample. Next, as e^+ possess both momentum and charge, it interacts with ions, electrons and even phonons. This stage is called the thermalization and lasts about few ps [1]. The elastic and nonelastic scatterings result in the loss of energy and information about initial direction of motion. At the end of thermalization, positron is in thermodynamical balance with environment and has energy of thermic vibrations about 25 meV. Since that moment so-called diffusion starts. In the longer time (between 100 and 500 ps) e^+ penetrates the area occupied by 10^7 atoms. The life of a positron ends in annihilation process with a random electron. In 99.7% cases it is annihilation process into two gamma quanta [2]. The possibility of annihilation on three or more photons exists but with very small probability. For example, the cross section on two gamma quanta annihilation is about 371 times as big as annihilation on three gamma quanta [3]. Additionally, only the former finds applications in material research. It is important that annihilation proceeds mainly with valence electrons because positron is situated in interstitial positions due to its electric charge. The probability of annihilation with electrons of atomic core is very small. In the central mass system of annihilating pair, the gamma quanta are emitted exactly in opposite direction while in the laboratory system some deviation from collinearity is observed. The bigger momentum of pair e^+e^-, the bigger the deviation.

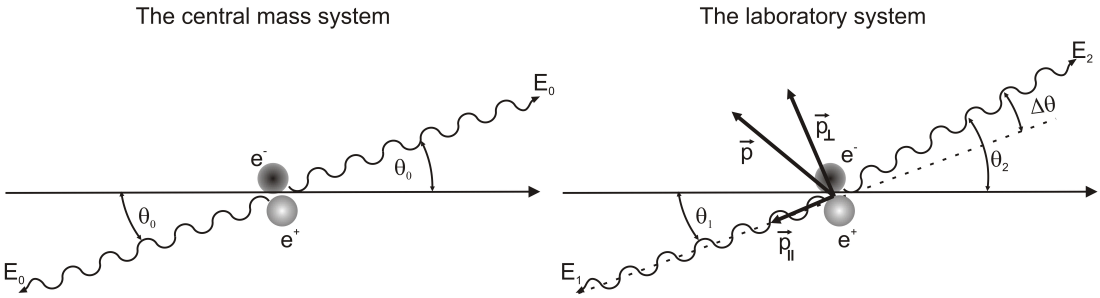

Fig. 2. The annihilation processes in the central mass system (left) and in the laboratory system (right).

In Fig. 2 the deviation from 180° is presented and it equals

$$\Delta\theta = \frac{p_\perp}{mc}, \tag{1}$$

where m is the electron mass, c is speed of light and $p_\perp$ is a transverse component of pair e^+e^- momentum. The momentum of annihilating pair finds its reflection not only in non-collinear emission of gamma ray, but also, as a result of Doppler effect, in its energy change. The energy depends on the value of parallel component of momentum of the pair e^+e^-

$$E_\gamma \simeq mc^2 + E_B \pm \frac{p_\parallel c}{2}, \tag{2}$$

where E_B is binding energy of e^+e^- in surrounding where the pair is placed and $p_\parallel$ represents longitudinal component of momentum.

During diffusion positron can pass the places where the density of electrons is changed. These places are defects of structure such as vacancies (atoms missing) and positron can be localized there. The electron density inside vacancies is lower in comparison to non defected area. Thus, the positron lifetime in a trap (defect), i.e. the time between positron generation in the source and annihilation, should be longer. The calculations supported by the reach experimental material show the mean positron lifetime in the crystal defect is proportional to its volume. In that way recognizing of single and multiple vacancies is possible. The fact that the momentum of annihilating pair inside traps is smaller makes the angle from Eq. (1) and energy from (2) smaller too. The momentum of the pair e^+e^- is in fact the momentum of an electron because the momentum of a positron is negligible and it can be omitted. These reasons make positron a good probe to determine momentum of electron and presence of vacancies and its concentrations in the matter.

III. POSITRON SOURCES

III.1. Standard experiments

In the case of PAS the most popular source is ^{22}Na. The isotope of ^{22}Na is characterized by a relatively long half life of about 2.62 years and maximal energy of emitted positrons of about 545 keV. Additionally, it is practically the sole source used in the positron lifetimes measurements. The ^{22}Na positron emission is accompanied by gamma quantum of 1274.5 keV delayed by 3.3 ps. The observation of this quantum informs about appearance of a positron.

