Cryst. Res. Technol.	34	1999	9	1091–1119

V. G. GRYAZNOV[A)], J. HEYDENREICH[B)], A. M. KAPRELOV[A)], S. A. NEPIJKO[B,C,D)],
A. E. ROMANOV[E)], J. URBAN[C)]

[A)] Institute for High Pressure Physics of the Russian Academy of Sciences, Troitsk, Russia
[B)] Max Planck Institute of Microstructure Physics, Halle (Saale), Germany
[C)] Fritz-Haber-Institute of the Max-Planck-Society, Berlin, Germany
[D)] Institute of Physics, Ukrainian National Academy of Sciences, Kiev, Ukraine
[E)] A.F.Yoffe Physico-Technical Institute of the Russian Academy of Sciences, St. Petersburg, Russia

Pentagonal Symmetry and Disclinations in Small Particles

A comprehensive review is given on experimental studies of small particles with fivefold symmetry accompanied by an in-depth theoretical description of their characteristics and computer modeling. The cases of uniform and nonuniform deformations (disclination model), stability and relaxation of elastic stresses in pentagonal particles and needle-like crystals, models of their formation are discussed.

Keywords: small particle, multiply twinned particle, five-fold symmetry, disclination, stacking fault

Contents

Abbreviations

SP - small particle
PSP - pentagonal small particle
DSP - decahedral small particle
ISP - icosahedral small particle
NC - needle-like crystal
PNC - pentagonal needle-like crystal
SF - stacking fault

1. Introduction

In the field of solid state physics it is well known that the size of the physical object is an important characteristic substantially determining its properties [FENDLER; HALICIOGLU 1988; KREIBIG; MOROKHOV 1977 and 1984; NEPIJKO 1985-1; PETROV 1986; ROMANOWSKI; SCHMID]. Almost every physical phenomenon has its own critical size beyond which the main characteristics of the observed phenomenon start to change radically. Such anomalies are usually considered to be size effects. As a rule, size effects are observed in thin films and needle-like crystals (NC), but are most noticeable in small particles (SP)[1]. Here we analyse one of the most specific size effects, i.e. the formation of 5-fold symmetry axes in SPs and NCs, which is forbidden according to the classical laws of crystallography.

1.1 Small Particles and their Size-dependent Physical Properties

The free surface of SPs greatly influences the formation of their structure and properties. In particular, the surface term of the free energy of SP enables stationary structural phases (including those of pentagonal symmetry), not typical of materials in a bulk state, [MOROKHOV 1984; NEPIJKO 1985-1; PETROV 1986] as well as a change (inhomogeneous in volume) of the lattice parameter [FRIEDEL 1977; MOROKHOV 1977 and 1984; NEPIJKO 1985-1; SAITO 1987]. Besides the change of lattice parameter [KLIMENKOV; NEPIJKO 1998-1; WOLTERSDORF] the change of lattice type [MOROKHOV 1977; NEPIJKO 1985-1] and different reconstruction of faces [NEPIJKO 1985-2 and 3] can occur in SPs. The growing role of the surface does not only influence the lattice, but also the electron subsystem [MOROKHOV 1977; NEPIJKO 1985-1]. For particles of ~100 Å in size the property classification in terms of "volume" and "surface" is rather difficult.

In general, SPs have several specific physical properties: thermal [BOGOMOLOV; NEPIJKO 1985-1], electric [BORZIAK 1965, 1981 and 1990], electronic [FREUND 1998; GORBAN´ 1991; NATSIK; NEPIJKO 1985-1], electron and photon emission [ADELT; BENDITSKII; BORZIAK 1965 and 1976; FEDOROVICH 1993 and 1994; KULYUPIN; NEPIJKO 1982-1, 1992 and 1998-2; VLADIMIROV 1991], optical [CHARLÉ; KREIBIG], magnetic [BUKHARAEV 1998-1 and –2; HADJIPANAYIS; HERNADO; NEPIJKO 1995; NIKITIN 1986 and 1995; PETROV 1996], superconductive [NEPIJKO 1985-1], etc. To a great extent they are associated with quantitative changes in the elementary excitation spectra sensitive to changes in boundary and symmetry. Correlations between particle size and electronic properties on the one hand, and adsorption behavior or catalytic activity on the other hand [FREUND 1997 and 1998; LAMBERT], are observed. Hence, it is quite natural to expect that many of the characteristics quoted are unusual in ensembles of pentagonal small particles (PSP)[2]. For example, it is reasonable to assume that the intersection of pentagonal axes with a PSP surface would yield a specific catalytic activity [WASHECHECK; YACAMÁN 1981].

The collective behaviour of SPs in ensembles influences and manifests the size effects. In this case the arising specific feedbacks lead to a new physical phenomenon. For example, during recrystallization of SP powders the exchange of particle boundaries for point defects drastically changes the solid phase reaction kinetics [GRYAZNOV, 1986]. If a SP ensemble is absorbing electromagnetic waves it will initiate a specific dipole interaction between SPs that qualitatively changes the electrodynamic characteristics of the ensemble [PERSSON].

---

[1] The terminology in this field is not finally determined. Small particles are also called highly dispersed particles, microparticles, fine particles, microcrystals, finely dispersed particles, submicron and ultrasubmicron particles,nanoparticles etc. In this review we use the term "small particles".

[2] Occasionally they are called multiply twinned particles

Collective size effects are investigated less than the properties of the individual SPs are. Nevertheless, in many cases the appearance of the 5-fold symmetry axis can qualitatively be regarded to result from the collective activity of a group of several SPs.

1.2 Pentagonal Symmetry in Small Particles and Quasicrystals

The pentagonal symmetry in SP substantially differs from the so-called quasicrystalline symmetry. The following particulars have been observed in quasicrystals [GRATIAS; POLUKHIN]:

1. Long-range orientational order with the absence of translational order. On the contrary, in PSPs there are some areas with crystallographic packing of atoms separated by low energy twin boundaries.
2. As a rule quasicrystals are made up of two or more kinds of atoms whereas PSP may consist of identical atoms.
3. Each "elementary cell" of a quasicrystal has a non-crystallographic symmetry axis (i.e. a quasicrystal has an infinite number of such axes) but a PSP has only one or six similar axes. (However, SPs of quasicrystalline phases as geometrical objects, generally have a few 5-fold axes [FRIEDEL 1976; MIAO; YU-ZHANG 1988].)

One can list several factors influencing the formation of pentagonal axes in SPs: 1. Small size of the object which makes the volume and surface energies comparable; 2. Anisotropy of surface energy; 3. Low energy of twin boundaries; 4. The original inclination of monocrystalline SPs to agglomeration.

Nowadays, researchers have collected substantial experimental information about decahedral and icosahedral small particle (DSP, ISP) properties and structures, their defects and elastic deformations. Despite the constantly growing interest in the properties of these particles (reflected in a great number of reports and conference proceedings on crystal growth, thin films and atomic clusters), there are not much reviews that intensely highlight this problem in literature. The scope of this review is to fill the gap in this field with special emphasis on bibliography and on a more detailed analysis of the results of recent publications and theoretical models for PSP. Furthermore, it should demonstrate the practical application of PSPs and pentagonal needle-like crystals (PNCs) to the production of new materials.

The present review will discuss the subjects as indicated below.

Section 2 is concerned with experimental methods of SP formation and structural characterization, and with the analysis of experimental results.

Section 3 discusses general features of the pentagonal symmetry in SPs and simple geometrical schemes of PSP structures. The well-known models of PSPs are analysed in comparison with experiments. PSP and PNC disclination models are described in detail along with corresponding size criteria and stability considerations based on these models. Elastic stress relaxation mechanisms in PSP are studied. The basic models of the PSP formation are presented.

Section 4 summarizes the results of PSP studies, with future potential PSP applications introduced.

2. Experimental Studies on Pentagonal Small Particles

This section discusses the fundamental ideas of the correlation between SP shape, composition, structure and conditions of their formation. The most effective methods of PSP structure analyses are examined. Here we have summarized the basic experimental data on PSP study. Particular attention has been given to description PSP defects.

2.1 Growth Characteristics

The physical and chemical states of SP depend on their respective formation processes. The methods applied comprise the plasma-arc method, the vapor condensation method (in vacuum or in inert gas), the electro-spark method, various chemical methods, etc. All these methods are completely listed and described in detail in [MAISSEL; MOROKHOV 1984; PETROV 1986].

The production of SPs is mainly performed at nonequilibrium conditions for formation and growth, which, however, inevitably influence their morphology. In some cases particles adopt structures being far from equilibrium despite the corrections made for size effects. Probably, in some cases SPs do not exhibit a crystallographic habit, faces appear after heat treatment [HEYRAUD]. Since SPs mainly consist of "surface", they may include increased content of impurities in condition that the impurities are localized only on the surface of a bulk crystal and are poorly soluble in its volume because of segregation effect. In other cases impurities easily leave SPs due to closely-spaced surface even if the temperature slightly increases [NOVIKOV]. More close to equilibrium conditions the SP shape is determined to a great extent by the temperature and the composition of the medium in which the particles are grown [WANG] as well as by their size and substrate in use [INO 1969-1; NEPIJKO 1982-2].

The SPs shape and structure can be essentially defined by the coalescence processes. For example, SPs may assume the shape of a dump-bell. Obviously, this is achieved by the fact that during the formation of the final SP geometry diffusion processes are still in progress. Another extreme is the formation of SPs with parallel twins [SMITH 1981-1]. This is probably due to the fact that originally cuboctahedral SPs nucleated in a stream usually share faces thus forming low energy twin boundaries [UYEDA 1973]. This process results in the formation of a system of parallel boundaries to a certain extent resembling the development of twin "stars" during the formation of PSPs by tetrahedrons [DE WIT]). Polyparticles are probably also the result of an incomplete coalescence process. The passive character of the twin boundaries (high angle boundaries disappear quickly [IIJIMA 1987-1]) guarantees the relatively stable state of polyparticles.

The physical characteristics of SPs in dependence on the conditions of their formation have been studied in numerous papers [BUCKLE; NEPIJKO 1985-1; RENOU 1985; UYEDA 1978; WANG]. In [RENOU 1985] the dependence of shape and structure of SPs on the substrate temperature has been determined and certain SP shapes (decahedral, icosahedral, octahedral, etc.) were correlated to defined temperatures. SP properties correlated to the parameters of evaporation in a jet of inert gas are analysed in [UYEDA 1978]. SP properties are shown to depend on the gas nature, its pressure and distribution of temperature in the jet zones. Impurities present in the gas are of particular interest as they influence the kind of the SP behaviour [WANG]. Oxygen is not desirable as it usually slows down the growth of PSPs [WAYMAN]. Special efforts have been made to get rid of it [HOWIE].

The presence of a second component in a solid solution may increase the possibility of PSP nucleation in certain metals, if the second component decreases the specific energy of twin boundaries [CHATTOPADHAYA]. Dendrite structures with several microns transverse size of NCs were obtained by anisotropic growth [BRIEU]. PNCs were experimentally observed in several metals of f.c.c. structure [MELMED 1959 and 1961; WENTORF(jr)]. PNCs may also have the shape of dendrites in a hard matrix, but their typical size will not reach the submicron range [WESTMACOTT]. In some cases aging of quasicrystals [MIAO; MIHAMA] results in precipitates of icosahedral phases.

2.2 Experimental Methods

Almost all analytical methods are used to study geometry and structure of SPs. Electron microscopy, Auger-spectroscopy, X-ray diffraction, nuclear magnetic resonance, positronelectron analysis, etc. are the methods most frequently used. A comprehensive list of experimental methods of studying SP is given in [PETROV 1986].

Usually, the experimental study of the SPs is complicated by their chemical activity owing to surfaces developing, their variation in size, artefacts connected with their tendency to aggregate, adsorption of impurities on their surface or the influence of a substrate. In resonance methods of specific peaks widen because of SPs small mass [GLEITER] as well as a "quasi long-range order" leads to broadening the diffraction reflections in some cases [MOROKHOV 1984; PETROV 1986; SOLLIARD 1981]. Variations in size and a comparatively small number of atoms in SPs result in an appreciable smearing out of critical characteristic parameters [HALICIOGLU 1988; MOROKHOV 1984; PETROV 1986]. Strong interactions of SPs with substrates and between SPs as well as poor vacuum can substantially influence the data of SP structure studies [IIJIMA 1987-2; MARKS 1986-1; VAINSHTEIN]. In general, the conditions listed above make it difficult to explain the experimental results unambiguously.

