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G. BRAUER
ZS. KAJCSOS
T. KEMÉNY

POSITRON ANNIHILATION IN METALLIC GLASSES
- A GENERAL SURVEY

Hungarian Academy of Sciences

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POSITRON ANNIHILATION IN METALLIC GLASSES - A GENERAL SURVEY

G. Brauer*

*Zentralinstitut für Kernforschung Rossendorf,
DDR-8051 Dresden, Postfach 19, German Democratic Rep.

Zs. Kajcsos, T. Kemény

Central Research Institute for Physics
H-1525 Budapest 114, P.O.B. 49, Hungary

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ABSTRACT

This report presents a review of the positron annihilation work on metallic glasses from the literature. For completion some general information and an overview on structural models of metallic glasses as well as a short description of the positron annihilation method itself are added. Conclusions regarding information on the structure of metallic glasses obtainable by positron annihilation are also given.

АННОТАЦИЯ

В работе обобщаются результаты исследований с помощью позитронной аннигиляции в металлических стеклах, имеющиеся в литературе. После общих сведений, касающихся металлических стекол, дается критический анализ структурной модели и затем методы позитронной аннигиляции. Дается оценка информации, получаемой с помощью позитронной аннигиляции, относительно структуры металлических стекол.

KIVONAT

Jelen cikkben összefoglaljuk az irodalomban fémüvegekre vonatkozóan található pozitron annihilációs vizsgálatok eredményeit. A fémüvegekre vonatkozó általános tudnivalók után a szerkezeti modellek kritikai elemzését, majd a pozitron annihilációs módszernek az ismertetését adjuk. Végül következtetéseket vonunk le a fémüvegek szerkezetéről pozitron annihiláció segítségével nyerhető információkra vonatkozóan.

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1. Introduction

Albeit glassy metals had been produced already \sim 150 years ago, the systematic study of the amorphous phase of metals and alloys had gained momentum only in the 50's. This delay was caused mostly by the lack of appropriate methods for the production of "glassy" samples, but recent techniques (e.g. "liquid metal rolling mill") enable us to obtain a continuous ribbon cooled rapidly enough ($10^5 - 10^{10} \text{ }^\circ\text{C sec}^{-1}$) to solidify in the noncrystalline state.

Since the metallic glasses ("undercooled liquids") are thermodynamically unstable, during heating transformation to stable crystalline phase(s) occurs; in some cases considerable changes had been detected even at temperatures much below the "crystallization temperature".

For the description of the amorphous solid structure some theoretical models have been suggested; the "dense random packing" model describes essentially noncrystalline configuration while in the "microcrystalline disorder" model, crystallites with completely uncorrelated orientation are assumed. Very recently the so-called "quasi-crystalline model" was suggested, meaning a random variation in the crystalline parameters of the basic structure.

For the experimental study of amorphous metallic systems many different methods have been applied, e.g. X-ray, electron and neutron diffraction, microscopy, measurements of ac-dc magnetic and electrical properties, density, elastic constants, hardness, etc.

As the power of positron annihilation methods became more and more established and demonstrated for the investigation of structural defects in solids, very recently they were also applied for studying the amorphous metallic alloys.

In this paper our aim is to give a short review both on the models and some experimental results on metallic glasses as well as on the positron annihilation methods applied for their investigation.

The metallic glasses exhibit the favorable properties of both metals and glasses in a level not easily reached by crystalline materials. For example they are among the strongest known engineering materials, they are not brittle, they have considerable ability to deform plastically. Some iron-based metallic glasses are as hard as fully martensitic steels. Resistance against chemical interaction, strength, ductility, toughness provide a very unusual combination of properties. These facts offer some application possibilities as e.g. reinforcing filaments in plastics, rubber and aluminium alloys. Mechanical oscillators and acoustic devices might also be constructed employing the low attenuation of acoustic waves in metallic glasses.

The nearly zero temperature coefficient and large absolute resistivity - as compared with well-known resistance alloys - make some metallic glasses suitable as electrical resistors, low temperature heating filaments, resistance thermometers, etc.

Favorable magnetic properties (low coercive force and high permeability) combined with mechanical hardness lend the metallic glasses for different applications as essential constituents in inversion transformers, current and pulse transformers, magnetic amplifiers, bistable switches, magnetic memories and even in consumer electronics as tape recording heads. In the future it is hoped that they can replace permalloy and silicon-iron in motors and generators much reducing the power loss in them.

2. Structure models for metallic glasses

Significant theoretical and experimental effort was devoted to the investigation of the structure of non-crystalline metallic materials. It is quite understandable, as the proper characterization of the atomic arrangement is the first step towards the description of the electronic structure and related properties (e.g. transport behaviour, magnetism, etc.) as well as dynamic features (phonon spectrum or diffusion characteristics). Despite the significant advances in this field a number of questions remained unclear. In this report an overview will be given of the main directions of the modelling activity with a special emphasis to the problems not yet solved.

A complete three dimensional characterization of a perfect crystal is given by referring to its elementary cell. By definition one cannot find long-range order in a non-crystalline material so we must accept a statistical description. The central quantity of the structural characterization is the atomic distribution function $\varrho(r)$. The number of atoms in the shell between r and $r+dr$ is $4\pi r^2 \varrho(r) dr$. One of the main limitations of this description is quite straightforward: We investigate only a one-dimensional projection of the real three-dimensional structure, so we cannot expect a one-to-one correspondence between $\varrho(r)$ and atomic arrangement. Despite this restriction practically all of the experiments are compared with models which are expressed in terms of quantities derived from $\varrho(r)$ namely the radial distribution function $RDF(r) = 4\pi r^2 \varrho(r)$ the pair correlation function $W(r) = \varrho(r)/\varrho_0$; and the reduced radial distribution function $G(r) = 4\pi r (\varrho(r) - \varrho_0)$ where $\lim_{r \rightarrow \infty} \varrho(r) = \varrho_0$ is the average atomic number density. The experimental determination of these quantities by either conventional diffraction methods (electron^[1-3], neutron^[4-5] or X-ray^[6-9]) or more sophisticated experimental techniques (anomalous X-ray scattering^[10], EXAFS^[11] etc.) will not be discussed here; we refer, besides original publications, to some excellent reviews^[12,13,14] and conference proceedings^[15]. Only one aspect of the experimental

problem is briefly mentioned here. Classical diffraction experiments can usually determine only the average distribution function while a physically meaningful description of a multi-component glassy alloy requires the knowledge of the partial correlation functions of different pairs of atomic species, $W_{ij}(r)$. Extreme care must be taken when a model calculation is compared with an experimentally determined average distribution function.

In order to discuss the most important requirements which must be fulfilled by a structural model we must start from a typical distribution function, which is shown in fig.1. Instead of the set of Dirac δ -functions which were found for a perfect crystal of infinite size one can observe for the amorphous materials broad distributions of atomic distances. Two radically different interpretations can be suggested for this fact:

A.) Microcrystalline model: The material consists of perfect crystals of very small size. The finite grain size causes such a broadening of the diffraction pattern, which is inversely proportional with the characteristic size [16]. A basic feature of this broadening is that every peak of the experimental interference function (the Fourier transform of the atomic distribution function) is broadened to the same extent. It was concluded by Cargill [17], that the microcrystalline model can not be valid for amorphous metallic materials where the first peak of the observed interference function is much sharper than the others.