In experiments with standard sources the isotope is enveloped into thin foils. Such prepared source is placed between two identical samples and through detection of gamma ray from the annihilation process the measurement is taken. Positron emitted directly from β^+ isotopes has the continuous energy spectrum. It means its energy is found in the range from 0 up to some maximal energy, specific to a given decay. For this reason the mean range of penetration of material by positron can be equal to a few dozen micrometers. For example, the mean positron implantation depth from ^{22}Na to Al equals about 90 μm. In this way, high energetic positrons cannot be used for materials where the thickness of defected layer is with the size of nanometers like in the case of thin layers, semiconductors, etc.

III.2. Positron beams

The detection of defects in the zone up to a few micrometers under the surface is possible by the use of monoenergetic positrons formed in the beam. The idea of creating the so-called slow positron beam with energy between few and a dozens keV is simple. Positrons are emitted usually from ^{22}Na source which is the starting point. Next, e^+ go through the moderator where some of them lose the energy. In most cases the thin foil like tungsten characterized by negative work function is used [4]. Sometimes the moderator is the solid rare-gas as Ne [5]. In the former the small amount of positrons annihilates in the foil, definitely more can leave it as fast positrons. There is also another possibility, namely, if thermalized positron appears near the surface, it can be re-emitted due to the negative work function. Similar situation occurs in solid Ne moderator. Both fast and slow positrons are obtained at the exit.

Next, the separation of these positrons before their utilization in the experiment must be done. It is realized in a few ways: using $\mathbf{E} \times \mathbf{B}$ Wien filter [6], external magnetic fields traverse to the flux or by the use of bending solenoids. The unmoderated positrons are stopped in the shield while the slow ones are formed in the beam with a small diameter by magnetic field or electrostatic lenses and accelerated to the desired energy. Next positrons go through the chamber where the sample to be studied is placed [7].

Slow positron beam obtained in that way is dedicated to DB measurements. Modern solutions such as the pulsed positron beams allow one to perform positron lifetime (LT) studies. In standard LT experiment the mean positron lifetime is calculated as a difference of time between emission of gamma quantum 1274 keV and annihilation. Alternative to registration of this quantum is the conversion of positron beam to very short pulses with a well-defined time structure [8]. The flux of moderated positron passes through a special set of bunchers and a chopper where particles are accelerated and deaccelerated and finally squeezed in the pulses.

IV. PAS TECHNIQUES

IV.1. Lifetime Spectroscopy (LT)

The positron annihilation rate λ (the reciprocal value of mean positron lifetime τ) is proportional to local electrons density n_e in the annihilation place

$$\lambda \approx \pi r_0^2 c n_e, \tag{3}$$

where c is the speed of light and r_0 is electron classic radius [9]. The electrons density inside micro traps, vacancies, pores etc. is lower in comparison to the area outside. So according to the above formula the mean positron lifetime in a defect is longer. For example, in pure iron

positron annihilating in a nondefected structure lives about 110 ps while the one captured in a vacancy lives 175 ps. Additionally, the longer the time, the bigger the volume of the trap. The measurement of positron lifetime components in the material allows us to detect defects, their size and concentration.

As a result of LT measurements, the LT spectrum can be obtained. It is the total sum of exponential distributions determined by the mean positron lifetimes in respective states $\tau_i = 1/\lambda_i$. The number of counts N in individual channels is the convolution of these distributions with the spectrometer spatial resolution function $g(t)$ in a shape of a single or double Gaussian function

$$N(t) = \int_{-\infty}^{+\infty} dt' g(t - t' - \Delta t_0) \sum_{i=1}^{n} \frac{I_i}{\tau_i} \exp\left(-\frac{t'}{\tau_i}\right), \tag{4}$$

where I_i is the intensity of a component corresponding to τ_i, while Δt_0 is the small shift of zero on the time axis in the timing spectrum.

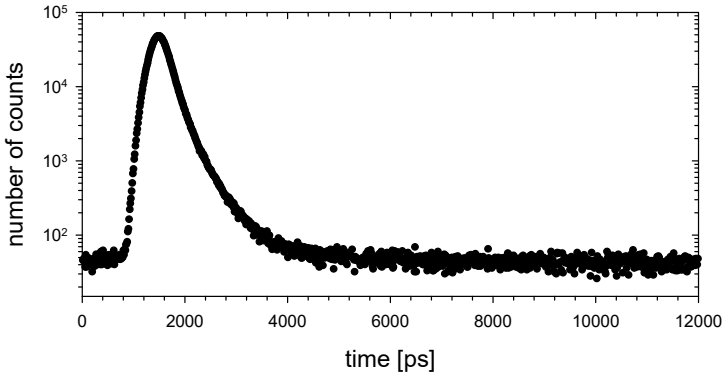

Fig. 3. Typical lifetime spectrum in the pure iron.