The methods of X-ray and neutron diffraction are often used to study the SP structure (requiring a considerable number of SPs). Despite the significant power of these methods they become unreliable if there exist particles of different structures in an ensemble of SPs. Electron microscopy enables to solve this problem and to study individual SPs. Nowadays, electron microscopy seems to be the most promising and informative method of studying SP geometry and structure. Computer simulations of image contrasts can be compared with the results of image processing [GAO 1987; GAO 1988; GIORGIO 1988; HEINEMANN 1980-1; IIJIMA 1985-1 and -2, 1986, 1987-2, -3 and -4; LANG; MARKS 1985-1 and 1986-1; NEPIJKO 1986; PETERFORD-LONG 1987-1 and 2; RENOU 1986; SHABES-RETCHKIMAN; SMITH 1986; SOLLIARD 1988; VAINSHTEIN; WALLENBERG 1985 and 1986].

Digital methods of filtration of the electron microscope images applied for improvement of their quality are described in [GIORGIO 1992; NIHOUL]. The possibility of combining different techniques for analysing individual SPs makes modern electron microscopy especially effective. In fact, by changing of the operation modes of the microscope individual particles can be studied by means of high resolution electron microscopy (HREM) [HIRSCH], selected zone dark-field method (SZDF) [HEINEMANN 1972; ALPRESS 1967], method of weak beam dark-field (WBDF) [COCKAYNE; HEINEMANN 1979-1 and –2 and 1980-2; YACAMÁN 1977, 1979-1 and –2], method of selected area electron diffraction (SAED), micro beam method (MBED) [IIJIMA 1985-2; MONOSMITH], method of double electron diffraction (Moiré pattern) [NEPIJKO 1984], etc. Extended description and comparative possibilities of the above-listed methods, as applied to SPs study, are given in [NEPIJKO 1985-1].

HREM is a precise method, which in principle may provide a comprehensive picture of the atomic structure of SPs. If requires, however, experimental image can be compared with calculated images. Simulated images of PSPs are presented in [FLUELI; MONOSMITH]. At the high beam current densities ($\sim 10^2$ A/cm^2) video recording at a time resolution of $\sim 10^{-2}$ s becomes attainable. This high time resolution makes it possible to study dynamics of processes in PSPs.

"In situ" method was applied in SPs study that enabled to observe the process of SPs growth in a transmission electron microscope [YAGI; SATO 1969 and 1971]. In order to study SPs "in profile" they are deposited on the particles having much larger sizes [IIJIMA 1985-1 and 1987-2]. In a high resolution transmission electron microscope vacuum up to 10^{-9} mbar was reached [VAINSTEIN], etc. In the section 2.2 we list the basic methods and even do not pose the problem to list all methods, their variations and combinations applied under SPs investigation.

Advances in PSP (materials and processes involved, formation mechanisms, stability, etc.) made by the above-mentioned methods as well as by some other ones are given in review [HOFMEISTER 1998]. Results of PSP investigation are presented in the next section 2.3 where defects have been received primary attention.

2.3 Experimantal Results

According to their morphology SPs can be divided into two classes: 1.Monocrystalline SPs (the perfect structure is sometimes damaged by stacking faults). 2.Polyparticles[3] [SMITH 1981-1] (dump-bells, biicosahedrons, bidecahedrons, twinned SPs, see section 2.1) and PSPs. SPs having shape of a pyramid, tetrahedron, cuboctahedron, and some more complicated ones should be placed in the first class [GILLET 1979; NEPIJKO 1985-1]. Usually, particles of this class are strongly bound with the substrate and precisely follow the conditions of epitaxial growth. As a rule, the particles of the second class have a weaker interaction with the substrate. They are close to free particles [NEPIJKO 1985-1] (for a weak epitaxy the PSPs grow more easily [HONJO]). Owing to the excess of the boundary energy in polyparticles, they are noticeably inclined to relaxation processes.

The first results of experimental study of PSPs (Au) were reported in the middle of the 60-s [ALPRESS 1967; INO 1966 and 1967; KIMOTO 1967-1 and 2]. Earlier, anomalous reflections in the diffraction patterns of electroprecipitated f.c.c. metals had been found [ALPRESS 1964; MIHAMA]. These reflections can also be explained on the assumption that there is a 5-fold symmetry axis in a bulk crystal. Even earlier, in the late 50-s pentagonal symmetry had been proved to be in NCs grown on a specially selected substrate [MELMED 1959 and 1961; WENTORF(jr)]. However, observation of structures with 5-fold symmetry was first described in [SEGALL]. Up to now PSPs have been evidenced for almost all f.c.c. metals [GILLET 1972; HAYASHI 1977-1; KOMODA; NEPIJKO 1985-1; OGAWA; UYEDA 1978] as well as for Ge and Si [HAYASHI 1977-2; SAITO 1979; WESTMACOTT] and some other elements [DAVERITZ; FARGES 1981; MATSUMOTO]. However, they have not been detected in metals of b.c.c. structure.

To sum up the results of the experimental studies, we list the main types of habits of SPs and NCs with pentagonal axes

1. Decahedral particles (Fig.1.a).
2. NCs in the shape of a right-angled prism with a pentagonal base (Fig.1.b).
3. Icosahedral SPs (Fig.1.c).

It seems that one DSP is the origin of two other ones. As it was mentioned above, SPs possessing the habit of a pentagonal dodecahedron in materials of quasicrystal structure have been identified (Fig.1.d) [MIAO; NISSEN; YU-ZHANG 1987 and 1988].

Usually, the PSP size or the diameter of PNCs was found to be tens to hundreds of Ångströms. These SPs have got a rather perfect structure, i.e. they have a minimum of internal defects. For larger sizes their regularity is disturbed: PSPs may have diameters of more than 1000 Å (see Tabl.1 in review [HOFMEISTER 1998]). It was observed that some PSPs of 300 μm in diameter were bound with the substrate [GEDWILL; NOHARA]. In some cases the PSP habit is modified (Fig.2). New faces are developed instead of vertices [MARKS 1984; NOHARA] (Figs.2.b,c). "Notches" appear along the PSP edges (Figs.2.a,c) [HOFMEISTER 1984; MARKS 1984; SAITO 1979; WHITE]. The growth of the notches implies the development of star-shaped particles [GALLIGAN 1972-1; GAO 1988; IIJIMA 1985-2; KOSTOV; WALLENBERG 1985; WENTORF(jr)]. The crystallographic analysis shows that the external faces of DSPs and ISPs are the close-packed {111} planes of the f.c.c. lattice that makes the formation of the pentagonal symmetry for small particles' sizes energetically favorable, PNC lateral faces are of {100} type (see Fig.1).

---

[3] The components of polyparticles can be formed by different phases [SHIOZAWA].

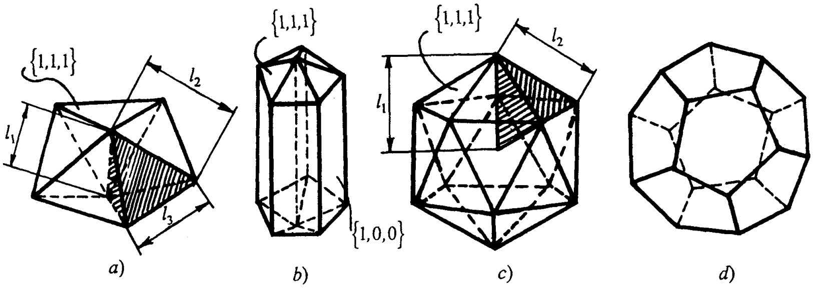

Fig. 1: Small particles of pentagonal symmetry:
a) decahedron - DSP; *b*) prism - PNC; *c*) icosahedron - ISP; *d*) dodecahedron. In *a*) and *c*) closely packed tetrahedrons are shaded.

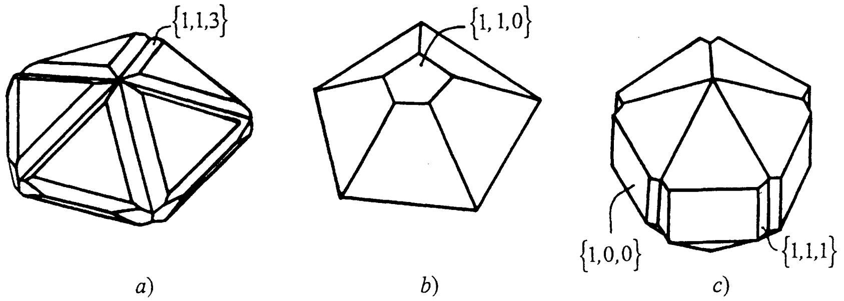

Fig. 2: Habit modifications of decahedral small particles:
a) formation of notches along the sides; *b*) formation of a new face perpendicular to the pentagonal axis; *c*) formation of faces and notches parallel to the pentagonal axis.

Besides differences between the physical and chemical properties of SPs and the same of a bulk material [Morokhov 1977 and 1984], there are differences in their defect structures: the most typical defects of crystal lattice, existing in the bulk materials, do seldom occur in SPs, and vice versa.

The possibility of elastic stress relaxation in PSPs is closely connected with crystal lattice defects. That is why the specific properties of the latter have to be analysed in SPs. In SP stacking faults (SF) are of the most frequent occurrence. The parallel arrangement of SFs to ISP faces is typical of ISPs. A SF is limited by the twin boundary or a Shockley partial dislocation [Marks 1981, 1983, and 1985-1]. It was found that the dislocations are noticeable in particles larger than 150 Å, with the number of defects increasing with SP size [Marks 1981, 1983, and 1985-1; Nepijko 1982-2 and 1986; Smith 1981-2].

Besides SFs and partial dislocations, there are some lattice rotations, however, their nature is difficult to explain. As a rule, in DSPs dislocations are localized near twin boundaries [Iijima 1987-3 and -4] (SFs are very close to twin boundaries). In ISPs dislocations may occur in the central part of a tetrahedron.

The defect structure of PSPs may influence the processes of coalescence. It is shown in [Renou 1977; Yagi] that particles, formed as a result of coalescence, retain the PSP symmetry. A larger-sized ISP is formed during the coalescence of two ISPs. If a DSP and a tetrahedron join, they produce a new DSP having two former orientations.

There are no literature data on any direct observation of point defects and impurities in SPs. However, it was noticed [Yang 1979-1 and -2] that owing to elastic and chemical forces the impurities are able to diffuse out of SPs. They segregate near the SP surface at relatively low temperatures. In [IIJIMA 1987-1] it is proposed that the migration of boundaries in polyparticles may be initiated by vacancies. According to the result of [JULG] the vacancy exchange between SPs plays an important role during recrystallization of an ensemble of SPs.

Up to now there exists only rather vague data on dislocation properties and structure [GAO 1987; IIJIMA 1985-2, 1986, 1987-3 and -4; MARKS 1981, 1983 and 1985-1; NEPIJKO 1982-2, 1985-1 and 1986; SMITH 1981-1; WALLENBERG 1985]. The difference pointed out should be between structural dislocations (they appear owing to the necessity to compensate elastic distortions in PSPs) being of static character and glissile dislocations (they adapt themselves to modification of a certain shape of SPs) being of dynamic character. Usually glissile dislocations are partial.

Refs.[HOWIE; MARKS 1985-1] demonstrate the use of electron microscopy with atomic resolution for studying dislocations in SPs. Using techniques, which is not quite adequate for the precise analysis of SP defect structures, the authors of some papers [HEINEMANN 1979-2; YACAMÁN 1979-1; YANG 1979-1 and -2] doubted the presence of dislocations in PSPs. But later on [SHABES-RETCHKIMAN] the presence of structural dislocations in PSP was proved.

