AUTHOR'S REFERENCE

of the scientific contributions in all works
of Associate Professor Dr. Dragomir Mladenov Tatchev

My current research activity is focused entirely at IPC-BAS, including two specializations in Germany - one one-year and one three-year, and covers scientific and applied research in the following areas:

Area 1 - Investigation of nanometric phase formation or characterization of nanometric phase in different media and materials.

Area 2 - Theory of small-angle X-ray scattering in multiphase systems.

Area 3 - Other articles.

I am a co-author of a total of 49 scientific papers concerning the above thematic areas. In 13 of them I am the first author, and in two of them the only author. These works have been published mainly in foreign journals, 23 of which are in journals in group Q1, 9 - in Q2, 3 - in Q3, 4 - in Q4, one publication is a chapter of a book and the the remaining 9 are published in full text in proceedings of symposia, congresses and conferences with Bulgarian and international participation. To date, a reference by author in Scopus gives 472 citations of my publications without taking into account the self-citations of any of the co-authors. My Scopus Hirsch index is 13, again without self-citation by co-authors. There are 439 citations of works with my participation in the Web of Science and the Hirsch index is again 13. The combination of the two sources gives a total number of citations equal to 488. The majority of the publications published so far correspond to the main thematic priorities of IPC-BAS.

The main contributions according to the above areas of scientific interest and research can be summarized by groups as follows:

Area 1, Investigation of nanometric phase formation or characterization of nanometric phase in different media and materials

The vast majority of my publications use small-angle X-ray scattering and, to a lesser extent, neutrons. The small-angle scattering experiments of all but one article were performed on one of the following synchrotrons: BESSY II in Berlin, DESY in Hamburg, or ESRF in Grenoble. Neutron scattering experiments were performed at the BER II reactor in Berlin and at the ILL reactor in Grenoble.

1.1. Primary crystallization of nickel in a hypoeutectic amorphous nickel-phosphorus alloy.

The emergence of the nanometric phase in the form of nucleation and growth is a traditional topic of IFH, which I have worked on since the beginning of my scientific career. Most articles on this topic are on a model system of hypoeutectic nickel-phosphorus alloy [2, 4, 5, 6, 11, 13, 14, 16, 17, 26], and then move on to gold particles in sodium-calcium glass [18, 20, 29] and to the study of crystallization products in glasses [30, 31, 32, 33, 34, 40]. Central to these systems is the small-angle X-ray Scattering (SAXS), but also of neutrons (SANS). The attractiveness of small-angle scattering is due to its ability to determine size distributions with high statistical reliability in the volume of solid optically opaque media. However, the analysis of the data from the small-angle scattering includes a mathematically incorrect inverse problem, which makes it impossible to simultaneously determine the particle size distribution and particle shape. This necessitates the use of transmission electron microscopy to determine the most suitable particle shape. The latter is used to calculate, usually in analytical terms, the scattering form factor, which is the core of the integral equation for determining the size distribution. Other methods have been used in the research, in particular, a thermomagnetic method has been developed for the study of nickel-phosphorus alloys - a variant of magnetic phase analysis, which has been compared with differential scanning calorimetry (DSC) [2, 4] and dilatometry [6]. Due to the high sensitivity and instantaneous response, the thermomagnetic method proves to be much more informative than the DSC in cases where it is applicable.

Studies of nickel precipitation in nickel-phosphorus alloy are covered mainly in the dissertation for the educational and scientific degree "Doctor" and are included in five publications [5, 8, 9, 11, 13]. Measurements of anomalous small-angle X-ray scattering (ASAXS) performed on the DESY synchrotron in Hamburg were used. The main contributions are as follows. It is shown that the "traditional" method of maximum entropy is completely sufficient for solving the integral equation related to the problem of determining the size distribution of spherical particles by small-angle scattering. The application of the maximum entropy method to the problem of determining particle size distribution by small-angle scattering has been extended so that several scattering curves can be analyzed simultaneously by several size distributions. A method for determining the average particle composition and/or the dependence of the particle composition as a function of their size simultaneously with their size distribution and the composition of the matrix containing them is indicated. For this purpose, the law of conservation of the number of monomers in a binary system has been used. For the process of primary crystallization in the amorphous $Ni_{83}P_{17}$ alloy, the size distributions of the released particles, the change in the composition of the particles with their size, the average composition of the

amorphous matrix and the volume fraction of the particles as a function of the annealing time were determined. The curve number of nuclei - time is constructed and the rate of nucleation, the effective diffusion coefficient and the parameters of the primary crystallization of the nickel-phosphorus alloy at 250°C are estimated.