The analysis of results of positron LT measurements involves the determination of values τ_i and its intensity I_i for two, three and even four components. In Fig. 3 an example of LT spectrum is presented. Physically interesting information lies on the right in the exponential decay part. The compilation of spectra obtained from LT experiment are done by the special programs prepared for this aim as Kirgegard's and Eldrup's POSITRONFIT, RESOLUTION [10] or Kansy's LT [11].

IV.2. Doppler Broadening of Annihilation Gamma Line (DB)

The Doppler phenomenon leads to change of energy of gamma quanta E_γ emitted in annihilation process. Its value registered in laboratory system depends on the pair momentum according to the formula (2). The negligence of the positron's momentum and the binding energy allows us to express E_γ of gamma quantum created in two gamma quanta annihilation process in the function of electron energy E

$$E_\gamma \cong mc^2 \pm \sqrt{\frac{1}{2} mc^2 E}. \tag{5}$$

In this way, if electron annihilating with positron has energy of about 11 keV (Fermi energy for iron), the change of energy of annihilating photon will equal about 1.68 keV. The broadening of gamma line 511 keV will be 3.36 keV.

The observation of DB is restricted by the energetic spatial resolution of a detector, which is determined as the full width at half maximum (FWHM) of a narrow nuclear line. Recently the HPGe detectors with high pure crystal allow one for measurements with the resolution of $1 \div 2$ keV. For this reason, the HPGe detectors have found a wide application in positron laboratories.

DB spectroscopy is mainly used to detect vacancies and their clusters as well as their concentration. The annihilation of a trapped positron gives the broadening of 511 keV line but relatively smaller than that which will appear in the case of annihilation of a positron with electrons of atomic core or conduction electrons. To simplify, the more defected sample the less broadened 511 keV line. The quantitative connection between these values describes the so called trapping model [12].

The shape of annihilating line depends on many factors, which are the reason why the analysis of this line consists in determining the proportion of annihilations with low and high momentum electrons by the use of so called S and W parameters. The most popular one is S parameter which determines the contribution in the spectrum from annihilation with low momentum electrons. It is a ratio of an area under the central part of annihilation line to the whole area under this line after the background subtraction.

The area under the line is selected arbitrarily, but the range wherein it is calculated should be predetermined within the framework of given measurement series. It allows one to monitor the behaviour of S parameter in dependence on the factor disturbing the structure, e.g. plastic deformation. This parameter is sensitive to the presence of defects and connected to their concentration. The bigger value of S parameter, the bigger concentration of defects such as vacancies.

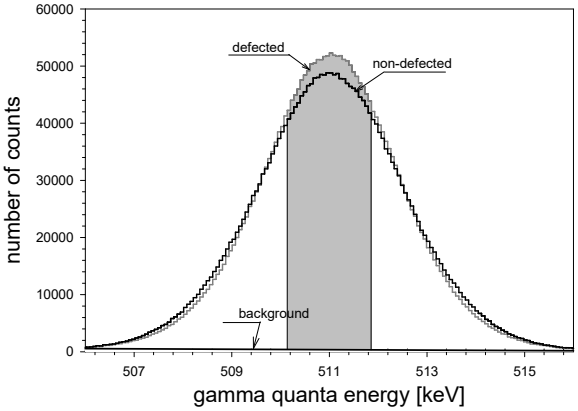

Fig. 4. The annihilation lines with marked area defining parameters S measured in pure iron. The grey line comes from the defected (by sliding) sample, while the black line represents the non-defected sample.

In Fig. 4 the annihilation lines of 511 keV for pure iron samples are presented. The black line represents the non-defected sample. The gray one comes from the sample defected by sliding.

The broadening in the case of the second sample is much smaller. It points that friction induced defects into the sample. In other words, the DB experiment consists of evaluation of broadening parameters, that allows one to conclude about concentration of defects and its distribution.