The development of electron microscopy enabled the observation of dynamic dislocations [GAO 1987; IIJIMA 1986; WALLENBERG 1985] in SPs concerning changes in the particle shape (Fig.3). The problem of the structural stability of PSPs was experimentally studied in [IIJIMA 1986, 1987-1, –2, -3 and -4]. SPs of $d = 2 \div 50$ Å were shown to repeatedly change their shape under the electron beam in the microscope in one second (Fig.4) [UGARTE]. This effect is typically associated with the size: the growth of SPs suppresses changes in the shape and the SP mobility on a substrate. The SP shape remains almost stable if the size of a particle is more than 100 Å.

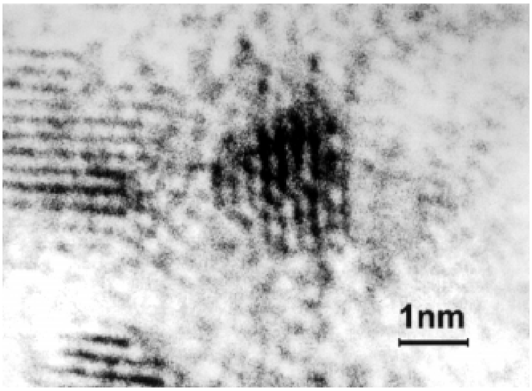

Fig. 3: A dynamic partial dislocation in a small particle of gold. The crystal is slightly tilted off the direction <110> (by courtesy of L.R.Wallenberg).

It has been proven [IIJIMA 1986 and 1987-2] that the structure fluctuations of SPs also occure without temperature effects. Obviously, changes in the SP shape are caused by charge effects as a result of the electron beam action. In fact, electrostatic forces overcome the yield stress if radius A is smaller than the typical value [GRYAZNOV 1989] $l_1^* = \left(q^2/\Theta_1 G b\right)^{1/3}$ on condition that the charge q is localized on a dislocation, or if radius A is smaller than $l_2^* = \left(q^2/\Theta_2 G\right)^{1/4}$ on condition that the charge is delocalized in a SP. Here, the numerical coefficients are: $\Theta_1 = \Theta_2 \approx 10^{-1} \div 10^{-2}$, where G is the shear modulus, b is the Burgers vector. In a typical case, i.e. for $q = 1\bar{e}$ ($\bar{e}$ is the electron charge) it follows $l_1^* > l_2^* \approx 10b$. These estimations are substantiated by the fact that changes in shape rarely occur in the case of conductive substrates when SPs can not maintain the charge [IIJIMA 1987-2].

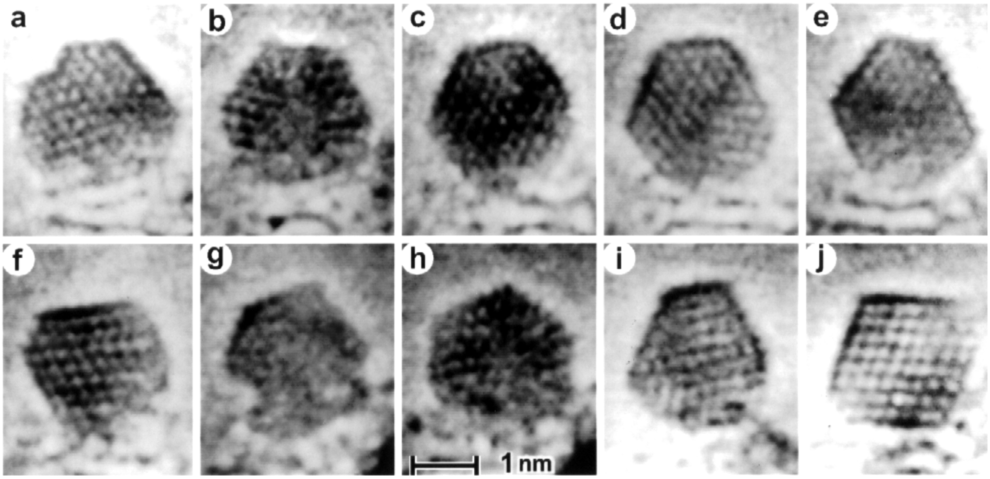

Fig. 4: Different shapes of a gold particle of ~20 Å, changing under the electron beam within five minutes. While in (*a*), (*d*) and (*i*) the particle appears as a single twin, in (*e*), (*f*), (*i*), (*j*) it assumes the shape of a cuboctahedron, and in (*b*) and (*h*) it assumes the shape of an icosahedron (by courtesy of S.Iijima).

As the size of the SPs increases, the structure of the latter acquires a static character. Nevertheless, the investigation of peculiarities of the elastic field in PSPs is a serious problem. The distribution of an elastic field in SP should be considered inhomogeneous that was proved by detailed electron microscope studies [MARKS 1981, 1983, 1985-1 and -2]. Ref.[MARKS 1985-2] critically analyses investigations in which researchers have not observed the inhomogeneity of lattice deformations in PSPs. Furthemore, it contains the conclusion that the inhomogeneously strained state is typical for PSPs. A disclination approach adequately explains the inhomogeneity of elastic deformation in PSPs [DE WIT; GRYAZNOV 1988; MARKS 1984; VLADIMIROV 1986].

With increasing PSPs size (or with increasing diameter for PNCs) no ideal pentagonal symmetry is retained owing to an essential increase in elastic energy. Energy relaxation starts with the formation of structural dislocations [IIJIMA 1987-3 and –4; INO 1969-1; NEPIJKO 1982-2 and 1986], which can form a wall (Fig.5.a). Another way of relaxation may be the formation of a wedge-shaped bulk defect consisting of twinned interlayers, which is located in one of the PSP tetrahedra (Fig.5.b) [HALL 1986; IIJIMA 1987-3 and –4; ISHIMASA]. The elastic energy relaxation in PSPs may also occur by a shift of the pentagonal axis towards the periphery [MARKS 1985-1]. This tendency is enhanced with the size of PSPs [GIORGIO 1988]. Finally, the energy of PSPs can be diminished by splitting the pentagonal axis (Fig.6). Respective structures were observed in [GAO 1988; HOFMEISTER 1984; RENOU 1986].

It should be pointed out that observations and interpretations of defects in the relaxed state of SPs are rather difficult. However, it is quite possible that all variants of the above-listed elastic stress relaxation, which were experimentally obtained mainly in DSPs, also occur in ISPs.

Despite the availability of numerous experimental data, stress relaxation mechanisms in PSPs have not been analyzed in detail. This problem will be discussed in the section 3.6.

3. Theoretical Description of Pentagonal Small Particles

The main geometrical characteristics of PSPs are given here. Theoretical approaches to the description of physical properties are formulated with a detailed analysis of theoretical models based on the continuum approximation. The main channels of the disturbance of the 5-fold symmetry caused by the increase of the PSP size are analysed.

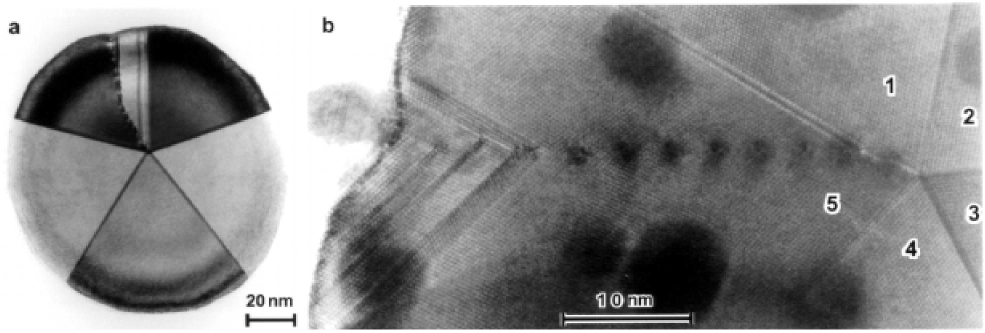

Fig. 5: A silicon decahedral small particle with lattice defects in one of the tetrahedrons:
a) general view of the particle; *b*) defect structure of a tetrahedron: a small-angle boundary consisting of edge dislocations connects the pentagonal axis with a wedge-shaped system of stacking faults. A defect structure occurred as the result of elastic stress relaxation, (by courtesy of S.Iijima).

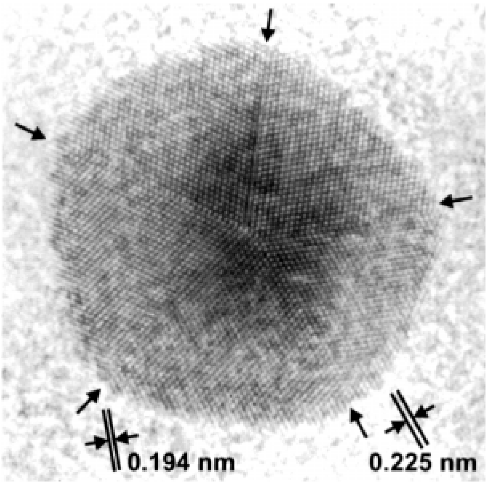

Fig. 6: High resolution micrograph of a decahedral small particle of palladium along the pentagonal axis. The splitting of the pentagonal axis into two nodes is clearly seen with the notches at the end of the twin boundaries indicated by arrows, (by courtesy of A.Renou).

3.1 Geometrical Characteristics

A DSP has 7 vertices, 10 faces, 15 edges, one 5-fold symmetry axis, one mirror symmetry plane perpendicular to it and five other planes containing this axis.

If the atomic planes of a DSP are completely packed, the structure of the DSP becomes most stable. The number of atoms of these "magic" DSPs is $N_\mathrm{d} = \frac{n}{6}\left(10n^2 + 15n + 17\right)$, where n - is the number of the atomic shell, forming the series: 7, 29, 76, 158, 285, etc. The DSP volume density is ~ 0.72 (an infinite cluster with an orthorhombic packing of atoms). It is somewhat lower than the packing density of a f.c.c. lattice (~ 0.74) [BAGLEY 1970]. This is also true for PNCs.

An ISP has 12 vertices, 20 faces, 30 edges, 6 five-fold axes passing through the vertices, 10 axes of the third order crossing the centers of the faces and 15 mirror symmetry planes perpendicularly crossing the edges. For of the shell model "magic" clusters have the number of atoms $N_\mathrm{i} = \frac{1}{3}\left(10n^3 + 15n^2 + 11n + 3\right)$, forming the series: 13, 55, 147, 309, 561, etc. [Nepijko 1985-1]. The volume density of ~ 0.69 of an ISP is rather low (an infinite cluster with the local rhombohedral packing of atoms) [Mackay].

The above mentioned polyhedra can be represented as joint tetrahedra with slightly deformed axes (because three-dimensional space cannot be closely packed with regular tetrahedra of equal size [Mackay; Nelson]). For DSPs (Fig.1.a) two types of relations between lengths l_1, l_2, l_3 of tetrahedron edges are possible: 1. $l_1 = l_2$, $l_3 = \sqrt{3}\sin\frac{\pi}{5} \approx 1.02 l_2$ (here $l_1 < l_3$); 2. $l_2 = l_3$, $l_1 = \sqrt{3 - \mathrm{ctg}^2\frac{\pi}{5}} \approx 1.05 l_2$, ($l_1 > l_3$). The distance from the center of an icosahedron to its vertices (Fig.1.c) is less than length l_2 of the edges belonging to its surface ($l_2 \approx 1.05 l_1$). Thus, during the packing of regular tetrahedra into icosahedra and decahedra inevitable gaps appear (a fixed-angle deficiency) (Fig.7). In case of a DSP the fixed-angle deficiency β_d is equal to $\beta_\mathrm{d} = 4\pi - 20\arcsin\frac{\sqrt{3}}{3} \approx 0.08\pi$; for an ISP, β_i is six times larger, i.e. $\beta_\mathrm{i} = 6\beta_\mathrm{d} \approx 0.48\pi$.