The existence of microcrystals would imply that a very significant fraction of the atoms in the amorphous material could be found at grain boundaries, i.e. high concentration of defects were expected. That is the point where positron experiments are traditionally claimed to be relevant for the decision between structural models. Our reservations in connection with these ideas will be mentioned where the experimental results are discussed.

B.) Essentially random models: It is generally accepted now that there is an element of inherent randomness in the structure of amorphous metallic materials. The extent and nature of this randomness is the central question of the modelling of amorphous structures.

B1; Dense random packing of hard spheres (DRPHS); With the apparent failure of the microcrystalline model, its opposite, the perfectly random model put forward originally by Bernal^[18] has been suggested for single component glasses by Cohen and Turnbull^[19] and was applied for amorphous metal-metalloid alloys by Cargill^[20]. The structure is set up as an assembly of hard spheres in close contact. The most significant feature of the structure is that it contains no holes large enough to accommodate a new sphere. The sophisticated computer procedures which are used to build the models are outside the scope of this report. The original Bernal model was realized historically first by steel balls in a plastic bag, and the procedure was refined later by Finney^[21] who achieved much better resolution. His calculated reduced radial distribution function is also shown for comparison in fig.1., scaled to the experimental result of Cargill^[17] on Ni-P. The only fitting parameter of this model is the diameter of the hard spheres. The comparison shows that the DRPHS construction is able to reproduce the main features of the measured distribution function.

B2; Relaxed models and molecular dynamics

There are two apparent inconsistencies between the results of DRPHS modeling and experimentally measured atomic distributions:

- When the hard sphere diameter is chosen to achieve the best agreement with the experimentally determined RDF the calculated packing fraction η of the model remains much too low. (A typical value^[21] is $\eta = 0.637$ while the measured density of the metallic glasses is only 2-3 % smaller than that of its crystalline counterpart. The packing fraction of an fcc or hcp close packed crystal structure is $\eta = 0.7405$).

- The intensity ratio of the split subpeaks of the second maximum of the pair correlation function is given in reversed order by the DRPHS model

in comparison with the measured ones (see fig.1.). This feature of the model can be removed by a somewhat modified model building algorithm which results in the formation of less distorted tetrahedra than those of the original model. By introducing a second parameter, the so-called tetrahedral perfection^[22], the intensity ratio of the subpeaks can be fitted to the measured one. There is nevertheless a severe drawback of this construction: the density of the model is further reduced, packing fractions as low as $\eta = 0.5$ are found.

There is an obvious refinement of the DRP modelling: The hard sphere result can be used as a starting point when the model is relaxed by a properly chosen pair potential. Due to the softer repulsive core and the attractive part of the potential, the minimization of the total energy leads to a more dense arrangement of atoms than that attainable in a sequential DRPHS modelling. The correct intensity ratio of the subpeaks results^[23] without making any recourse to tetrahedral perfection. The packing fraction is somewhat increased ($\eta = 0.66$) but is still much smaller than that of a close packed crystalline structure.

The final step in the hierarchy of completely random models is the molecular dynamics (MD) calculation. The decrease of kinetic energy (i.e. reduction of temperature) in a molecular dynamic computer model of a liquid (100-1000 atoms interacting through a pair potential) reproduces the basic features of a real glass transformation. On account of the increased density the atomic mobility decreases and the liquid is solidified to a glassy state^[24]. The pair correlation function is very similar to the experimental one, and the packing fraction is the highest among the random models, $\eta = 0.70$.

B3; Inherent problems of random modelling

Despite the definite successes of the random modelling some conceptual difficulties must also be mentioned. One must not forget that the distribution function averaged over different atomic species, is only a necessary

but by no means sufficient test for the applicability of a given model. The close similarity between the distribution functions of a completely random single sized spheres model and the Ni-P glass (fig.1.) can not be interpreted as an indication of the random local (nearest neighbour) coordinations. Several experimental techniques which are able to determine the partial distribution functions of the different pairs of atomic species [5,10,25] show in good agreement with each other that metalloid atoms are surrounded by metal atoms only, so there are no first neighbour metalloid-metalloid pairs.

In order to account for this general feature of the metal-metalloid glassy alloys a somewhat different variant of the DRPHS models is frequently referred to. It was recognized by Polk [26] that beyond the simple geometrical constraints expressed by the possible structures of hard spheres, the formation of metallic glasses is mainly determined by the covalent-like chemical bonding between metal and metalloid atoms. This observation, together with the fact that metalloid atoms are usually smaller than the transition metal atoms, leads naturally to the so-called Polk-model. In a randomly packed assembly of transition metal atoms the holes which are smaller than the diameter of a metal atom can nevertheless accommodate the smaller size metalloids. Although this structure is in qualitative agreement with the results of diffraction experiments, quite a number of inconsistencies remain.

It was recognized by Cargill [12] that the holes are significantly smaller than the figures originally supposed. Besides, as it was pointed out by Nagel [27], the coordination number of the larger Bernal holes varies from 4 to 6 while the coordination of metalloids is found as 9 ± 1 transition metal in e.g. Pd-Si or Co-P glasses. It follows, that the metalloid atoms can not be introduced to the holes without the severe distortion of the DRP structure of transition metal atoms. It was shown recently by Hayes et.al. [25] that in a $\text{Pd}_{80}\text{Ge}_{20}$ glass the nearest neighbour Pd atoms of a Ge are located within a root mean square half width of less than 10^{-2} nm which is almost as narrow as the distribution in the crystalline reference material and is definitely inconsistent with a random arrangement.

B4; Model with Fixed Chemical Short Range Order (CSRO)

In the previous parts of this chapter we have formulated some basic features which should be expected from a successful model. An element of inherent randomness (see paragraph A, on the failure of the microcrystalline model) must be reconciled with the existence of fixed local coordinations. The first step in this direction was made by Maitrepierre^[28], who has suggested that the structure of Pd-Ni-P and Pd-Fe-P glasses should be described by a quasi-crystalline model based on Pd₃P. This idea, namely the intermetallic compound-like chemical short range order of the metallic glasses is the basis of the whole group of random models with fixed local coordinations.

The existence of a well defined local symmetry around the metalloid site is also detected experimentally by a recent nuclear magnetic resonance study^[78]. Quadrupolar effects give conclusive evidence that the building units of the amorphous structure can be found in the crystalline counterparts.

The essential assumption of the quasi-crystalline models is the existence of special compositions (say TM:P=3:1 in the previous example) where the glass is characterized by a perfect chemical short range order. It has nothing to do with the microcrystalline model, as there is no long range order beyond the first coordination shell. It is reflected in the fact that the shape of the pair correlation function can be calculated from the crystal structure of the compound and from the assumed distribution of atomic distances, the width of the nth peak is an increasing function of n^[29], in agreement with the experimental results not reproduced by microcrystalline models. The structure of a metallic glass is described by two terms^[30].

The disorder of the glass of special composition is a consequence of the distribution of atomic distances and bond angles only, that is what we call topological disorder. In a glass of arbitrary composition there is no perfect order even in the first neighbour shell, due to the off-stoichio-

metry there are A atoms on B sites which is called chemical disorder.