V. PAS AT JINR

At the Dzhelepov Laboratory of Nuclear Problems at JINR the slow positron beam based on a positron injector used in previous project [13] is used. The method of positron flux formation is the following. Positrons after emission from ^{22}Na source with 30 mCi pass through the solid neon gas. It plays a part of a moderator causing the wide part of positrons at elastic scatterings to slow down to thermal energies. The cryogenic source dedicated to experiments is closed in a special stand which includes neon and liquid helium lines. The ^{22}Na isotope is placed in the chamber with vacuum of 4×10^{-9} Torr. The cryocooler guaranties low temperature of about 7 K. Second line delivers neon which creates condensed layer of moderator without cloud. In this way the amount of positrons obtained in flux is 10^6 e^+/s and its average energy equals 1.2 eV while width of the spectrum is 1 eV.

Next, the separation of slow and fast positrons is done by the use of 100 Gs longitudinal magnetic field for transport of slow positron continuous beam. Slow positrons follow "slalom" trajectory when fast positrons hit the aperture diafragma.

The negative potential applied to the sample allows us to accelerate positrons up to initial energy of 40 keV. In this way monoenergetic positrons are implanted into the sample [14].

The LT spectrometer based on photomultipliers Hamamatsu H3378-50 with BaF_2 scintillators, digital unit APV8702 made by TechnoAP Co., Ltd. in Japan and power supply electronics is used at JINR in positron lifetime studies. Its time resolution is 180 ps. The ^{22}Na isotope enveloped into 5-μm thick titanium foils is the positron source. Its activity equals 27 μCi. The positron source is placed between two samples in each measurement. The LT spectrum usually contains 10^6 counts.

The standard spectrometer is used in DB measurements. It consists of a HV supply, a HPGe detector, a preamplifier, a multichannel analyzer and a PC computer. The gamma quanta from annihilation process are registered in the coaxial HPGe detector made by ORTEC with following parameters: the relative registration efficiency at 1.33 MeV γ-photon (at the standard IEC 60973) equals 30 %; energy resolution (FWHM at the 511 keV) is 1.1 keV; the peak to Compton ratio (the height of the 1.33 MeV peak to the average Compton plateau) is 65:1. The detector will be supplied by 1.5 kV high voltage power supply in NIM standard made by the same company.

The signal, after passing through the detector is amplified in ORTEC 572 A amplifier and reaches the 16k multichannel analyzer ORTEC 927 ASPEC which cooperates with a PC computer. In this way energetic spectrum from annihilation processes is be obtained.

The mentioned apparatus working at JINR was used to perform many investigations in the field of material science [15–22].

VI. Example of application

VI.1. Zeolite

Zeolite ZSM-5 (Zeolite Socony Mobil–5) is aluminosilicate material which has widely applied in many industrial areas as catalytic, absorption and ion-exchange materials [23]. It is also

indicated as a promising material for the treatment of radioactive isotopes of ^{152}Eu, ^{137}Cs, ^{131}I and ^{90}Sr from the liquid waste associated with the operation of the nuclear reactor [24,25]. The ability of radioactive isotope treatment depends strongly on the number of absorption and ion exchange centres which are relative to defects in this material [25]. The modification of ZSM-5 structure by irradiation is recently an important topic in material science. It should be also mentioned that Vietnam possesses huge reserves of kaolin being a source of raw materials for producing zeolite ZSM-5.

The positron lifetime spectrometer at JINR was applied to studies of structure changes generated by 10 MeV electrons in the ZSM-5 characterized be Si:Al ratio equal 30. The irradiation with the dose 10^{16}e/cm^2 was performed using LINAC accelerator (UERL-10-15S2) established at Vinatom (Vietnam).

Table 1. Positron lifetimes and their intensities before and after irradiation of ZSM-5 samples.

Sample	τ_1 **[ns]**	τ_2 **[ns]**	τ_3 **[ns]**	τ_4 **[ns]**	$\mathbf{I_1}$ **[%]**	$\mathbf{I_2}$ **[%]**	$\mathbf{I_3}$ **[%]**	$\mathbf{I_4}$ **[%]**
reference	0.160	0.447	1.90	3.83	21.80	57.61	16.88	3.71
irradiated	0.186	0.465	2.05	4.66	24.7	61.7	11.59	2.02

In measured positron lifetime spectra four components τ_i (and their intensities I_i) were found both for reference (unirradiated) and irradiated samples. τ_1 and I_1 are related to annihilation of free positron and p-Ps; τ_2 and I_2 give information of positron annihilation in characteristic molecules of ZSM-5 zeolite (constructed by the double five-membered rings); τ_3 and I_3 are attributed to annihilation of ortho-Positronium in channels; τ_4 and I_4 are considered as annihilation of ortho-Positronium in intersection of channels/small void. The irradiation causes increase of all positron lifetime components as well as intensities of I_1, I_2 and decrease of I_3, I_4. It confirms that structure of ZSM-5 is significantly affected by irradiation with the 10 MeV electron beam. Another interesting observation is a lack of positron lifetime component longer than 10 ns before and after irradiation.