There are some other ways of a geometrical description of icosahedra and decahedra. Methods of spherical trigonometry can be used to demonstrate that at the edges of an octahedron the icosahedron can be constructed (Fig.8.a) [Berger]. It is not difficult to eliminate the fixed-angle deficiency which also occurs with the packing of tetrahedra. The surface of thus constructed icosahedron is formed by $\{111\}$ planes and $\{1-\tau, \tau, 0\}$ planes (with $\tau = \frac{\sqrt{5}+1}{2}$), which are of non-crystalline character. That is why single-component ISPs without internal stresses can not be formed.

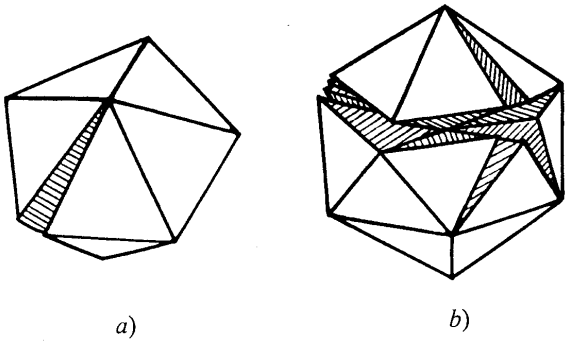

Fig. 7: Solid angle deficiency in SP constructed of regular tetrahedrons.
a) A decahedron with a vertical split.
b) An icosahedron with a split in its complex configuration.

One more regular polyhedron having 5-fold symmetry axes, i.e. a dodecahedron, should be mentioned here. It has 12 faces, 20 edges, 30 vertices, 6 axes of the fifth order passing through the centers of the faces, 10 symmetry axes of the third order passing through the vertices and 15 mirror symmetry planes perpendicularly crossing the edges. The characteristics listed show the geometrical similarity between an icosahedron and a dodecahedron. This conclusion is also drawn from the principle of duality [Berger] (i.e. an icosahedron can easily be transformed into a dodecahedron, and vice versa). Hence, it seems strange that dodecahedral single-component SPs have not yet been observed.

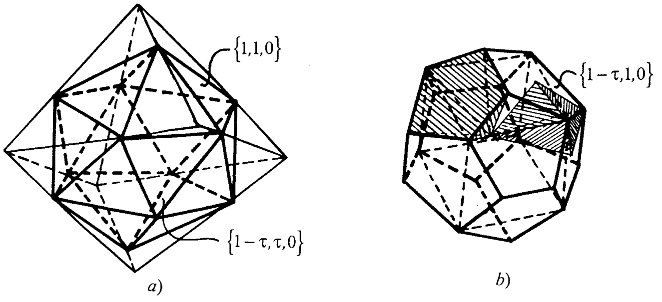

Fig. 8: Crystallogeometric description of polyhedrons with a symmetry axis of fifth order.
a) An icosahedron built on octahedron.
b) A dodecahedron built on a cube. A pyramid with a pentagonal base and a hexahedron are shaded.

In principle, a dodecahedral particle can be formed in several ways. A relatively simple algebraic analysis shows that a dodecahedron can be built on the base of a cube [Berger] (Fig.8.b). But in this case the particle gets faces of non-crystalline nature $\{1-\tau,1,0\}$. This is not true for traditional single-component materials. A dodecahedron can also be made of multiply twinned hexagons (Fig.8.b). At first sight, it may be most beneficial to b.c.c. structures: in this case closely packed planes $\{110\}$ emerge onto the particle surface with the twinning process taking place along low-energy boundaries $\{112\}$. Nevertheless, it does not occur in practice because the formation of dodecahedra by the twinning of b.c.c. crystals along the boundaries $\{112\}$ causes a physically unusual large elastic deformation of ~40% of the crystals.

As reported above, quasicrystalline dodecahedral SPs were recently discovered [Miao; Nissen; Yu-Zhang 1987 and 1988]. We can suggest that, like PSPs, these particles can be formed by the mechanism of sequential twinning of pyramids having a pentagonal base (Fig.8.b), when most closely packed "quasicrystal faces" emerge on to the SP surface. However, a more detailed study of quasicrystalline SPs would be beyond the scope of this review.

3.2 Computer Simulations

Numerical simulations of clusters consisting of $N \sim 10^1 \div 10^3$ atoms provides a possibility of the accurate study of some SP characteristics, such as the energy of the ground state, the binding energy, the evolution of the SP structure, etc. As a rule, any simple interaction potential is used, and the atomic configurations guaranteeing a minimum thermodynamic potential for the prescribed number of interacting atoms is determined.

First fundamental studies [Alpress 1970; Fucano] implied semiquantitative estimations based on the calculation of atoms in a SP volume and on the surface. They were preceded by some calculations using the method of molecular dynamics for clusters [Valkealahti], containing a small number of atoms ($N \sim 10^2$) whose interaction was described by the pair of central potentials [Burton; Hoare 1972; Petrov 1986; Uppenbrink]. In some cases the use of methods of quantum chemistry was rather effective [Bonissent; Gaspard; Gordon; Julg], as it was also proved by some authors in a modified form [Blaisten-Barojas; Briant; Cyrot-Lackmann; Farges 1977, 1980 and 1987; Halicioglu 1981; Hoare 1979 and 1983; Khanna]. Calculations have been carried out for polyparticles (biicosahedra, triicosahedra) [Farges 1987], and it was demonstrated that these SPs (contrary to ISPs [Gillet 1976]) grow rather slowly owing to the presence of high internal stresses.

In recent years the development of powerful computers largely extended the potentialities of numerical simulations. It became possible to study SPs containing several thousands of atoms [HALICIOGLU 1988]. It was proved that in "magic" icosahedral clusters the energy of the ground state is separated from the level of excited state by a perceptible energy gap. The SP state corresponding to the high energy levels can be classified as quasi-liquid because in this state many physical characteristics are substantially changed [HALICIOGLU 1988; HONEYCUTT]. However, such calculations are now possible only for simple systems (inert gases). Nevertheless, these results are very useful because they reveal important properties of clusters (for example, the inhomogeneously stressed state of icosahedral clusters [FARGES 1980; LEE; SHABES-RETCHKIMAN], a higher packing density relative to that of octahedra [SHABES-RETCHKIMAN]). These results contradict the presumption of a homogeneous deformation of the SP crystal lattice [BAGLEY 1965; MACKAY] (see sections 3.1, 3.3).

The method of molecular dynamics also revealed a inhomogeneously stressed state of the pentagonal two-dimensional clusters [DOYAMA; MIKHAJLIN; ZHIGILEJ]. These clusters were formed by a perfect disclination being inserted into an initially unstressed triangular lattice.

The major result of the above mentioned papers is the conclusion that the small icosahedral and decahedral clusters are stable relative to their transformation into the embryo of usual crystal structures. However, even for simple interatomic potentials it is impossible to accurately obtain the critical size of the PSP transforming into an ordinary structure [HALICIOGLU 1988; HONEYCUTT; LEE]. However, there exist a molecular dynamics calculation for Cu clusters [VALKEALAHTI] which predicts a critical size for the transition of icosahedral to cuboctahedra f.c.c. structure.

It should be noted that the microscopic approach has some further drawbacks. First, the interaction potentials are generally applicable only to qualitative analyses [UPPENBRINK]; second, within this approach it is very difficult to study reliably the structure of large clusters ($N \sim 10^3$) or SPs.

Another possibility of describing the SP structure is the use of macroscopic material parameters (elastic moduli, surface energy, energy of twin boundaries, etc.) initially calculated from the first principles or experimentally measured. The macroscopic approach allows to observe the evolution of the structure and development of the crystal lattice defects in SPs over the whole range of the SP sizes (if $A >> a$, where a is the lattice parameter).

3.3 Models of Homogeneous Deformation

The PSP stability [BRIEU; INO 1966, 1969-1 and -2; OGBURN] was first explained on the basis of a homogeneous deformation of the PSP crystal lattice: the tetrahedra forming the PSPs are considered to be homogeneously deformed. They are deformed either towards one of the vertices in the case of ISPs, or towards one of the edges in the case of DSPs. DSPs are formed by 5 tetrahedra joining along 5 twin boundaries, ISPs - by 20 tetrahedra forming 20 twins. All known DSPs and ISPs have twin boundaries {111} and external faces {111}. The habit may be modified by the formation of new faces,see section 2.3.

In this model the elastic energy is calculated in a trivial way. The simplest analysis of a PSP structure transformation into the nearest crystalline shapes reveals the two characteristic sizes A^{m}, i.e. the size of the highest stability of PSP structure, and A^*, i.e. the critical size of the PSP stability. (The inequality $A^{\mathrm{m}} < A^*$ is always obeyed. For example, for the transition of an icosahedron to a tetrahedron $A^{\mathrm{m}} = \frac{2}{3} A^*$ satisfies this inequality). The calculations [INO 1969-1] show that value A^* is very large for DSPs. However, this contradicts the experimental data and the results of computer simulations [ALPRESS 1970; HALICIOGLU 1988; NEPIJKO 1985-1; WAYMAN]. In addition, the accuracy of the estimations [INO 1969-1] was repeatedly questioned (for example [MARKS 1985-1]).

In [YANG 1979-1 and -2] it was proven that PSPs consist of tetrahedra, the lattice of which was undergone a phase transformation. In fact, DSPs can be produced from tetrahedra having an orthorhombic base centred structure [BAGLEY 1965 and 1970; MACKAY] (the initial f.c.c. lattice is deformed by the value up to 5% along <110>, see section 3.1). ISPs can be composed of tetrahedra of rhombohedral structure (the initial f.c.c. lattice is deformed along <111>). In principle, according to these models PSPs should be able to grow up to infinitely large sizes. However, this does not correspond to the experimental data.

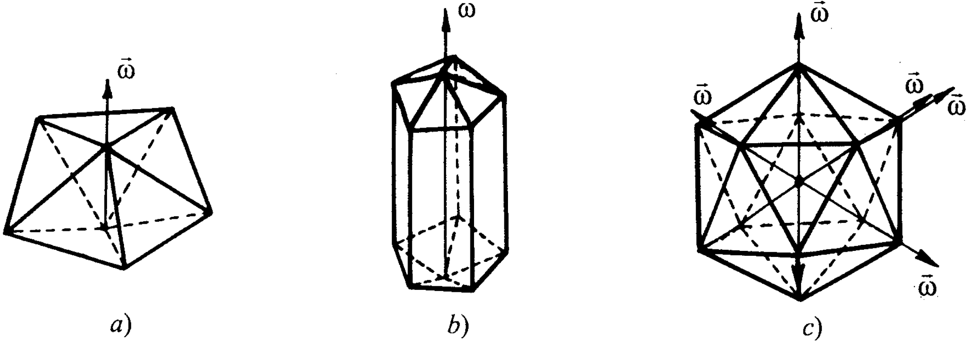

Fig. 9: Disclinations in pentagonal small particles and needle-like crystals. The disclinations are parallel to the pentagonal axes: *a*) in a decahedron; *b*) in a pentagonal needle-like crystal; *c*) in an icosahedron.

3.4 Disclination Models of Inhomogeneous Deformations

A fixed-angle deficiency in packed tetrahedra forming a PSP (Fig.7) necessarily leads to a disclination in a particle in order to eliminate this deficiency. In fact, according to the definition there is a linear wedge-shaped disclinations at the edges of a wedge, which is either inserted into or taken out of the material [VLADIMIROV 1986]. For PSPs, this procedure actually corresponds to the removal of some wedge-shaped material from a particle and the gluing together of the faces of cut. In the wedge there is a linear positive disclination, with parameter ω denoting the wedge angle. For DSPs and PNCs the material has one disclination coinciding with the 5-fold symmetry axis. The disclination has the wedge angle $\omega = \frac{\beta_\mathrm{d}}{2} = 7^\circ 20'$ (Figs.9.a,b) [UYEDA 1973]. For an ISP, it is necessary to introduce even 6 disclinations of this kind connecting the opposite vertices of the icosahedron (Fig.9.c) [WAYMAN]. It is essential that in the icosahedron surface of the cut is not smooth owing to the introduction of disclinations. This surface consists of the three conjugate plane areas. This situation leads to the difference in disclinations between an icosahedron, a decahedron and a PNC.