There are several successful attempts to describe structure and physical properties of metallic glasses with a variant of chemically coordinated random models. The structure of Pd-Si is reproduced by Gaskell^[31] with the aid of packing polyhedra characteristic to the cementite structure. The structure and thermal stability of transition metal-transition metal (e.g. W-Fe, Mo-Co, Mo-Ni) glasses are interpreted by Wang^[32] in terms of the basic structural unit of the intermetallic compounds i.e. the Kasper polyhedra.

The study of ferromagnetic glasses is highly relevant to the structure, as magnetic properties are sensitive to short range order. The investigation of Fe-based glasses can also be supported by Mössbauer spectroscopy in order to characterize the nearest neighbour environment of an Fe atom. The crystallization behaviour of Fe-B glasses has been shown^[33] to be closely connected to the structure. The hyperfine field distribution of Fe₇₅B₂₅ glass was successfully derived^[34] from the hyperfine field pattern of its crystallization product, b.c. tetragonal Fe₃B intermetallic compound. The close relation between hyperfine field patterns indicates the similarity of chemical short range order in the metallic glass and in the intermetallic compound. A quasi-crystalline model of the glass was constructed, and the composition dependence of the hyperfine field distribution and the saturation magnetization calculated from this model together with that of a DRP construction was compared to the experimentally determined quantities^[35]. Both, hyperfine field distribution and saturation magnetization are definitely in better agreement with the chemically correlated model.

It has been demonstrated recently^[29] that the experimentally determined radial distribution function of Fe-B glasses can also be described by the quasi-crystalline model. We can conclude that both random and chemically correlated models can be used for interpreting the results of diffraction experiments, but the proper characterization of short range order is neces-

sary for using structural models to explain other physical properties.

3. The positron annihilation method

In the following chapter the principles of positron annihilation and some general problems in the application of the positron method to the study of condensed matter are briefly summarized. Investigations by positron annihilation have been developed in many laboratories in three main fields:

i.) measurements of the lifetime of positrons

ii.) measurements of the γ - γ angular correlation of the 2γ -annihilation

iii.) measurements of the Doppler-broadening of the annihilation γ -line.

Positrons, injected into a sample are thermalized on a time-scale which is short compared to their lifetimes. The annihilation rate of a positron-electron pair into gamma quanta is proportional to the electron density sampled by the positrons at the time of annihilation. In condensed media most positrons annihilate with an electron into two gamma quanta, each with an energy $m_0c^2=511$ keV, in the center of mass frame of the annihilating positron-electron pair. Since momentum is conserved before and after the annihilation the two gamma quanta emerge from the site of annihilation approximately 180° apart in the center of mass frame. The momentum of the positron after thermalization can be neglected in first order, therefore the electron momentum is carried away by the annihilation γ -quanta. This fact results in deviations from 180° of the angular correlation between the two gamma quanta as well as in a Doppler broadening of the 511 keV annihilation radiation in the laboratory frame.

In this sense, measurements of positron annihilation characteristics can give information about the distributions of density and momentum of the electrons in the sample and thus contribute to the elucidation of basic problems in the physics of condensed matter.

Positrons employed in the preceding techniques are obtained from the β^+ -radiation emitted during the decay of unstable neutron-deficient nuclei (e.g. ^{22}Na , ^{58}Co , ^{64}Cu) and have a continuous kinetic energy spectrum reaching up to a maximum value E_{max} . In the sample they are stopped with an implantation profile. The number of positrons reaching a depth x in the sample depends on E_{max} and the positron absorption coefficient μ_+ of the sample. The mass absorption coefficient μ_+/ρ for positrons from ^{22}Na and ^{64}Cu have been experimentally determined in the literature [36,37].

$$I = I_0 \exp(-\mu_+ x)$$

$$\begin{aligned} \mu_+/\rho &= (34 \pm 3) \text{ cm}^2\text{g}^{-1} & \text{for } &^{22}\text{Na} \quad (E_{\text{max}}=0.54 \text{ MeV}) \\ \mu_+/\rho &= (29 \pm 1) \text{ cm}^2\text{g}^{-1} & \text{for } &^{64}\text{Cu} \quad (E_{\text{max}}=0.65 \text{ MeV}) \end{aligned}$$

Mostly volume effects are studied by positron annihilation, where the depth dependence of the annihilation events in the sample due to the implantation profile of the positrons does not play any role. One must be sure that all of the positrons are stopped in the sample. If a sample is not thick enough to stop all the positron from a source - a single amorphous metallic alloy ribbon - several layers of the same material have to be placed together until a sufficient thickness is reached. The choice of a positron source may depend on several practical conditions (possibility of production by particle accelerators or reactors, commercial availability, costs, half-life, handling restrictions regarding activity, etc.) but is also determined by physical reasons. For positron lifetime measurements (fig.2.) it is essential to have a strong gamma emission coincident with the positron emission, as in the case for ^{22}Na . The positron source of (10-50) μCi activity is evaporated on a thin plastic or metallic foil which is then covered by a foil of the same kind. Such a "source sheet" has to be sandwiched between two identically treated pieces of the sample under investigation (in order to maximize positron absorption) and this source can be used many times. The minimum surface area required for a measurement depends on source preparation and has to be generally equal or larger than a spot of about 2-3mm in diameter. The fraction of annihilation events, P_f in the source sup-

porting foil depends on the atomic number Z of the sample and on foil thickness, d and has to be taken into account in the evaluation of positron lifetime spectra [36].

$$P_f = \frac{\alpha(1-\beta)}{1-\beta(1-2\alpha)}$$

$$\alpha = (\mu_+/\rho) d$$

$$\beta = 0,342 \lg Z - 0,146$$

(where d is the foil density and β is the reflection coefficient).

The measuring technique requires fast timing which is already commercially available. The obtained time spectra have to be treated mathematically as a sum of decaying exponentials folded by the actual time resolution function of the equipment. Besides the correction of any spectrum for source supporting foil contributions and background mainly two problems have to be solved. The first is an estimation of the time resolution function of the measuring system (the so-called "resolution" or "prompt curve") by a ^{60}Co source and the analytical description of this function for computational reasons. This effort is necessary, because the lifetimes to be measured (100-500 ps in metals, alloys and other solids) are of the order of the time resolution which can be achieved by the present techniques (170-350 ps). Different attempts exist in the literature to describe the prompt curve, e.g. by a Gaussian [38,39], by a sum of Gaussians [40] or by a convolution of a Gaussian with a double-sided exponential [41]. The second problem is to relate the parameters of a "good fit" with a physical meaning or model. For a "good enough" statistics the measuring time required for a spectrum is about (6-24 h).

For angular correlation measurements (fig.3) it is necessary to have as little coincident gamma radiation from the source as possible to avoid background problems, otherwise all kinds of positron sources are suitable

for this investigation. Usually the positron source (of 10-100 mCi activity) is a few millimeters away from the sample and shielded by lead in all directions not pointing to the sample surface. In general the sample should not be smaller than about 10 mm in diameter. To improve the measuring efficiency 0.5-0.8 T magnets can be used to focus positrons from the source onto the sample. (In this way smaller samples can also be investigated.) The angular resolution of the equipment is mainly determined by the geometry of the detectors and collimators, but the implantation profile of the positrons in the sample must also be taken into account in high resolution measurements. Usually an angular resolution of (0.5-1) mrad is easily achievable. The measuring time is of the order (1-7) days.