The most significant of these contributions is the development of a method for the simultaneous determination of particle size distribution and composition. Thus, it turns out that the smallest particles precipitates are not pure nickel, as the equilibrium phase diagram suggests, but contain a significant amount of nickel (up to 14 at.%), which is pushed out during growth. This result is in agreement with the non-classical theory of nucleation of Jürn Schmelzer (Generalized Gibbs approach) and is often cited as its confirmation.

The analysis of in situ data from ASAXS measurements was compared with the results of DSC in a subsequent publication [26], which completes the series of studies on the primary crystallization of nickel in an amorphous nickel-phosphorous alloy. It is shown that the kinetics of nickel separation in the amorphous matrix determined by the data from ASAXS agrees perfectly with the theory of Kolmogorov and Avrami for overall crystallization. The nucleation and growth of a new phase usually take place simultaneously and it is impossible to separate them by most methods of examination, including the DSC or thermomagnetic method, but it would be too laborious with microscopy. SAXS allows direct determination of the curve (number of nuclei)-time, from which the rate of nucleation can be determined, to be used in the extended volume of Kolmogorov-Avrami theory, whence to determine the growth rate. The article [26] also shows that the initial stage of the kinetics of nickel crystallization is in poor agreement with the Kolmogorov-Avrami theory in the case when data from DSC measurements are used. The latter is explained by the change in the composition, and respectively of the thermal effect, with the increase of the particles.

1.2.   Metal nanoparticles in soda-lime glass.

Similar to those for the nickel-phosphorus alloy, ex situ and in situ measurements of ASAXS and SAXS were performed for gold-doped soda-lime glass [18, 20, 29]. After cooling the melt, a supersaturation with gold is obtained, which is released into spherical particles with a new increase in temperature. In this case, no change in the composition with the particle size is observed. The system corresponds to the theoretical model of spherical particles with a small volume part in a matrix and is particularly favorable for small-angle scattering studies. A complete quantitative characterization of the release of gold particles in the soda-lime glass, ie. depending on the annealing time, the change in the number of particles, the average size and their volume fraction are determined.

The glass is sensitive to X-rays, which accelerates the kinetics of particle separation. In the samples annealed at 550°C and constant X-ray irradiation, the process begins about 20 minutes earlier, the number of particles is about an order of magnitude larger, but their size is about 2.2 times smaller, while their final volume is the same as in the samples annealed without irradiation. The curve of the number of particles depending on the annealing time has a maximum in annealing without irradiation, ie. there is a moment (between the 30th and 40th minute at 550°C), after which Oswald ripening is observed - the small particles dissolve and give material with which the large ones grow, and their total number decreases. Such a maximum, ie. Oswald ripening is not observed when heated under X-ray irradiation [29].

The result has a fundamental and applied aspect. Such behavior of delayed Oswald ripening was predicted by Bartels, Schmelzer, Gutzow and Paskova, but was first observed in one and the same system under virtually the same conditions. The explanation is twofold. On the one hand, X-rays create defective centres, so called "colour centres", in the glass, which cause heterogeneous nucleation, and on the other hand, reduce the gold ion to a significantly more mobile gold atom. The result is a larger amount of gold particles with a smaller size and very narrow distribution. Because Oswald ripening depends on the difference in particle size, the narrow size distribution causes a delay. In particular, a hypothetical monodisperse particle system would not undergo Oswald ripening.

In an applied aspect, irradiation with measured doses of X-rays would allow manipulation of the number and size of gold particles. This could even be done locally with X-ray lithography methods. This makes the gold-soda-lime glass system particularly attractive for optoelectronics, in which gold particles find application.