The possibility of describing PNC structure and properties with regard to disclinations was first mentioned in [GALLIGAN 1972-2; HALL 1973; UYEDA 1973]. Ref. [UYEDA 1973] gives the scheme (Fig.10) of a cross-section perpendicular to a pentagonal symmetry axis in PNCs. This cross-section is crossed by the five twin boundaries. In f.c.c. crystals they are $\{111\}$ planes, with the misorientation of these boundaries being $\sim 7^\circ 20'$ (i.e. the pentagonal symmetry axis corresponds to a disclination of $\omega = 7^\circ 20'$). This disclination is called partial disclination [VLADIMIROV 1986]. Its typical characteristic is the presence of five disclinational "stacking faults", i.e. twin boundaries intersecting the pentagonal axis. This property justifies these defects in PNC called "star" disclinations. In the same way a defect of configuration in ISP (Fig.9.a) may be called a "hedgehog" disclination. It should be pointed out that point disclinations (called "hedgehog", too) are defects typical of the systems of directors in nematic liquid crystals [KLEMAN]. In our case the "hedgehog" has a small number of needles (twelve), i.e. lines of disclinations.

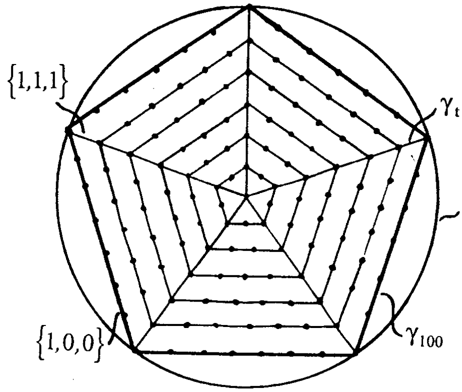

Fig. 10: Atom sites in the section of a pentagonal needle-like crystal (a "star"-disclination).

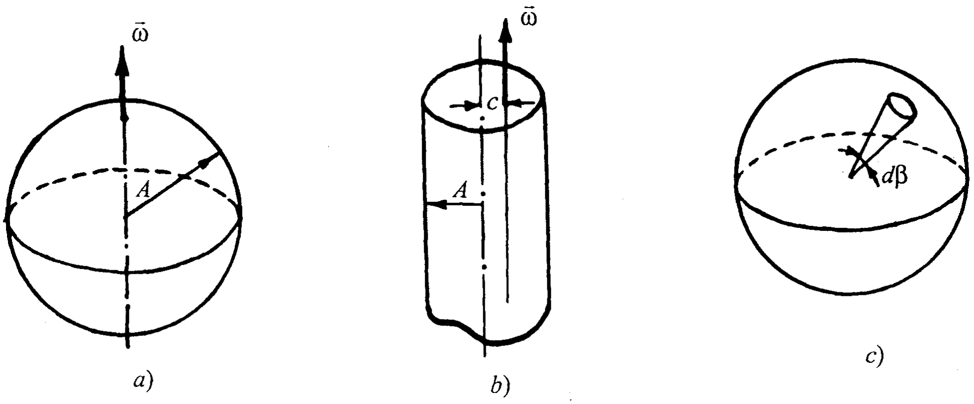

Fig. 11: Continuum models of disclinations in pentagonal small particles and needle-like crystals: *a*) a disclination passing through the center of a sphere; *b*) a disclination shifted from the axis of a cylinder; *c*) a cone disclination in a sphere.

A disclinational approach to the analysis of the elastic-stressed state of PSPs and PNCs is most attractive because the presence of a disclination in a material automatically leads to inhomogeneous stresses, thus corresponding to findings of recent experiments (see section 2.3). Besides, the well-developed mathematical apparatus of the theory of disclinations allows one to analyze rather complicated situations for deviations from an ideal five-fold symmetry (an abnormal position of the pentagonal axis, its splitting, presence of other defects, etc.). The above-mentioned reasons show the effectiveness of the disclinational approach.

The elastic field and the elastic energies of disclinations are calculated with consideration for the boundary conditions on the surface of a particle or a NC. Very often it is possible to derive the shape of PSPs and PNCs from that of close geometry (Fig.11). For example, the approximation of NCs to infinity by an isotropic cylinder is quite natural (Fig.11.b). To analyze the elastic field in DSPs a slice of an infinite cylinder was considered [DUNDURS;

GRYAZNOV 1988; MARKS 1986-2]. A sphere is the most appropriate approximation for all PSP shapes (Fig.11.a). A disclination intersects the diameter of the sphere or the axis of the cylinder. It can also be displaced from the sphere diameter or the cylinder axis (Fig.11.b). Finally, one more way of eliminating a gap in PSPs is to use disclinations [WAYMAN], where the cone-shaped material is removed from ISPs (Fig.11.c). Several such cones of a total fixed angle deficiency β_{i} (or an infinite number of cones with an infinitesimal fixed angle $\delta\beta_{\mathrm{i}}$) can be removed from the ISPs that corresponds to the formation of point disclinations (Marks-Yoffe model [MARKS 1986-1]).

Elastic fields and energies of disclinations in an infinite elastic cylinder have been studied in detail [DUNDURS; HUANG; LURJE; MARKS 1986-2; RICHTER; ROMANOV; VLADIMIROV 1986]. In particular, [RICHTER] gives the tensor components of elastic stresses for a cylindrical PNC of radius A with a disclination of ω displaced from the axis to the periphery at distance c. The corresponding linear elastic energy [DUNDURS; HUANG; LURJE; RICHTER; ROMANOV; VLADIMIROV 1986] is given by

$$\varepsilon^{(\mathrm{D})} = \frac{G\omega^2 A^2}{16\pi(1-\nu)}\left[1-\left(\frac{c}{A}\right)^2\right]^2 , \tag{1}$$

where ν is Poisson's ratio.

Radius A^* of PNC stability relative to the transition into a monocrystal is given by

$$A^* = \frac{32\pi(1-\nu)}{G\omega^2}\left[f\bar{\gamma} - \frac{5\gamma_{100}}{\pi}\sin\frac{\pi}{5} - \frac{5\gamma_{\mathrm{t}}}{2\pi}\right] , \tag{2}$$

here $\bar{\gamma}$ is the effective surface energy of a monocrystal, γ_{100} is the surface energy of the (100) face (Fig.10), and γ_{t} is the energy of twin boundaries.

Coefficient f is equal to 1 if a change of the surface energy is analyzed for a transformation from the pentagonal prism to the cylinder of the same radius; $f \approx 0.87$ - if areas of their sections are equal.

The formation of disclinations in SPs and NCs causes the compression of material to be in the centre of a SP, but not deformation towards the periphery. However, the calculations made within the linear theory of elasticity predict a zero total dilatation caused by the disclinations [ZHIGILEJ]. The occurrence of total dilatations is particularly a non-linear effect. For its estimation it is necessary to analyze a non-linearity influence on the elastic characteristics of the disclination [VLADIMIROV 1988]. The inhomogeneous deformation of the PNC and PSP lattices may influence the character of the local positions of the lattice defects. Their occurrence diminishes the PNC and SP elastic energies. The inhomogeneity of the deformed state influences the inhomogeneous distribution of other components, thus causing the specific features of phase growth as well.

The disclinational approach allows one to analyze various situations arising during the growth of heterophase PNCs in materials, requiring the study the elastic energy of the disclination in a heterophase of NC, for example in a two-phase NC. In this case the line of a disclination coincides with the axis of a cylinder. Inside the area of radius A_1 the elastic moduli are given by G_1, V_1 and in the layer of $A_1 < r < A_2$ they are G_2, V_2, respectively. There are essentially different situations: 1. The boundary is coherent, i.e. there is a disclination in area "2" (pentagonal symmetry intergrows from phase "1" into phase "2", which can be an oxide shell, a segregation layer, etc); 2. The boundary loses its coherency, there is no disclination occurring in area "2" (for example, in case of the NC growth in the matrix); 3. There is no disclination in the internal area "1" (a new phase of normal symmetry is growing at the place of the disclination core).

For the following cases the elastic energy is written [GRYAZNOV 1988]:

$$\varepsilon^{(1)} = \varepsilon_0^{(1)}\left[1-k^2+\frac{(1-\nu_2)}{(1-\nu_1)}\Gamma k^2-\frac{4\bar{b}}{\bar{a}-\bar{b}k^2}k^2\ln^2 k\right], \tag{3a}$$

$$\varepsilon^{(2)} = \varepsilon_0^{(2)}\left[1+2(1-\nu_1)\frac{\bar{b}k^4-(\bar{a}+\bar{b})k^2+\bar{a}}{(\bar{a}-\bar{b}k^2)^2}\right], \tag{3b}$$

$$\varepsilon^{(3)} = \varepsilon_0^{(3)}\left[1-k^2-4k^2\,\frac{\bar{b}\ln^2 k+(1-\nu_2)/2(1-2\nu_1)\Gamma\left(k^2+2\ln k^2-1\right)}{\bar{a}\text{ - }\bar{b}k^2}\right], \tag{3c}$$

where $\varepsilon_0^{(1,2)} = \dfrac{\omega^2 G_{2,1}A_{2,1}^2}{16\pi(1-\nu_{2,1})}$, $k=\dfrac{A_1}{A_2}$, $\Gamma=\dfrac{G_1}{G_2}$, $\bar{a}=1-2\nu_1+\Gamma$, $\bar{b}=1-2\nu_1-\Gamma(1-2\nu_2)$. Corresponding dependencies for energies $\varepsilon^{(1)}$, $\varepsilon^{(2)}$ and $\varepsilon^{(3)}$ are shown in Fig.12. With the passage of disclination through both phases, a coherence will break (the formation of misfit dislocations) for $k > k_{\mathrm{c}}$, with $k_{\mathrm{c}} = \exp\left[-\dfrac{2\pi(1-\nu_2)\bar{a}\sigma_{\mathrm{c}}}{G_2\bar{b}\,\omega}\right]$ and σ_{c} is the stress necessary for a misfit dislocation to form.

The analysis of relation (3b) shows that in a very stiff matrix ($\Gamma \longrightarrow 0$) PNC growth is strongly suppressed relative to that of free PNCs. In fact, for $\nu_1=\nu_2=\nu$ it follows $\varepsilon^{(2)} = \dfrac{(3-4\nu)}{(1-2\nu)}\varepsilon_0^{(2)}$. For example, if $\nu=\dfrac{1}{3}$, the linear energy of a PNC in a stiff matrix is five times higher than that energy of a free PNC.

Eq.(3c) for $\Gamma=0$ can be reduced to a common equation [VLADIMIROV 1986] (a cylindrical pore of a certain size having a minimum of total energy appears in PNCs). Fig.12d shows $\varepsilon_0^{(4)} = \varepsilon_0^{(3)} + 2\pi G_2 A_2^2 kQ$ as a function of k and of the specific energy Q of the boundaries between areas "1" and "2" ($Q=\dfrac{\gamma}{G_2A_2}$) for $\Gamma=1$. For small values of Q (i.e. for small values of the surface energy of the boundary γ or large values of external radius A_2) there will be a preferential structure transformation in the area containing a disclination, if a saddle point is reached ($k_{\mathrm{s}} \approx 0.6$). For $A_2 \approx 10^2 a$, the substitution of corresponding parameters shows that the activation energy of the PNC transition into a "nondisclinational" state may assume a rather reasonable value of ~1 eV per atom.

In [DUNDURS; MARKS 1986-2] the following general statement is given: the stressed state in a sphere caused by a linear defect (which does not contain non-plane components of a self-deformation) lies in the intermediate area between the stressed state in an infinite cylinder (plane deformation) and the stressed state in a plane disk (plane stress). It should be noted that the components of the deformation tensor for a screw dislocation do not correspond to these conditions.