In Doppler-broadening studies (fig.4) practically the same source-sample arrangement as in lifetime measurements can be used, all kinds of positron emitting isotopes are suitable for this purpose. The information contained in Doppler-broadening and angular correlation results is similar, since both techniques respond to the same physical quantity i.e. the final momentum of the annihilating positron-electron pair in the laboratory frame. The best energy resolution achievable by semiconductor detectors is about 1 keV at 514 keV (natural γ -line of ^{85}Sr) which is a factor of 10 to 20 times worse than that of achievable in angular correlation studies. The Doppler-broadening technique has nevertheless distinct advantages as compared to the angular correlation method: only one detector is required, no coincidence circuitry is necessary and thus rapid data collection is possible. The counting statistics is very good and it may more than compensate disadvantages connected with poor resolution for certain applications like measurements at very high temperatures, high pressures or the study of annealing or reaction kinetics. The measuring time for one spectrum is of the order 0.5-2 h.

As a charged probe, positrons disturb the wave function of the sample under study, but due to theoretical efforts it is possible to make conclusions for the unperturbed material. The advantage of the positron

methods in electronic structure studies of solids compared to other methods is their independence of the mean free path of electrons. This way these methods are neither restricted to low temperatures nor to high purity, defect-free materials. They are successfully used to get information e.g. about the electronic structure of non-dilute alloys and of rare earth metals at higher temperature in their paramagnetic phase.

Besides the electronic structure studies most applications of the positron methods belong to the following two groups. In the first set the charge of the positrons is used to study their interaction with crystal defects and surfaces mainly in metals and alloys, but also in molecular solids. In this case their response to electric fields and its dependence on morphology is exploited. The second set employs the spin of the positrons. In this manner the interaction with external magnetic fields and internal paramagnetic states of matter, and the interaction of positronium (a bound state between an electron and a positron) with its surrounding is studied, mainly in ionic crystals and amorphous solids like glasses.

To study crystal defects one needs information at different distinct levels. In the first stage we have to know the fundamental aspects of positron-electron interaction in perfect materials. The next step is to show that there is a change in the positron annihilation characteristics caused by the presence of a single type of defect at a sufficiently high concentration. Having solved the problem of the coexistence of different types of defects, one can start to study the complex characteristics of materials in practical use.

Positrons are attracted and trapped by all kinds of crystal defects having effective negative charge. The annihilation at defects is influenced by the electronic structure of the defects, e.g. the decreased density of conduction electrons around a vacancy. This fact results in an increase of the positron lifetime as well as in an increase of the peak height of the angular and energy distribution curves. From the relative changes of these parameters the fraction of positrons annihilating in defects can be esti-

mated. In the trapping model this fraction is connected with the trap rate of a given defect type which is assumed to be proportional to the defect concentration. If the temperature dependent proportionality factor (the defect-specific positron trapping rate) is known, the relative changes of the measuring parameters can be used to calculate absolute defect concentrations.

In metals the sensitivity range for vacancies is from 10^{-7} to 10^{-3} vacancies per atom and for edge dislocations from 10^8 to 10^{12} cm line length per cm^3 . The maximum change in the measurable parameters is around 10 % but it naturally depends on the material under investigation and also on the sample handling and investigation procedures [45]. Other defects seen by positrons are grain boundaries, voids and impurity-vacancy complexes. Because of the high technological interest in irradiation damage, fatigue, work hardening and creep, positrons are frequently applied in the study of metals to determine vacancy formation energies (measurements in thermal equilibrium), to investigate and clarify the processes in different recovery stages and to study the formation of voids, because processes are difficult to investigate by electron microscopy.

For more extended and detailed descriptions of the principles, measuring possibilities and limitations of the positron methods we refer to some excellent review articles and books [42-45].

The accumulated experience that the defect structure and especially the vacancy-type defects in crystalline metals and alloys can be successfully studied by positron methods has significantly stimulated their application also to amorphous metallic materials.

4. Positron annihilation studies on metallic glasses - a literature survey

In the following chapter we briefly report the main results obtained from positron annihilation studies on metallic glasses.

Regarding the basic constituents of a metallic glass one usually makes a distinction between metal-metalloid (M2) and metal-metal (M1) glasses, where especially for the M2 glasses the basic constituents are often composed of many different kinds of atoms. For clarity we only cited here the chemical constituents of a system, but for easier comparison with our data collected here we note some corresponding commercial names in Table 1. The main points of the general information on positron annihilation investigations in the literature are collected in Table 2 (M2 glasses) and Table 3 (M1 glasses). The abbreviations for the positron methods are the following: lifetime measurement=LT, $2\theta^*$ -angular correlation=AC, Doppler broadening=D.

As there is at present no theory of positron annihilation in amorphous alloys it is natural to apply the experiences from investigations on defected crystalline materials (trapping model, see chapter 3) to explain the measured data.

From a comparison of the results on different as-received iron - based metallic glasses with crystalline, well-annealed and vacancy-rich Fe [74,75] it has been concluded, that the positron annihilates from a definite state associated with the iron atoms in the glassy alloys. This vacancy-like state is intermediate between a pure bulk and a pure vacancy state of the crystalline Fe and explains also the remarkable independence of the annihilation parameters of the type and concentration of the metalloid atoms [65]. The existence of such a definite state has been concluded also for the Pd-Cu-Si system when compared with crystalline Pd [53]. In principle this type of conclusion might have been drawn from all of the studies of metallic glasses in the as-received state although it is not always explicitly shown and concluded by the corresponding authors. From the application of the trapping model [56,65] it follows that in most amorphous alloys the study of the deformation and irradiation - generated defects by means of positron annihilation is of restricted significance because the positron is probably always localized at defects. It explains why negligible changes are detected in the bulk lifetime of e.g. electron-irradiated Pd-Ni-Si [54] as compared to the as-quenched state after production. It

suggests that no stable defects are induced in this way which are observable by positrons. It was supposed that "vacancy-interstitial" pairs created during irradiation recombine either by diffusive processes analogous to those observed in the crystalline phases or through local atomic regroupings similar to those associated with the plastic flow during cold rolling in the Pd-Cu-Si system^[51,53]. A remarkable influence of neutron irradiation has been reported for Mo-Ru-B^[73] and a similar sensitivity of the positron parameters to induced defects is predicted for Ti-Be-Zr in^[65].

Much effort has been spent by complex experiments including heating and cooling of the samples, thus obtaining the temperature dependence of the positron annihilation parameters. From the similarity of these temperature dependences to those of defected crystalline materials the view that vacancy-like defects exist in the glassy material has been concluded e.g.^[59,60]. Theoretical studies^[79] indicate that a single vacancy might not be energetically advantageous in an amorphous medium. It indicates that the defects observed by positron annihilation studies must be more complex entities than the classical monovacancy.

On the other hand it has been proved by this type of experiment that relaxation processes, i.e. the change of chemical short range order, can be followed in the amorphous state, e.g.^[51-53, 61,62,64,66,72]. Extending the temperature range up to the crystallization of the glassy alloys very detailed information regarding the crystallization process was obtained, e.g. a proposed crystallization model^[67] has been confirmed^[46,48] and the activation energy of the crystallization^[69] has also been estimated.

Regarding annealing and/or crystallization of amorphous alloys at a first look some results of different authors obtained on materials of the same nominal composition seem to be contradictory:

- On commercially available $\text{Fe}_{80}\text{B}_{20}$ no difference between the measurable parameters of the amorphous and the crystalline state was found in

[59,60,63,69], whereas for materials produced otherwise a pronounced difference was reported in [58,61,62].