A second studied system of metal particles in soda-lime glass with potential application in optoelectronics is the system of gold-silver alloy or bimetallic particles of the core-shell type [23]. They are obtained by ion implantation of gold and silver ions without further processing. According to high-resolution transmission electron microscopy (HRTEM) observations, the resulting metal particles are spherical in shape, the larger of which are of the core-shell type, with the core having a lower density. By means of anomalous small-angle scattering (ASAXS), a complete quantitative characterization of three samples was made, and for this purpose a new two-stage method of data analysis was developed. The first stage consists in fitting the scattering curves and determining the relationships between the scattering contrasts of the nucleus and the shell of the particles at different energies, compared to those at one of the energies. In this respect, the composition of the core and the shell is calculated. In the second stage, the values of the scattering contrasts are calculated with the compositions thus determined, and the number of particles is determined by subsequent fitting. The

structure of the nucleus turns out to be interesting. In the case when gold is implanted first, the core is completely hollow, and when the silver is implanted first, the core is again of reduced density, but above that of the glass. The latter is interpreted as "looseness", ie. Not as one, but many small cavities. Thus, it turns out that the nucleus is a stock of vacations arising from the ionic bombardment. This is also suggested by the uniform composition of the small, completely dense particles and the shell of the core-shell particles.

1.3.   Crystallization of $Mn_xFe_{1-x}Fe_2O_4$ particles in oxide glass

Studies of the crystallization of spinel nanoparticles in oxide glass from the SiO_2/Na_2O/Fe_2O_3/MnO system [30, 31, 32, 33, 34] are more routine insofar as this can be said for the small-angle scattering method. The main task is to determine the average size, size distribution and average composition of nanoparticles in thermally treated samples. By anomalous small-angle X-ray scattering [30, 31, 32, 34] and small-angle neutron scattering [33, 34], the particle size as well as their increase with the annealing time were determined. The scattering form factor used, which successfully fits the data, is of a spherical particle in a shell. In this case, the core is denser and enriched in iron, and the shell is depleted of iron. The shell is interpreted as a diffusion yard of the nucleus. The core is a magnetite-based crystal in which there is a partial replacement of iron with manganese, $Mn_xFe_{1-x}Fe_2O_4$. Thus, when annealing glass with a composition of $13.6Na_2O$– $62.9SiO_2$–$8.5MnO$ – $15.0Fe_2O_3$-y (mol%) at 550 ° C, the proportion of manganese atoms in the nucleus, x, changes between 0.03 and 0.07 with an increase in the annealing time from 40 to 180 minutes. These results became an essential part of Vikram Singh Raguvanshi's PhD dissertation, which I had the opportunity to mentor during my stay in Berlin and my subsequent visits there.

1.4.   Nanoparticles in confinement

Apoferritin is a hollow spherical macromolecule with an inner diameter of 8 nm and an outer diameter of 12 nm. The preparation of a metal or oxide particle in the cavity of apoferritin or ferritin-like molecules is used to control the particle size. Particles of Fe_3O_4-γFe_2O_3 (magnetite/maghemite) [21, 24], silver [28], Pt, CoPt, Pd, CdS, CdSe, ZnSe and a number of oxides were thus obtained. The crystallization of metal or oxide-filled protein molecules forms a three-dimensional crystal lattice, which is particularly interesting, for example, for the study of magnetic interactions between nanoparticles with strong magnetic properties such as iron oxide.

The characterization of such systems with small-angle scattering differs from the simple determination of size distributions. Protein molecules are practically monodisperse. Their scattering at small angles consists of maxima separated by sharp minima, the depth of which is limited by the

background scattering and / or the resolution of the small-angle scattering apparatus. At the same time, the particles in the protein cavity are not monodisperse, but their maximum size is limited by the protein cavity. This makes it impossible to use both standard distributions, such as Gaussian or lognormal, which have a large tail, and standard software such as SASFit to fit the scattering curves.

The problem is solved by analytically deriving the scattering form factor of a spherical particle attached to the wall of a hollow sphere and using a size distribution of the type of the Lorentz distribution, limited above by the size of the cavity [28, 28_Sipporting_Info]. The distribution and mean size thus obtained are compared with those measured by analytical ultracentrifugation and are in good agreement. The mean size determined by SAXS is slightly less than 1.7 ± 0.9 nm versus 2.1 nm from ultracentrifugation, but the accuracy of the SAXS experiment suggests that the two methods agree.