VI.2. Swift heavy ion irradiated gold

The ion irradiation of materials is well-known process of structure modification. Energetic ions introduce a large number of structural defects being responsible for physical, mechanical and chemical properties of given target. These defects can be successively easy observed using PAS techniques. In the aim of demonstration slow positron beam to the defects detection the results of studies of pure gold samples are cited [22]. Two discs with 10 mm in diameter and 3 mm thick of 99.95 % purity gold were annealed at 800˚C for 3 hours in vacuum conditions of 10^{-5} Torr and slowly cooled down to the room temperature. This procedure allowed us to removed defects introduced during sample preparation. Then one disc was irradiated with 167 MeV Xe^{26+} heavy ions and dose 10^{14} ions/cm^2. On the basis of theoretical calculations the implanted thickness was about 8 μm. However, according to equation $\bar{x} = AE^n/\rho$, where $\bar{x}$ is mean implantation depth, E is positron energy, A=6.73 μgcm^{-2}keV^{-n}, n=1.408 are Makhov's parameters and ρ is density equal 19.30 g/cm^3 the layer studied by positron beam (0.1 – 40 keV) was close to 0.63 μm [26].

In Fig. 5, the dependence of S parameter on positron energy is shown. The top axis reflects the mean implantation depth. In case of both profiles S parameter decreases with energy and saturates. The fast decreasing of S parameter for low energies is attributed to back diffusion of

positrons and their annihilation at the surface. The saturation of $S(E)$ plot for irradiated sample (white circles) appears faster in comparison to nonimplanted one (black circles). Moreover, level of S parameter saturation is higher for implanted gold. In this way we can conclude about the presence of irradiation-induced defects in studied sample.

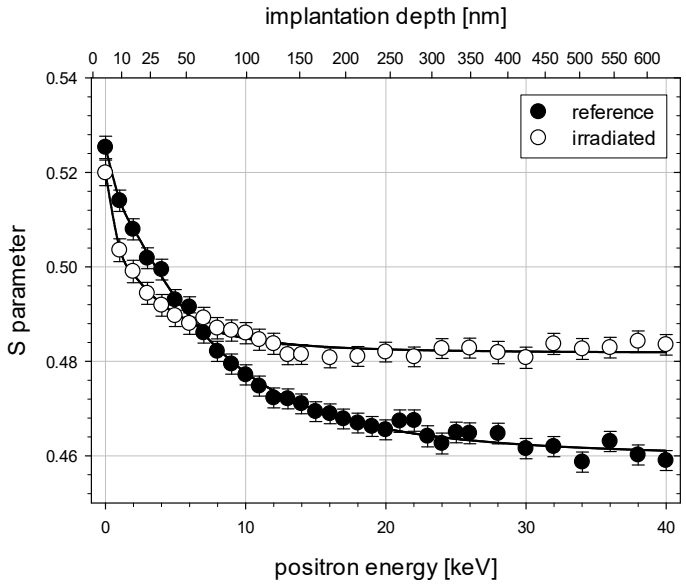

Fig. 5. The measured S parameter as a function of the positron incident energy E for studied gold samples. The top axis represents the mean positron implantation depth. The solid lines represent the best fit of model function to the experimental points [22].

Fitting so called positron diffusion equation [27] to experimental points (solid lines represent the best fits) we obtain the values of positron diffusion lengths (L_+). For unimplanted specimen L_+=84$\pm$3 nm was noted. However, irradiation caused the reduction of this parameter to 29$\pm$2 nm. It confirms the existence of open-volume defects with some concentration in irradiated samples. It should be noticed that values of positron diffusion lengths make possible to evaluate the defect concentration insofar as we know the kind of defect. More details related to these studies are available in Ref. [22].

VII. SUMMARY

The positron annihilation spectroscopy is a very sensitive method dedicated to the detection of points defects in materials. It allows to recognize their type, concentration and changes of their concentration, e.g. in depth function. It is a technique interesting both from scientific and practical points of view. This method has been developing rapidly recently and number of centres which use it is still growing.

The new point on the map of these centres is Joint Institute for Nuclear Research in Dubna. Here, the properties of high quality positron beam and other apparatus used in measurements are

comparable to similar devices in the world. The direction of works focuses on the task of solid state physics and practical applications of obtained results in engineering.

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