- On $\text{Cu}_{57}\text{Zr}_{43}$ some authors found two lifetime components [65], whereas other authors [48] report only one.
- From the model analysis of their AC data in the Pd-Si system according to the theory of positron annihilation in metals some authors [68] conclude a localization of the positron in the amorphous state near to Si atoms and near to Pd atoms in the crystalline state, whereas other authors [48] definitely exclude such a preference.
- On commercially available $\text{Fe}_{32}\text{Ni}_{36}\text{Cr}_{14}\text{P}_{12}\text{B}_6$ some authors [59,60] found a difference in the measurable parameters between the amorphous and crystalline state, whereas others [58,61-63] did not do so.

The last example could be an indication of the effect of different measuring conditions (measuring temperature: 80 K [59,60] or room temperature [58,61-63] plus a possible influence of etching the samples before each measurement [59,60]. In our opinion all the other examples point to the strong influence of the technological parameters (i.e. the conditions of sample preparation) on positron annihilation parameters, which can easily mask the possibly small composition effects. Such an influence seemed to be noticed by other authors [71] too, but has not been published in details.

In order to test this hypothesis a systematic investigation of the influence of different preparation conditions for the same chemical composition ($\text{Fe}_{40}\text{Ni}_{40}\text{Si}_{14}\text{B}_6$) has been performed, which confirms our hypothesis, and will be presented in details elsewhere [77].

5. Conclusions

The positron annihilation methods (LT,AC,D) have already been widely applied to the investigation of amorphous alloys.

Studies of the as-quenched state have demonstrated the possibility to detect changes of chemical short range order.

From a comparison of results on samples of the same nominal composition a strong influence of the conditions of sample preparation (i.e. technological parameters) on measurable positron annihilation characteristics could be concluded.

Regarding the decision between the two extreme structural models for amorphous alloys, the dense random packing and the microcrystalline model, the positron annihilation method is limited by the fact that positrons prefer to be trapped by vacancy-like defects in contrast to free annihilation and thus changes are to be expected in the measurable parameters only in a given concentration range of defects. It has been observed that in most amorphous alloys positrons are always trapped at defects, i.e. the defect concentration must be very large. At present it seems to be impossible to draw any definite final conclusions regarding the structural models for amorphous alloys from positron annihilation studies.

6. Acknowledgements

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7. Tables

Table 1. Commercial name and chemical composition of some amorphous alloys from Allied Chemical Co., Morristown/NJ, USA

Metglas	chemical composition
2605	$\text{Fe}_{80} \text{B}_{20}$
2605 A	$\text{Fe}_{78} \text{Mo}_2 \text{B}_{20}$
2605 S	$\text{Fe}_{82} \text{B}_{12} \text{Si}_6$
2605 SC	$\text{Fe}_{81} \text{B}_{13.5} \text{Si}_{3.5} \text{C}_2$
2605 Co	$\text{Fe}_{67} \text{Co}_{18} \text{B}_{14} \text{Si}_1$
2826	$\text{Fe}_{40} \text{Ni}_{40} \text{P}_{14} \text{B}_6$
2826 A	$\text{Fe}_{32} \text{Ni}_{36} \text{Cr}_{14} \text{P}_{12} \text{B}_6$
2826 MB	$\text{Fe}_{40} \text{Ni}_{38} \text{Mo}_4 \text{B}_{18}$

Table 2. Collected main information obtained by positron annihilation on M2 glasses. Numbers in the table indicate the corresponding reference number.

system	POSITRON METHOD USED			Significant changes in measurable parameters upon crystallization		Temperature dependence		Crystallization process	influence of a-irradiation 1-electrons 2-neutrons b-cold rolling
	LT	AC	D	yes	no	amorphous state	crystal- lized st.		
Pd-Si	47,48	46,47,48, 68	48	-	46,48,68	47	-	46,48	-
Pd-Cu-Si	49,51,53	50,51,52, 68	-	-	49,50,51, 53,68	52	-	-	51 ^b , 53 ^b
Pd-Ni-Si	54	-	-	-	-	-	-	-	54 ^{a1}
Ni-P	46,48	46,55	-	-	46,48,55	-	-	46,48	-
Ni-Si-B	65	-	56,65	-	-	-	-	-	-
Ni-Al-P-B	52	-	-	-	-	52	-	-	-
Co-P	-	55	-	-	55	-	-	-	-
Co-Fe-Si-B	57	-	57	-	57	57	-	57	-
Fe-B	56,61,62, 65,74,75	61,62,63, 69	56,58,59, 60,61,62, 74,75	58,61,62	59,60,63, 69	56,58,59, 60	59,60	-	-
Fe-Mo-B	56,74,75	69	56,59,60, 74,75	56,60,69, 74,75	-	59,60	60,74	69	-
Fe-Ni-B	57,65	-	56,57,65	-	57	-	-	-	-
Fe-Ni-P-B	61,62,64, 72,74,75	63	58,61,62, 72,74,75	64,72	58,61,62, 63	63,72	-	-	-
Fe-Al-P-B	52	-	-	-	-	52	-	-	-
Fe-Ni-Cr-P-B	61,62	63	56,58,59, 60,61,62	59,60	58,61,62, 63	59,60	-	-	-
Mo-Ru-B	73	-	-	-	-	-	-	-	73 ^{a2}

Table 3. Collected main information obtained by positron annihilation on M1 glasses. Numbers in the table indicate the corresponding reference number.

system	POSITRON METHOD USED			Significant changes in measurable parameters upon crystallization		Temperature dependence		Crystallization process	influence of a -irradiation 1-electrons 2-neutrons b -cold rolling
	LT	AC	D	yes	no	amorph. state	cryst. state		
Cu-Zr	48	48	48	66	48	66	66	66	-
	65	66	65						
Ni-Zr	-	66	-	66	-	66	66	66	-
Ti-Be-Zr	65	-	65	-	-	-	-	-	-
(RE)-Co with RE=Nd, Sm,Gd,Dy,Er	-	66	-	66	-	66	66	66	-
with RE=Nd, Sm,Gd,Tb, Dy,Er	-	70	-	70	-	70	70	70	-
Mg-Zn	-	71	-	-	-	76	-	-	-
		76							
Ca-Mg	-	71	-	-	-	-	-	-	-
Ca-Al	-	71	-	-	-	-	-	-	-

8. Figures

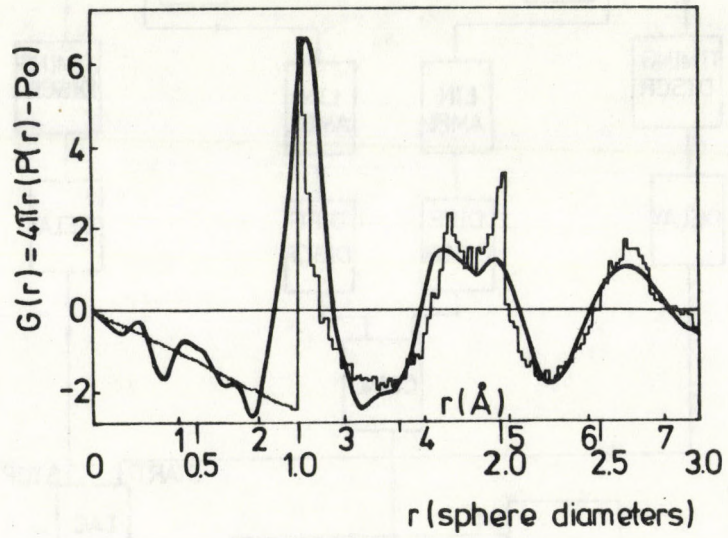


Fig. 1.