The task is complicated when the particle-filled protein molecules are crystallized. Since the molecules are nanometric, the lattice period of the protein crystals is of the same order. Therefore, diffraction peaks from the crystal lattice appear on the SAXS scattering curve. The problem is equivalent to the diffraction one with the difference that instead of the atomic form factor the scattering unit is the form factor of the protein molecule with the particle in it. Small-angle scattering has no atomic resolution. In this case, the data analysis requires a separation of the so-called scattering factor and the structural factor describing the interference causing the diffraction peaks. This was done by SAXS and SANS for two types of solid ferritin samples - crystalline and conditionally called - "amorphous" [24]. It was found that the difference in the distance between the protein molecules (respectively between the magnetic crystals in them) in the crystal and in the amorphous sample is about 0.6 nm. This difference, as well as the lack of order, have a significant effect on the magnetic properties of the samples.

A relatively complex task solved by a combination of a large number of methods, including anomalous small-angle X-ray scattering, is the determination of the position of copper added to silicoaluminophosphate (SAPO-5) [47]. Silicoaluminophosphates are a type of molecular sieves which, with the addition of small amounts of copper, are a promising catalyst for various purposes. However, copper can occupy different positions in the SAPO-5 crystal - on its surface, embedded in the crystal lattice or in one of its channels, the largest of which has a diameter of 1.13 nm. In this case, however, ASAXS did not confirm the presence of particles in the confined space of the channel. Two of the three samples tested showed no anomalous effect near the copper absorption edge - these were the samples with less copper 2.3 and 2.6 wt%. This shows that the copper is evenly distributed throughout the sample. The sample with 9.6 wt% copper shows an anomalous effect, but at the smallest angles, where structures larger than 80 nm scatter. This could mean that copper accumulates on the surface

of large blocks, most likely in the form of CuO. In combination with EXAFS (Extended X-ray absorption fine structure) it was found that during hydrothermal synthesis of SAPO-5 copper is embedded in the lattice, during impregnation the copper enters the channels of the crystal lattice, and when impregnated with a large dose of copper, CuO is obtained on the outer surfaces. In different positions, copper has different reduction-oxidizing properties, which allows them to be varied by the method of production.

1.5. Platinum based catalysts

Catalysts on a powder support, which for the most part is some form of carbon, have a specific scattering curve at small angles. It consists of predominant scattering by the support, the intensity of which decreases in an indicative function with distance from the transmitted beam and a 'hump' to the larger angles due to the metal or oxide particles of the catalyst. Separating the scattering of the catalytic particles from that of the support is a major task in this case, and anomalous X-ray scattering offers significant advantages, including for determining the composition of the particles. Often the size distribution of the catalytic particles turns out to be bimodal. In terms of volume, large particles or clusters predominate, but in terms of number and catalytic surface they are a negligible percentage. Most methods, such as XRD, XPS or EDS, do not distinguish small from large particles and give a general picture. ASAXS can distinguish particles by composition and size, which is a significant advantage.

By anomalous X-ray scattering, it has been found that the composition of presumed nickel particles deposited on a carbon and/or TiO_2 powder carrier is closer to that of NiO, $Ni(OH)_2$ and NiOOH than on pure nickel, without excluding small amounts from the latter. This result is confirmed by X-ray electron spectroscopy (XPS), which detects traces of the same nickel compounds. After treatment with a platinum solution for galvanic substitution, these nickel oxide particles dissolve and the deposited platinum particles do not contain nickel [35]. The method of determining the composition is an advanced modification of that used for silver-gold particles in [23]. Again, the ratios of the scattering contrasts are used, but not to the contrast at a selected energy, but to their average value. This reduces the dependence of the measurement error result on the selected one energy.

Area 2 - Theory of small-angle X-ray scattering in multiphase systems

Anomalous small-angle X-ray scattering (ASAXS) uses variable X-ray energy near the absorption edge of any of the chemical elements in the sample. Thus, part of the intensity of the primary beam undergoes inelastic scattering, which is added mainly as an angle-independent background, but the

intensity of the elastically scattered rays decreases. In this way, the small-angle scattering acquires sensitivity to the chemical elements. In practice, ASAXS is a method of varying the scattering contrast.