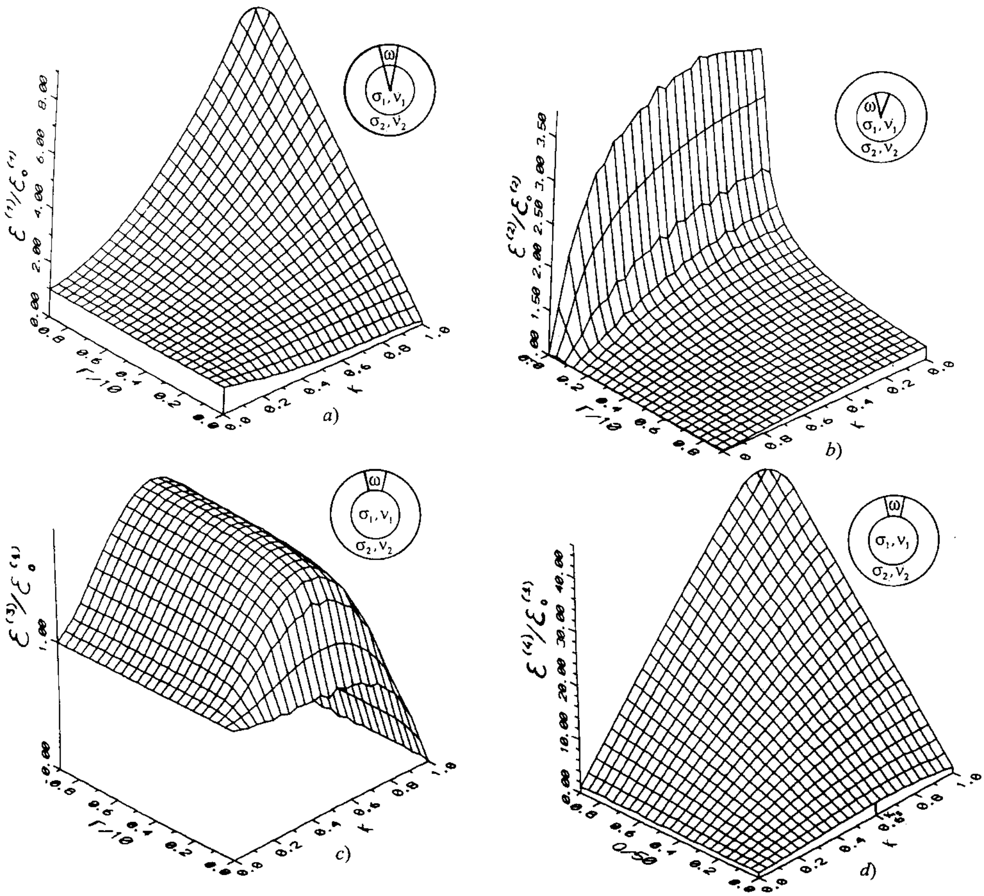

Fig.12: Dependencies of the linear energy of pentagonal needle-like crystals on characteristics of the inhomogeneity of their structures. The linear elastic energy for *a*) a disclination passing through two regions; *b*) a disclination situated in an inner region; *c*) a disclination situated in an outer region; *d*) the same taking into account the energy of a boundary; the saddle state: $k_s = 0.6$, $k = \frac{A_1}{A_2}$ is the relative size of internal area, $\Gamma = \frac{G_1}{G_2}$ is relative modulus of elasticity.

The energy of wedge disclination (like the edge dislocation energy) of the plane stress differs from the energy of a plane deformation by a factor of $(1-\nu^2)$, which yields ≈ 0.9 for the common Poisson's ratio $\nu \approx 0.3$. Thus, the full energy of a wedge disclination $E_c^{(D)}$, shifted from the center of a sphere by distance c lies within the relatively narrow interval: $2(1-\nu^2)\sqrt{A^2-c^2}\,\varepsilon^{(D)} < E_c^{(D)} < 2\sqrt{A^2-c^2}\,\varepsilon^{(D)}$. In principle, the problem of the axially symmetrical position of a disclination in a sphere at Neumann boundary conditions can be solved by the Lamë method for the axial problems of the three-dimensional theory of elasticity.

If this solution is known, the elastic fields in ISPs arise from the superposition of elastic fields of six disclinations, i.e. the "hedgehog" disclination.

However, stresses in an ISP can approximately be described using the concept of Marks-Yoffe point disclinations. It allows one to obtain quite simple expression for the tensor component of stresses in ISPs [WAYMAN]. The corresponding elastic energy of ISP [GRYAZNOV 1988; WAYMAN] is given by:

$$E^{(\mathrm{I})} = \frac{G\beta^2(1+\nu)}{216\pi(1-\nu)} A^3 \ . \tag{4}$$

In [AJAYAN; WAYMAN] based on the disclinational approach ISP and DSP stability is given relative to the transition of ISP and DSP structures in a state with the normal crystal structure. Two types of habits are being discussed: a model of "strong faceting", and an isotropic model, taking into account the surface energy dependence on deformation. As a result, ISPs are more stable than monocrystals within a small size range of $d \le 10^2$ Å, and DSPs occupy an intermediate place. The disclinational approach makes it possible to avoid an overestimation of the critical size A^* of the PSP stability in relation to the DSP transition in the usual monocrystalline state. Actually, taking into consideration the stability of the SP volume during this transition, one may obtain the following estimation for ISP, from (4) for the model of "strong faceting":

$$A^* \approx 1944\pi \frac{(1-\nu)}{(1+\nu)} \frac{(\gamma - 1.06\gamma_{111} - \gamma_{\mathrm{t}})}{G\beta_{\mathrm{i}}^2} \ . \tag{5}$$

Typical radii A^* of the ISP stability for a number of metals are given in Table 1. For PNC and ISP these estimations have been derived in isotropic approximation from expressions (2) and (5), respectively. Values A^* for ISP slightly differ from the results in [WAYMAN]. However, it is essentially smaller than this value obtained in [MONTANO], where homogeneous deformations are suggested. For Cu-clusters these results are in good agreement with recent HREM data [URBAN 1996 and 1997].

Inaccuracy of the experimental results for γ appreciably influences the data in Table 1, leading only to rough estimations. But, as expected, criteria (2) and (5) cause substantially different values of A^* for PNC and ISP since the density of elastic energy in ISP is one and a half order higher than in PNC. The reason is that ISP has 6 disclinations, unlike to PNC with only one, and that the elastic energy E is proportional to β^2. It is quite possible that the defects reducing the elastic energy are created in PNCs before the PNC reaches the value of A^* (see section 3.6).

3.5 Models of Pentagonal Small Particle Formation

Fig.13 demonstrates all well-known mechanisms of PSP formation studied experimentally and with the help of theoretical models. Historically, a model of sequential joining of tetrahedra was first presented (Fig.13a) in [INO 1966]. However, this model does not guarantee the formation of regular DSPs and ISPs since there is only little probability for five or twenty tetrahedra of equal size to join and to form regular figures. Nevertheless, the detection of PSPs in a non-ideal tetrahedral arrangement [GAO 1988; HOFMEISTER 1984; RENOU 1986] does not eliminate this possibility, since the diffusion processes smooth these imperfections of the PSP structure through a diffusive matching of the tetrahedra.

Investigations of crystallites with pentagonal axes in thin films led to the model of sequential twinning [FAUST; HALL 1986; SMITH 1968] (Fig.13.b). This process is certainly caused by the presence of shear stresses in the planes perpendicular to the film surface. The well-known model of PSP formation from a small atomic cluster of the initially pentagonal structure [Burton; Hoare 1972; Kostov] is shown in (Fig.13.c). A DSP can be formed from a 7-atom embryo or, if Verfelmeier's series is realized (tetrahedron-decahedron-icosahedron, i.e. a 7-atom embryo becomes a 13-atom one) an ISP can be formed. Small decahedral and icosahedral clusters are rather stable with regard to the process of their transition to embryos of usual crystal structures. Obviously, this fact had been pointed out for the first time in [Frank].

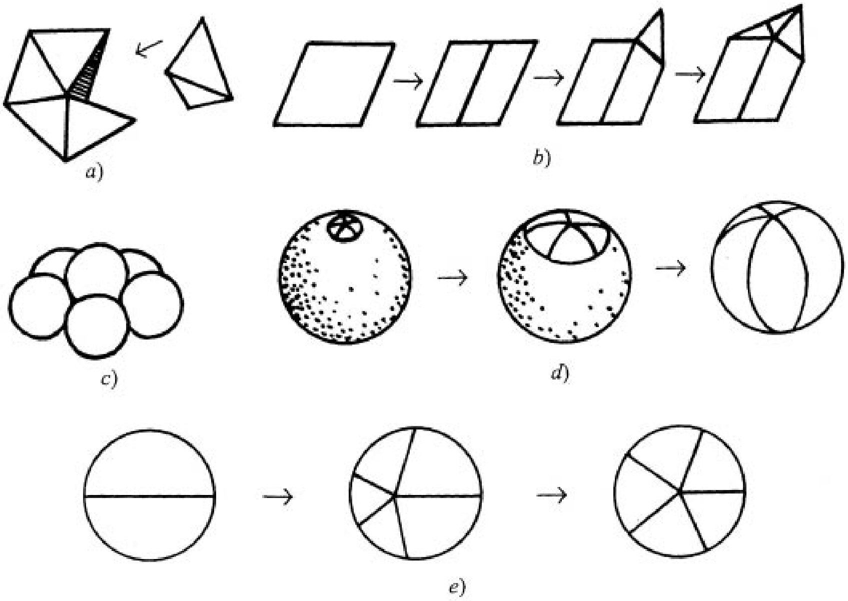

Fig. 13: The mechanisms of development of pentagonal symmetry in small particles: *a*) sequentially joint tetrahedra; *b*) the sequential twinning in thin films; *c*) the formation and growth of a pentagonal embryo; *d*) stabilization of the intermediate SP structure with a disclination.

When the SP formation passes the liquid-solid boundary, the presuppositions for an embryo of the five-fold symmetry to originate are enhanced. During SP cooling this embryo intergrows inside, thus transforming the SP into the decahedral one [Iijima 1987-3 and -4] (Fig.13.d). Obviously, this model is not applicable if a SP is formed by avoiding the liquid phase.

For SP formation under conditions implying a highly mobile crystal structure, during the growth one of the intermediate stages of SPs of the five-fold symmetry can be fixed [Iijima 1986; Marks 1986-2] (Fig.4.b,j) The stable position of the disclination with five twin boundaries as it was shown in [Marks 1986-2] is in the center of a SP. Here it is relatively stable because it is necessary to overcome the potential barrier to displace a disclination to the periphery of SP. The mechanism of the formation of pentagonal axes has been proved for ISPs as well.

3.6 Stability and Relaxation of Elastic Stresses

In comparison with a bulk crystal a variety of stationary structure defects is essentially diminishing with decreasing crystal size. Generally speaking, the SP crystal structure is more perfect than the equivalent volume of a bulk crystal under the same conditions. The increasing perfection of the SP crystal structure is particularly reflected by the fact that only defects, which do not substantially lower the SPs symmetry, remain. The origination of crystal lattice defects of the low symmetry in SPs is mainly connected with the growth of SPs. In the small-size range stacking faults and twins are typical for SPs, but with increasing SP size, the dislocations, dislocation dipoles, point defects (non-perfections) may be formed, i.e. SPs become unstable with regard to the conservation of the high symmetry.

Several variations in the particle's geometry and their structure can be assigned to SPs: 1.Variation in shape produced by the effect of electrostatic forces (A_1^* ~ 10 Å) [GRYAZNOV 1989]. 2.Instability caused by the transition from PSP to monocrystal (A_2^* ~ 10^2 Å) [INO 1969-1; WAYMAN]). 3.Instability of PSPs induced by the formation of defects (structural dislocations, disclinations, etc.) leading to the degeneration of five-fold symmetry ($A_3^* \geq 10^2$ Å) [GRYAZNOV 1988]. 4.Instability of glissile dislocations in SPs ($A_4^* \geq 10^2 \div 10^3$ Å) [GRYAZNOV 1989].

Here, the PSP instability, connected with the formation of defects compensating the internal stresses, is most important. Fig.14 presents the main mechanisms of the relaxation of internal stresses in PSPs.