Comparison of the measured $\text{Ni}_{76}\text{P}_{24}$ distribution function (continuous line with the histogram derived from DRPHS modelling [12])

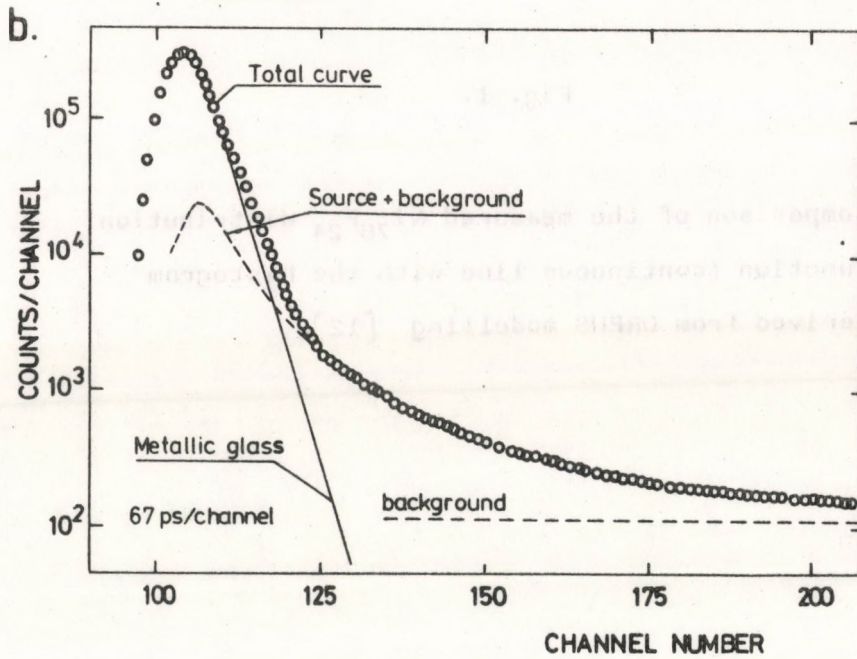
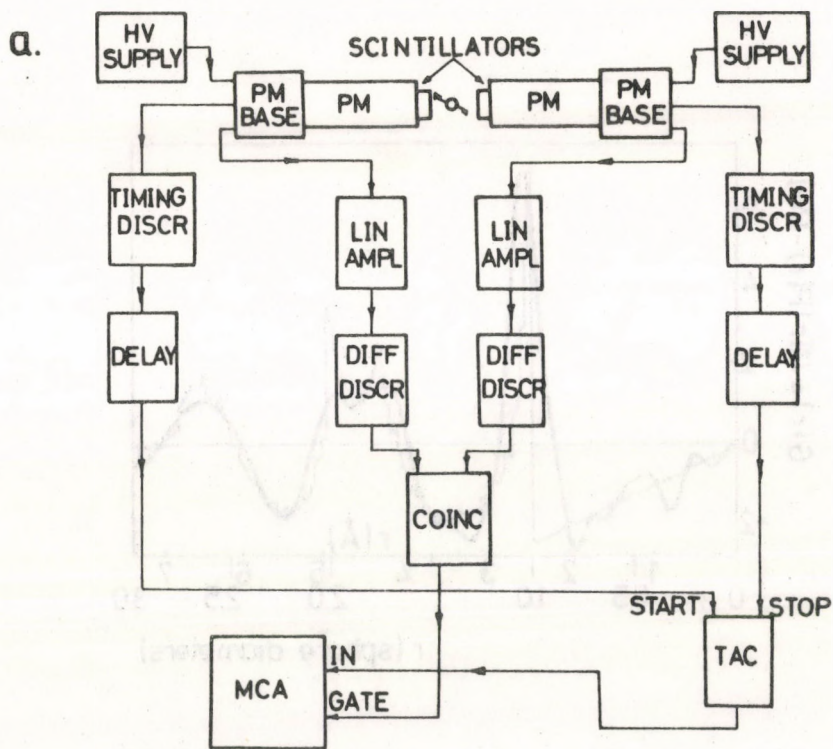


Fig.2. Block diagram (a) and typical spectrum (b) for positron lifetime measurements

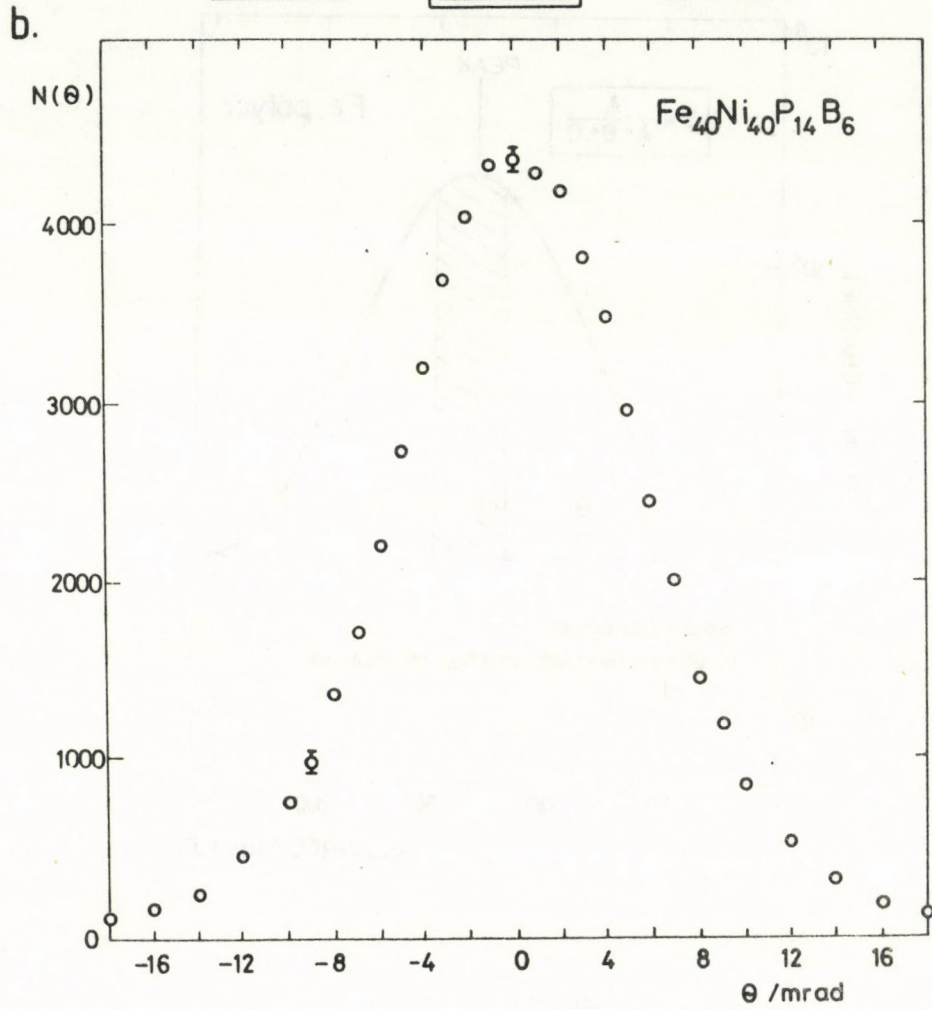
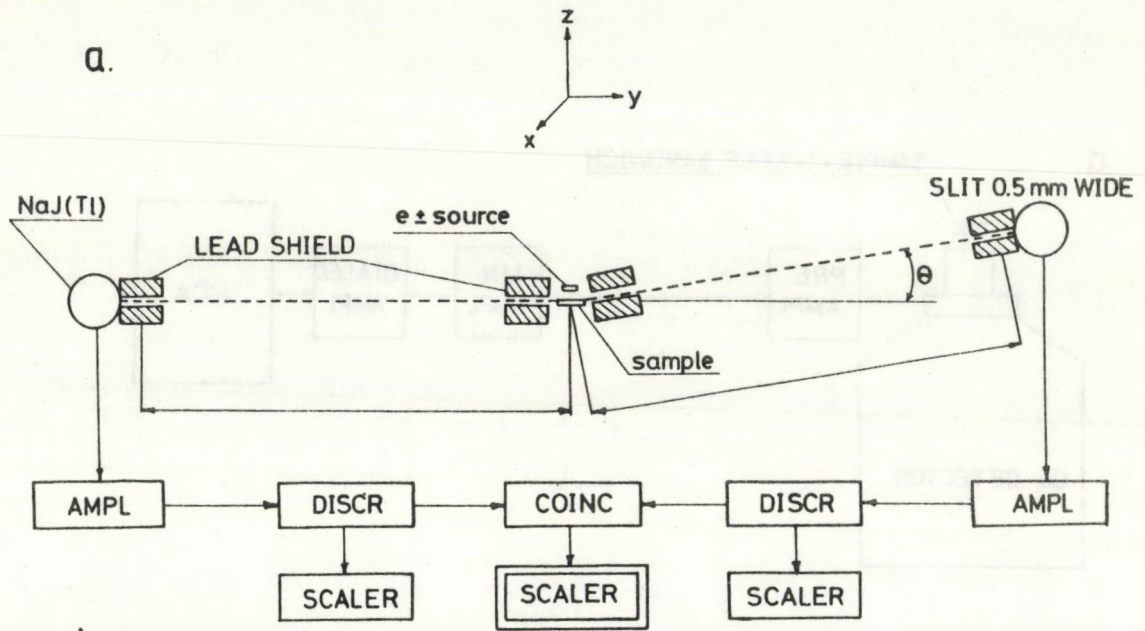