The theory of small-angle scattering, as developed by Guine, Debye, Kratky, and Porod in the first half of the last century, applies to two-phase systems. However, the two-phase system makes all experiments on contrast variation meaningless, but such experiments have been used successfully for several decades. Theory lags behind practice. An attempt to fill this gap are the two articles of which I am the sole author [19, 25]. They have developed a theory of small-angle X-ray scattering by multiphase multicomponent systems.

To describe the scattering of multiphase systems, single phase scattering functions have been introduced, which represent the scattering of this phase as it would be if it existed alone in vacuum and interphase scattering functions taking into account the interference between a pair of phases. Single-phase scattering functions can be treated with the entire low-angle scattering apparatus for two-phase systems. The interphase scattering functions carry information about the surface between the pair of phases to which they refer.

A generalized expression for the scattering invariant of a multicomponent multiphase sample is derived. Typically, ASAXS experiments consist of measurements at 3 or 5 X-ray energies near one edge of absorption. This suggests that the absorption edges of all other elements in the sample are far enough away that they do not cause an anomalous effect. This is not always the case. Furthermore, a multicomponent system cannot be solved by measuring only the absorption edge of one element. The developed theory allows to determine measurement schemes using several edges of absorption, to determine their number and the minimum number of energies at which the measurements should be performed. The theory is not limited to ASAXS, but applies to arbitrary methods of contrast variation.

The validity of the concept of partial structural scattering factors in the analysis of ASAXS data and determination of the "resonance" scattering curve, which is also a single phase scattering function in case the resonant element is contained only in this phase is proved by the study of Al89Ni6La5 alloy [22]. The resonance scattering curve, determined when measured near the nickel absorption edge, is also treated as a scattering function of a nickel-containing phase. At the same time, for this alloy the possible neutron scattering contrasts are such that the scattering from the nickel-containing phases determines the neutron low-angle scattering curve. It was found that the resonance scattering curve for nickel is proportional to the neutron scattering curve, but differs significantly from the resonance curve defined near the absorption edge of lanthanum [22]. This means that the sample is not two-phase (in which case all scattering curves are proportional to each other), that the nickel-containing

phase is only one, that the resonance scattering curve can be reliably determined, and that it coincides with the scattering function of nickel-containing phase.

The theory of X-ray scattering from multiphase samples developed in this way covers in a consistent way the methods of contrast variation used so far, gives a new vision for their interpretation and reveals possibilities for constructing new schemes for scattering contrast variation. The exact approximations and assumptions in which the equations for an n-component system are reduced to those used in practice, including for two-phase systems, are also given. There are already publications in the literature that actively use equations from the theory just described. The approach to multiphase systems applied to X-ray scattering could also be applied to neutron scattering, taking into account their specificity - magnetic contrast and the possibility of polarization analysis.

Area 3 - Other articles

In several of my publications X-ray computed tomography [37, 40, 41, 43, 45, 48, 49] with the SkyScan 1272 device available in IPC-BAS was used. A significant result was obtained for laser-treated and subsequently coated with chemically deposited nickel or platinum biocompatible polymer [37, 43] and for aluminium-ion battery [45].

The result of laser irradiation of a polymer depends on the wavelength and power of the laser. Laser irradiation of dimethylsiloxane was intended to selectively "activate" the polymer for chemical deposition of a metal, in particular platinum or nickel. The potential application of such systems is the creation of eye implants to restore vision. When passing a certain power of the laser, the known process of ablation is observed - removal and ejection of the material of the irradiated object. However, before ablation occurs, swelling or negative ablation occurs in polymers. In the case of irradiation of dimethylsiloxane with KrF excimer laser, swelling is not a homogeneous process. Conical cavities in the irradiated volume were observed by computed tomography [37]. These cavities are open on the surface of the specimen, but are closed in its volume. Their specific shape is associated with the shape of the beam in its focus, but could also be due to self-focusing. The form of chemically deposited nickel on laser-treated dimethylsiloxane was also monitored by X-ray computed tomography [43].