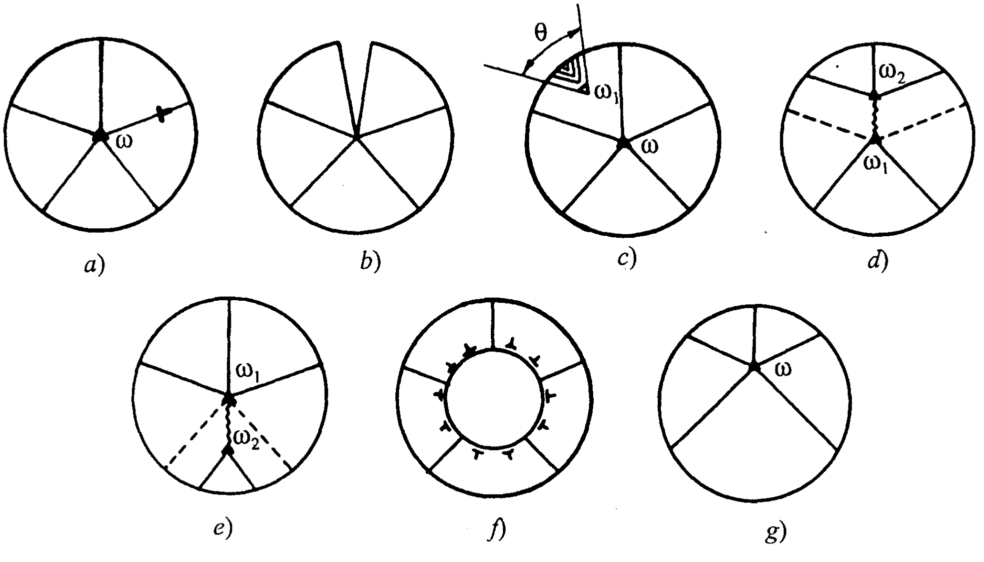

Fig. 14: The channels of elastic energy relaxation in pentagonal small particles: *a*) origination of a structural dislocation compensating the disclination elastic field; *b*) opening of a gap; *c*) origination of a negative disclination of power ω_1 with a system of stacking faults in one of the tetrahedrons; *d*), *e*) different ways of decomposing the disclination of power ω into two others linked by a "disclinational" stacking fault; *f*) formation of a region without a disclination inside the SP; *g*) shifting of the pentagonal axis towards the periphery.

The formation of edge dislocations with a Burgers vector perpendicular to the radius-vector substantially lowers the elastic stresses in PSPs. The most probable position for a dislocation to form is the twin boundaries [NARA] where the inhomogeneous stresses are increased (Fig.14.a). The corresponding elastic linear energy of a disclination + dislocation system in PNCs is as follows:

$$\varepsilon = \varepsilon^{(2)} + \frac{Gb^2}{4\pi(1-\nu)}\left[\ln\frac{1-x^2}{r_\mathrm{c}/A} + \frac{x^2}{4}\right] + \frac{G\omega bA}{4\pi(1-\nu)}x\ln x\ , \tag{6}$$

where $x = \frac{c}{A}$, c is the distance between disclination and dislocation, and r_c is the radius of the dislocational core. This expression is easily derived from the results of [VLADIMIROV 1986].

Analysis of the dependence $\varepsilon - \varepsilon_0$ shows that there is a critical radius $A_\mathrm{c} \sim \frac{b}{\omega}$ of PNC (the respective estimation for PSP is given in [INO 1969-1]), starting with which a dislocation begins to originate. PNC structurally modifies to a monocrystal, for $A_\mathrm{c} < A^*$. The effect of dislocation formation was realized by the computer simulating of the full disclinations [ZHIGILEJ]. To do this, the method of molecular dynamics to two-dimensional clusters consisting of 500 interacting atoms was applied. These results are probably correct for PSP as well.

In [GILLET 1977; KOMODA] it is supposed that the elastic energy in PSPs can be relaxed by opening some gaps (Fig.14.b). In principle, they may disappear later owing to the diffusion processes. However, the existence of this channel has not yet been reliably evidenced.

The micrograph of Fig.5b shows that in one of the DSP tetrahedra a wedge-shaped area is formed by a system of twin boundaries. This presumebly implies the formation of the partial negative wedge disclinations of the wedge angle ω_1, connected with the surface by a system of plane defects in one of the tetrahedra (Fig.14c). For PNCs, this corresponds to the following elastic linear energy:

$$\varepsilon = \varepsilon_0^{(2)} + \frac{G\omega_1^2 A^2}{16\pi(1-\nu)}\left(1-x^2\right)^2 + \frac{G\omega_1\omega}{8\pi(1-\nu)}\left[2x^2\ln x + 1 - x^2\right] + \gamma_\mathrm{v}A^2\left[2(\chi - \sin\chi) + \sin^2\chi\,\mathrm{ctg}\,\theta\right], \tag{7}$$

where $\chi = \pi - \theta - \arcsin(x\sin\theta)$, θ is the angle of the vertex of a wedge-shaped defect (Fig.14.c), and γ_v is the specific volume energy in the defect area. Eq. (7) was derived from the formulae obtained for the energy of interaction of a pair of disclinations in a cylinder [RICHTER; ROMANOV].

Another channel of stress relaxation in PSPs can be the splitting of a disclination core as it is shown in Figs.14.d,e (see also Fig.6). This phenomenon was observed in [GAO 1988; HOFMEISTER 1984; RENOU 1986]. On the basis of the disclination model it can be explained in the following way. First, under certain conditions the square-law dependence of the linear energy of PSPs and PNCs on disclinations causes an energetically favorable decomposition of initially one disclination into two ones of smaller angles $\omega = \omega_1 + \omega_2$. Second, after the decomposition of the initial disclination the products of the disclination reaction approach markedly closer to the surface of PNCs or PSPs, additionally lowering the elastic energy of the system. At last, the length of twin boundaries is shortening with a disclination decomposing. That is the reason why the decomposition according to Fig.14.d is particularly preferable to that in Fig.14e. In Figs.14.d and 14.e the initial positions of twin boundaries are marked by dashed lines

In general, two factors hinder the motion of disclinations over large distances (in extreme cases, up to the free surface of a particle): 1.The origination of the disclination boundaries between the disclination angles ω_1 and ω_2; this high-angle boundaries have a higher energy of boundaries γ_d. 2. A change in the particle shape (not shown in Fig.14.d) caused by the disclination displacement leads to a change in the free surface energy. Neglecting the last parameter one can yield the linear energy ε of PNCs with the split disclination [Gryaznov 1988]:

$$\varepsilon = \varepsilon_0^{(2)} + \frac{G\omega^2 A}{8\pi(1-\nu)}\left[\omega_1 x^2 \ln x^2 + (\omega_1+\omega_2)x^2 + \omega_2 \frac{x^4}{2}\right] + \gamma_\mathrm{t} A\sqrt{1-\sin^2\frac{\pi}{5}x^2} + \gamma_i A x\,,\ i = 1{,}2 \tag{8}$$

Here, $\gamma_1 = \gamma_\mathrm{d} - \gamma_\mathrm{t}\left(1+\cos\frac{\pi}{5}\right)$, which corresponds to the scheme of Fig.14.d. $\gamma_2 = \gamma_1 + \gamma_\mathrm{t}$ corresponds to the scheme of Fig.14.c. The most probable values of the partial disclinations are $\frac{3}{5}\omega$ and $\frac{2}{5}\omega$.

Fig.14.f shows another way of elastic energy relaxation in PSPs: in the center of SPs another phase grows without the five-fold symmetry axis. The "non-pentagonal" phase is separated from a pentagonal one by a boundary (in details, see section 3.4). This situation was probably observed in [Marks 1983].

A shift of a disclination from the center of PSPs (Fig.14.g) [Giorgio 1988] is accompanied by the elastic energy decrease (in accordance with eq. (1)).

In a number of papers [Ajayan; Berry; Hoare 1972; Iijima 1986; Montano] this process is supposed to be important for the phenomenon of SP "quasi melting" (the possibility of this process is theoretically described in [Hoare 1972]). It turned out that this situation can be presented as the formation of a disclination on a SP surface and its propagation through the particle [Dundurs; Marks 1986-2]. In the centre of a SP the disclination occupies a site of local equilibrium caused by the anisotropy of the surface energy [Marks 1986-2].

These results show that a temperature rise diminishes the contribution of the surface energy anisotropy to the total energy of a SP. Then the dependence on the disclination energy (1) is more and more decreasing, and the local minimum of energy in the centre of a particle becomes smaller.

Here, we should point out again that the models of elastic energy relaxation listed above may be strictly applied to PNCs. However, relaxation processes in PSPs should qualitatively be similar.

4. Conclusions

The present analysis demonstrates the role of topological defects (disclinations and dislocations) in describing of some physical properties of pentagonal small particles.

Over the size range of $A \le 10^2 \div 10^3$ Å PSPs are typical for almost all f.c.c. metals as well as for a number of other materials. Within this size range the surface energy alredy exceeds the losses of energy, caused by the origination of elastic stresses owing to the presence of non-crystalline symmetry axes This conclusion is not quite correct for quasi-crystals.

The pentagonal symmetry of PSPs and PNCs can be described most adequately in terms of disclinations. This allows one to analyse almost all data known of PSP structures in a general way. Pentagonal small particles and needle-like crystals are unique physical objects enabling one to study the direct influence of isolated disclinations on the properties of solids.

There is a critical size A^* for PSPs (for PNCs it is the diameter) below which the gain in the surface energy compensates the losses in the volumetric elastic energy. As a result, the pentagonal symmetry is retained up to size A^*.

The disclination approach allows one to clearly describe the relaxation of the elastic energy accumulated in PSPs. The PSPs show another critical size A_c above which the dislocations, screening of the elastic field of disclinations, originate. Other channels of elastic energy relaxation in PSPs are also important: the splitting of the PSP disclination core, the origination of the compensating disclination, the displacement of disclinations from the centre of SPs, the creation of a disclination-free region.

The properties of the defect structures of SPs may be decisive for practical applications. It is possible to create materials of specific properties by compacting PSPs powders. In fact, plastic processes in such materials with average stresses $G\omega \approx 1$ GPa in a grain may proceed in an unusual way. Particularly, a change of the Hall-Petch law is possible, if there is no grain boundary flow: dependence $\sim A^{1/2}$ of the obtained stress on the grain size may turn into $\sim \ln A$ owing to the topological properties of the main defects.

The production of composites on the basis of piezoelectric and piezomagnetic materials by using PSPs may be most promising for the creation of materials of new electromagnetic properties. For example, as simple estimations show, high internal stresses in piezoelectric PSPs of a composite cause an average electric field of the same strength as on top of a charged needle of a radius of ~100 Å.

The authors believe that the use of PSPs as components of the so-called nanocrystalline materials [BIRRINGER] is most promising for modern materials science.

Acknowledgments

The authors are most obliged to V.I.Vladimirov whose ideas inspired them to write this review. The authors thank L.I.Trusov for this constant encouragement to and interest in this review and V.M.Ievlev for his critical comments and also H.Hofmeister for useful suggestions and critical discussions.