Fig.3. Block diagram (a) and typical spectrum (b) for 2γ -angular correlation measurements

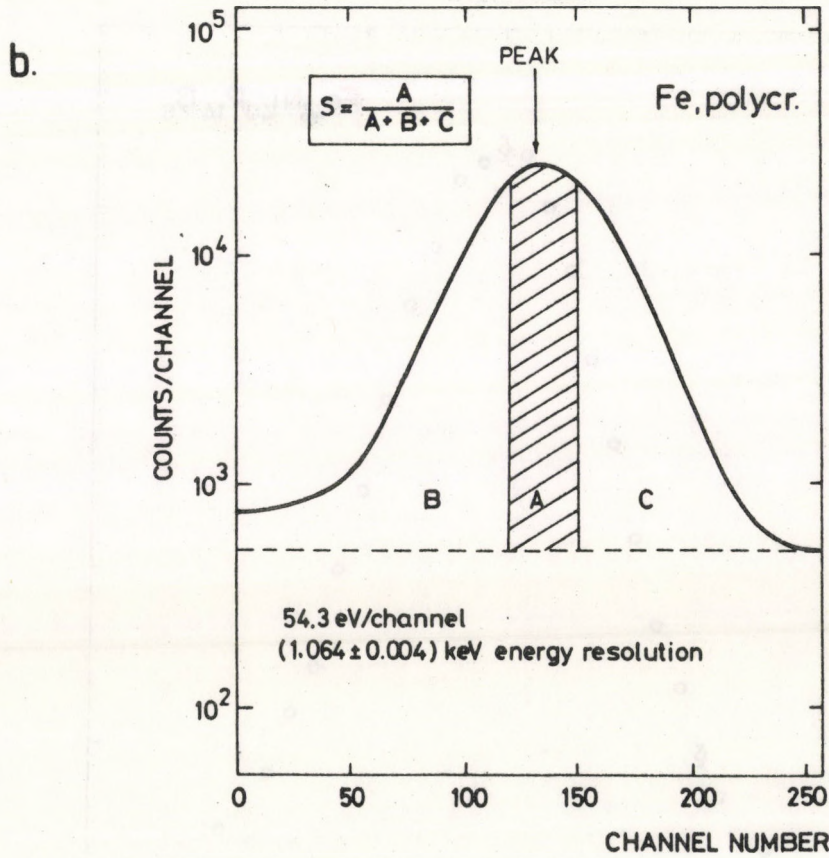
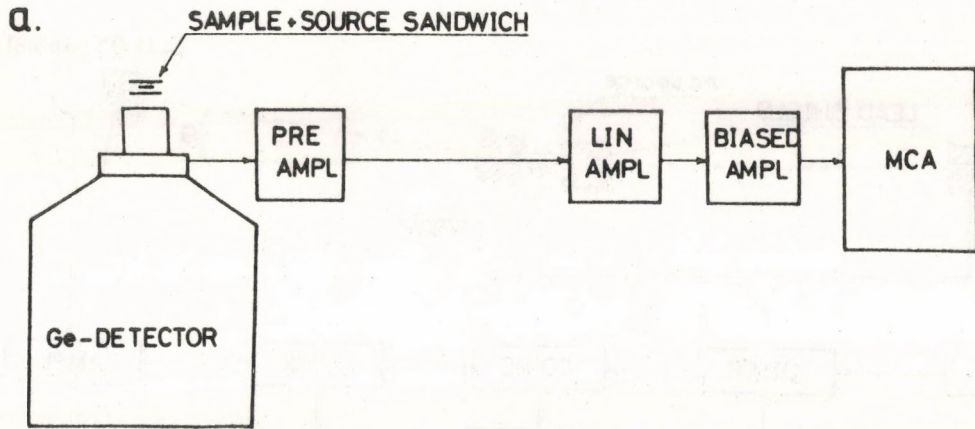


Fig. 4.