One of the current trends in research on electrochemical power sources is the use of multielectron chemical reactions. This means that when an ion is transferred inside the battery, several electrons flow into the external circuit. Such is the aluminum-ion battery, which uses as a charge carrier a trivalent aluminum ion Al^{3+} and is a potential competitor to lithium-ion batteries. The anode of the battery is aluminum, which when discharged is oxidized to Al^{3+}. The aluminum ion reacts with $AlCl_4-$

ions entering the electrolyte from the cathode to form $Al_2Cl_7^-$. When the battery is charged, the opposite reaction takes place: aluminum is released at the anode, and $AlCl_4^-$ ions intercalate at the cathode. The intercalation of these ions in highly oriented pyrolytic graphite was studied by low-angle scattering, X-ray diffraction and X-ray computed tomography [45], in order to determine the reasons for the loss of aluminum-ion battery capacity during the first charge and discharge cycle.

During battery charging, the diffraction peak (002) splits into two peaks, which can be used to determine the so-called intercalation degree, representing the number of graphene planes between the planes of intercalating ions. Since the distance between these two planes is relatively large, a diffraction peak appears in the small-angle scattering curve. As charging intercalation progresses, this peak shifts to larger angles as more and closer interplanar spaces are filled with intercalating ions. Conversely, upon dilution, the planes filled with ions are released and the peak shifts to smaller angles. Thus, SAXS allows for direct determination of the degree of intercalation.

Computed tomography did not detect changes in the morphology of the graphite electrode, but when the battery was charged it showed a decrease in porosity, an increase in its thickness and an increase in its ability to absorb X-rays [45]. A direct relationship was found between electrode thickness and degree of intercalation.

The three methods used gave a consistent result, including equal degrees of intercalation within the accuracy. Thus, it was found that after discharging the battery, the graphite cathode does not return to its original state. The loss of capacity after the first cycle is due to the retention of $AlCl^{4-}$ ions in the graphite. The deformation of the peak in the small-angle scattering curve and the change in the porosity at the micro level imply inhomogeneous expansion of the electrode and therefore the generation of mechanical stresses and structural changes in the electrode, which lead to the capture of $AlCl^{4-}$ ions. The high orientation of the base planes of the graphite used and the need for diffusion of $AlCl^{4-}$ ion along the intergranular boundaries perpendicular to these impenetrable planes justify such an explanation.

The small-angle scattering is performed exclusively in the transmission geometry, ie. the x-ray passes through the sample. Although less commonly used, the use of geometry creating conditions for total external reflection is known as Grazing incidence small-angle x-ray scattering (GISAXS). The method is extremely complex as sample preparation, sample adjustment and analysis of the obtained data. GISAXS is very rarely used for in situ temperature experiments, as thermal expansions and changes in density (density changes the critical angle for total external reflection) change the parameters of the experiment geometry and make the scattering curves incomparable to each other.

This problem was solved by using the Yoneda peak to determine the location of the pattern from the 2D detector from which to take horizontal sections equivalent to the scattering curve in the transmission geometry [27]. In this way, the changing conditions of the geometry of the experiment are eliminated, since the Yoneda peak always appears at an angle to the plane of the sample equal to the critical one for full external reflection. This modification of the analysis of 2D images was used to characterize the changes of the sol-gel yttrium-zirconium layers obtained by heating and annealing at 1000°C. Separation of yttrium-enriched and depleted areas has been found to occur, and the scattering phase undergoes Oswald ripening.

In one of the articles, a small-angle scattering was performed on the Empirian laboratory X-ray machine at IPC-BAS to study the structure of a uresilicate polymer [46]. A change in the distances between solid segments of the molecule of one of the polymer components was found when the ratio in the quantities of the starting components for polymer production changed.

In the publications not mentioned so far, I either have a smaller share compared to the co-authors or the achieved result is outside my main areas of scientific interest. The latter include studies with small-angle neutron scattering of rocks from Antarctica [36], the study of deciduous teeth with computed tomography [41] and studies of relaxation of mechanical stresses in metal glass [7].

Many of my publications are include chemical or electrochemical preparation of layers or nanoparticles, to which I have no contribution. My participation in these articles consists in characterization by physical methods - mainly magnetic measurements [3, 10, 15, 42], data analysis [38, 39], heat treatment [39] or preparation of polymer layers of dimethylsiloxane [44] (as well as for those already described [37, 43]).