Block diagram (a) and typical spectrum (b) for Doppler-broadening measurements

9. References

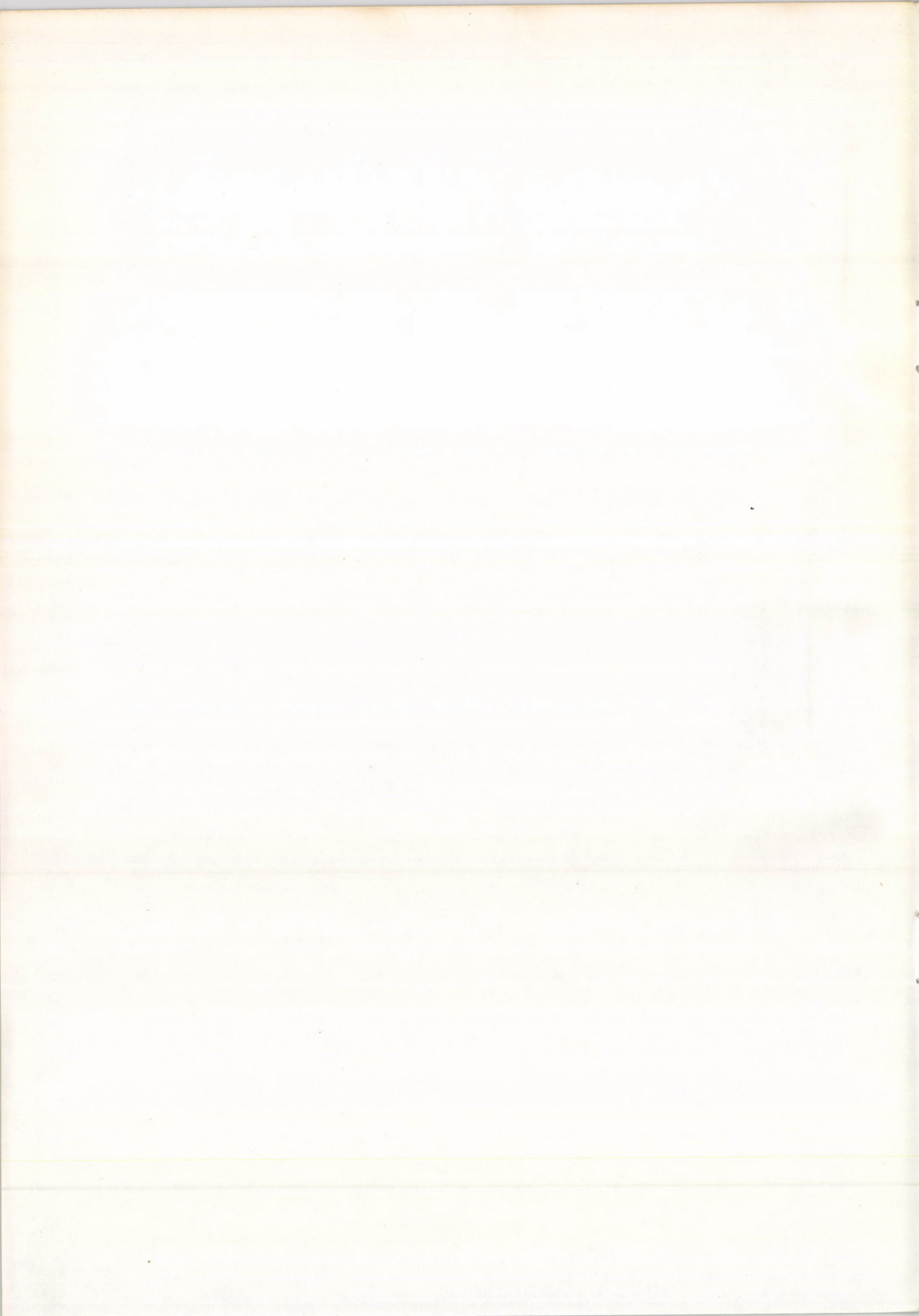
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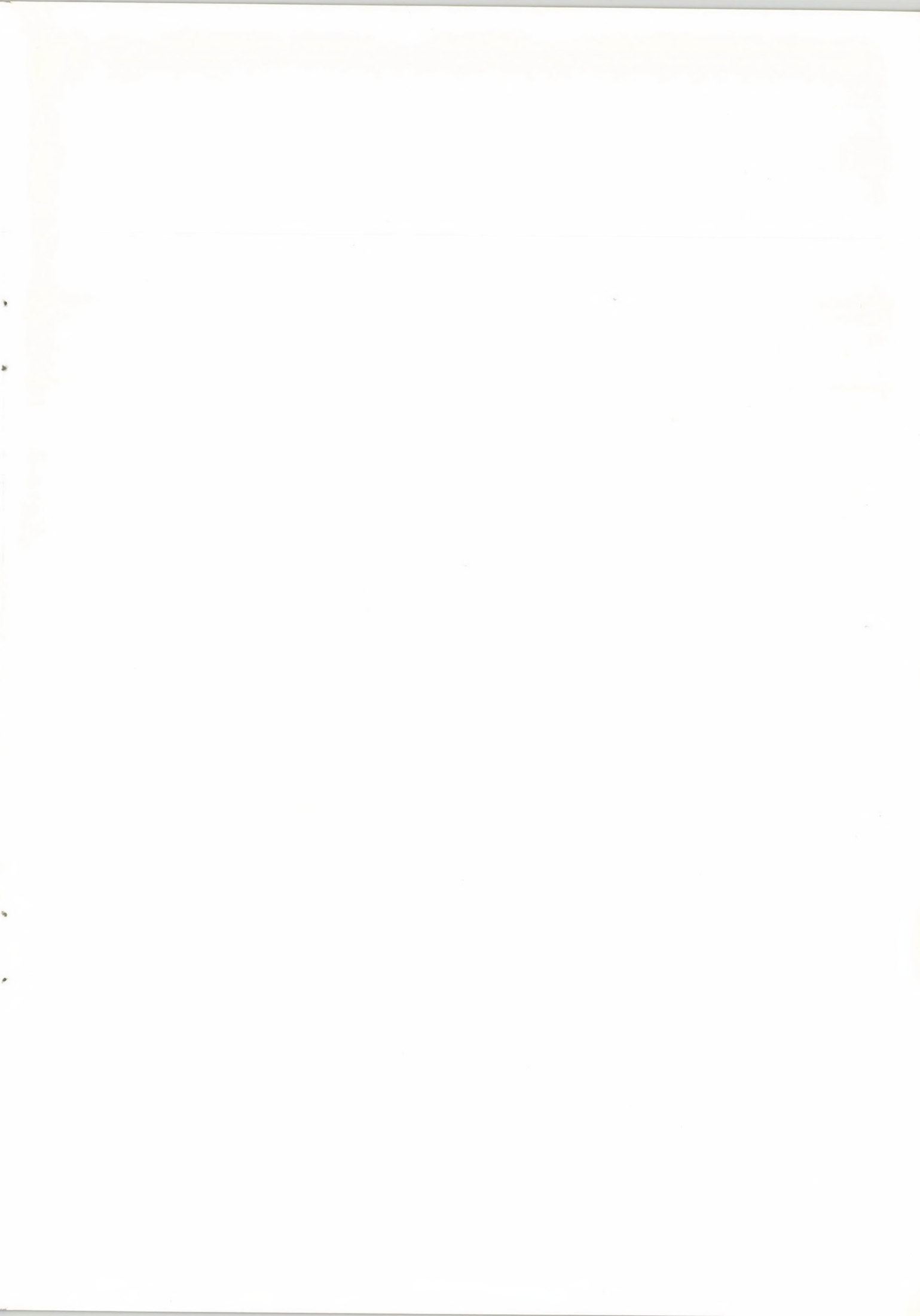
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Kiadja a Központi Fizikai Kutató Intézet
Felelős kiadó: Szegő Károly
Szakmai lektor: Nagy Dénes Lajos
Nyelvi lektor: Nagy Dénes Lajos
Példányszám: 670 Törzsszám: 81-471
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