References

ADELT M., NEPIJKO S., DRACHSEL W., FREUND H.-J.: Chem.Phys.Lett., **291** (1998) 425
AJAYAN P.M., MARKS L.D.: Phys.Rev.Lett., **60** (1988) 585
ALPRESS J.G., SANDERS J.V.: Phil.Mag., **19** (1964) 645
ALPRESS J.G., SANDERS J.V.: Surf.Sci., **7** (1967) 1
ALPRESS J.G., SANDERS J.V.: Austr.J.Phys., **23** (1970) 23
BAGLEY B.G.: Nature, **208** (1965) 674
BAGLEY B.G.: Nature, **225** (1970) 1040
BENDITSKII A.A., DAN´KO D.B., FEDOROVICH R.D., NEPIJKO S.A., VIDUTA L.V.: Int.J.Electronics, **77** (1994) 985
BERGER M.: Geometry, vol. 1, Mir, Moscow (in Russian)
BERRY J., JELLENIK J., NATANSON J.: Phys.Rev.A, **30** (1984) 919
BIRRINGER R., GLEITER H.: Encyclopedia of materials science and engineering, vol.1, Ed.R.W.Cahn, Pergamon Press 1988 (p.339)
BLAISTEN-BAROJAS E., GORZON I.L., AVALOS-BORJA M.: Phys.Rev.B, **36** (1987) 8447
BOGOMOLOV V.N., KLUSHIN N.A., OKUNEVA N.M., PLACHENOVA E.L., POGREBNOI V.I., CHUDNOVSKII F.A.: Fiz.Tverd.Tela, **13** (1971) 1499 (in Russian)
BONISSENT A., MUTAFTSCHIEV B.: J.Chem.Phys., **58** (1973) 3727
BORZIAK P.G., SARBEJ O.G., FEDOROWITSH R.D.: phys.stat.sol., **8** (1965) 55
BORZIAK P.G., KULYUPIN YU.A., NEPIJKO S.A., TOMCHUK P.M.: Bull.Acad.Sci.USSR, Phys.Ser.(USA), **40** (1976) 139

BORZIAK P.G., KULYUPIN YU.A., NEPIJKO S.A., SHAMONYA V.G.: Thin Solid Films, **76** (1981) 359

BORZIAK P.G., GORBAN´ S.A., GRIGORIEVA L.K., NAGAEV E.L., NEPIJKO S.A., CHIZHIK S.P.: Sov.Phys.JETP, **70** (1990) 347

BRIANT C.L., BURTON J.J.: J.Chem.Phys., **63** (1975) 2045

BRIEU M., GILLET M.: Thin Solid Films, **100** (1983) 53

BUCKLE E.R., TSAKIROPOULOS P., POINTON K.C.: Int.Met.Rev., **31** (1986) 256

BUKHARAEV A.A., OVCHINNIKOV D.V., NURGAZIZOV N.I., KUKOVITSKII E.F., KLEIBER M., WIESENDANGER R.: Phys.Solid State (USA), **40** (1998) 1163

BUKHARAEV A.A., OVCHINNIKOV D.V., NURGAZIZOV N.I., KUKOVITSKII E.F., KLEIBER M., WIESENDANGER R.: Scanning, **20** (1998) 3

BURTON J.J.: Nature, **229** (1971) 335

CHARLÉ K.-P., KÖNIG L., NEPIJKO S., RABIN I., SCHULZE W.: Cryst.Res.Technol., **33** (1998) 1085

CHATTOPADHAYA K., RAMACHANDRORAO P.: J.Cryst.Growth, **36** (1976) 355

COCKAYNE D.J., DAY I.L.F., WHELAN M.J.: Phil.Mag., **20** (1969) 1265

CYROT-LACKMANN F., GORDON M.B.: J.de Phys.Coll., **41** (1980) 263

DAVERITZ L., HEY R., BERGER H.: Thin Solid Films, **116** (1984) 165

DE WIT R.:, J.Phys.C, **5** (1972) 529

DOYAMA M., COTTERIL R.M.J.: Phil.Mag.A., **50** (1984) L7

DUNDURS J., MARKS L.D., AJAYAN P.M.: Phil.Mag.A, **57** (1988) 605

FARGES J., DE FERAUDY M.F., RAOULT B., TORCHET G.: J.de Phys.Coll., **38** (1977) 47

FARGES J., DE FERAUDY M.F., RAOULT B., TORCHET G.: J.de Phys.Coll., **41** (1980) 263

FARGES J., DE FERAUDY M.F., RAOULT B., TORCHET G.: Surf. Sci., **106** (1981) 95

FARGES J., DE FERAUDY M.F., RAOULT B., TORCHET G.: Physics and chemistry of small clusters, NATO ASI Ser.B, **158**, Plenum Press, New York-London 1987 (p.15)

FAUST J.M., JOHN H.F.: J.Phys.Chem.Solids, **25** (1964) 1409

FEDOROVICH R.D., NAUMOVETS A.G., TOMCHUK P.M.: Progr.Surf.Sci., **42** (1993) 189

FEDOROVICH R.D., KIYAYEV O.E., NAUMOVETS A.G., PILIPCHAK K.N., TOMCHUK P.M.: Phys.Low-Dim.Struct., **1** (1994) 83

FENDLER J. (Ed.): Nanoparticles and nanostructured Films, Wiley-VCH, Weinheim-New York-Chichesterr-Brisbane-Singapore-Toronto 1998

FLUELI M., SPICHER R., STADELMANN P.A., BUFFET P.A., BORREL J.-P.: Europhys.Lett., **6** (1988) 349.

FRANK F.C.: Proc.Roy.Soc.A, **215** (1952) 43

FREUND H.-J.: Angew.Chem.Inst.Ed.Engl., **36** (1997) 452

FREUND H.-J., BÄUMER M., LIBUDA J., KUHLENBECK H., RISSE T., AL-SHAMERY K., HAMANN H.: Cryst.Res.Technol., **33** (1998) 977

FRIEDEL J.: Ann.Phys., **7** (1976) 257

FRIEDEL J.: J.de Phys.Coll., **38** (1977) 7

FUCANO Y., WAYMAN C.M.: J.Appl.Phys., **40** (1969) 1656

GALLIGAN J.M.: Phys.Lett.A, **39** (1972) 407

GALLIGAN J.M.: Scr.Met., **6** (1972) 161

GAO D., GLEITER H.: Acta Met., **35** (1987) 1571

GAO P.Y., KUNATH W., GLEITER H., WEISS K.: Scripta Met., **22** (1988) 683

GASPARD M.B., HODGES C.H., GORDON M.B.: J.de Phys.Coll., **38** (1977) 63

GEDWILL M.A., ALTSTETTER C.J., WEYMAN C.M.: J.Appl.Phys., **35** (1964) 2206

GILLET E., GILLET M.: J.Cryst.Growth, **13** (1972) 212

GILLET M.: J.Cryst.Growth, **36** (1976) 239

GILLET M.: Surf.Sci., **57** (1977) 139

GILLET M., RENOU A.: Surf.Sci., **50** (1979) 91

GIORGIO S., URBAN J.: Appl.Phys.Lett., **52** (1988) 1467

GIORGIO S., NIHOUL G., URBAN J., SACK-KONGEL H.: Z.Phys.D, **24** (1992) 395

GLEITER H.: Dislocations 84, Paris 1984 (p.457)

GORBAN´ S.A., NEPIJKO S.A., TOMCHUK P.M.: Int.J.Electronics, **70** (1991) 485

GORDON M.B., CYROT-LACKMANN F., DESJONGUWRES M.C.: Surf.Sci., **80** (1979) 159

GRATIAS D.: Usp.Fiz.Nauk, **156** (1988) 347 (in Russian)

GRYAZNOV V.G., NOVIKOV V.I., TRUSOV L.I.: Poverkhnost.Fiz.Chim.Mech., No.1 (1986) 133 (in Russian)

GRYAZNOV V.G., KAPRELOV A.M., ROMANOV A.E.: Disclinations and rotational deformation of solid state, Ed. V.I.Vladimirov, Fiz.Tekhn.Inst., Leningrad 1988 (p.47) (in Russian)

GRYAZNOV V.G., KAPRELOV A.M., ROMANOV A.E.: Zh.Tekh.Fiz.Pisma, **15**, No.2 (1989) 39 (in Russian)

HADJIPANAYIS G.C., PRINZ G.A. (Eds.): Science and Technology of Nanostructured Magnetic Materials, NATO ASI Ser.B, **259**, Plenum Press, New York-London 1991

HALICIOGLU T., WHITE P.J.: Surf.Sci., **106** (1981) 45

HALICIOGLU T., BAUSCHLICHER(jr) C.W.: Rep.Prog.Phys., **51** (1988) 883

HALL C.R.: Scr.Met., **7** (1973) 73

HALL C.R., FAUZI S.A.H.: Phil.Mag., **54** (1986) 805

HAYASHI T., OHNO T., SHIGEKI Y., UYEDA R.: Jap.J.Appl.Phys., **16** (1977) 705

HAYASHI T., SAITO Y., YATSUYA S., MIHAMA K., UYEDA R.: J.de Phys.Coll., **38** (1977) 191

HEINEMANN K., POPPA H.: Appl.Phys.Lett., **20** (1972) 122

HEINEMANN K., YACAMÁN M.J., POPPA H.: phys.stat.sol.(a), **54** (1979) 675

HEINEMANN K., YACAMÁN M.Y., YANG C.Y., POPPA H.: J.Cryst.Growth, **47** (1979) 177

HEINEMANN K., AVALOS-BORJA M., POPPA H.: Electron Microscopy and Analysis Group, Inst.Phys.Conf.Ser., **52**, Bristol 1980

HEINEMANN K., POPPA H., YACAMÁN M.J.: J.Vac.Sci. and Technol., **17** (1980) 461

HERNADO A. (Ed.): Nanomagnetism, NATO ASI Ser.E, **247**, Kluwer Academic Publishers, Dortrecht-Boston-London 1993

HEYRAUD J.C., METOIS J.J.: J.Cryst.Growth, **82** (1987) 263

HIRSCH P.B., HOWIE A., NICHOLSON R.B., PASHLEY D.W., WHELAN M.J.: Electron Microscopy of Thin Crystals, Butterworth, London, 1965

HOARE M.R., PAL P.: J.Cryst.Growth, **17** (1972) 77

HOARE M.R.: Adv.Chem.Phys., **40** (1979) 49

HOARE M.R., MCINNES J.A.: Adv.Phys., **32** (1983) 791

HOFMEISTER H.: Thin Solid Films, **116** (1984) 151

HOFMEISTER H.: Cryst.Res.Technol., **33** (1998) 3

HONEYCUTT J.D., ANDERSEN H.C.: J.Phys.Chem., **91** (1987) 4950

HONJO G., TAKAYANAGI K., KOBAYASHI K., YAGI K.: phys.stat.sol.(a), **55** (1979) 353

HOWIE A., MARKS L.D.: Phil.Mag.A, **49** (1984) 95

HUANG W., MURA T.: J.Appl.Phys., **41** (1970) 5175

IIJIMA S.: Surf.Sci., **156** (1985) 241

IIJIMA S.: J.Electr.Micr., **34** (1985) 249

IIJIMA S., ICHIHASHI T.: Phys.Rev.Lett., **56** (1986) 616

IIJIMA S., ICHIHASHI T.: Surf.Sci., **192** (1987) L872

IIJIMA S.: Microclusters, Eds. S.Sugano, Y.Nishina, S.Ohniski, Springer-Verlag, Berlin-New York-London-Paris-Tokyo 1987 (p.188)

IIJIMA S.: Jap.J.Appl.Phys., **26** (1987) 357

IIJIMA S.: Jap.J.Appl.Phys., **26** (1987) 365

INO S.: J.Phys.Soc.Jap., **21** (1966) 346

INO S., OGAWA S.: J.Phys.Soc.Jap., **22** (1967) 1365

INO S.: J.Phys.Soc.Jap., **27** (1969) 941

INO S.: J.Phys.Soc.Jap., **26** (1969) 1559

ISHIMASA T., FUKANO Y.: Surf.Sci., **156** (1985) 241

JULG A., BENARD M., BOURG M., GILLET M., GILLET E.: Phys.Rev.B, **9** (1974) 3248

KHANNA S.N., BUCHER J.P., BUFFET J.: Surf.Sci., **127** (1983) 165

KIMOTO K., NISHIDA I.: J.Phys.Soc.Jap., **22** (1967) 940

KIMOTO K., NISHIDA I.: Jap.J.Appl.Phys., **6** (1967) 1047

KLEMAN M.: Points, lines and walls, John Wiley&Sons, New York 1983

KLIMENKOV M., NEPIJKO S., KUHLENBECK H., BÄUMER M., SCHLÖGL R., FREUND H.-J.: Surf.Sci., **391** (1997) 27

KOMODA T.: Jap.J.Appl.Phys., **7** (1968) 27

KOSTOV P.I., KOSTOV I.: Cryst.Res.Technol., **23** (1988) 973

KREIBIG U., VOLLMER M.: Optical Properties of Metal Clusters, Springer-Verlag, Berlin-Heidelberg-New York 1995

KULYUPIN YU.A., NEPIJKO S.A., STYOPKIN V.I.: Bull.Acad.Sci.USSR, Phys.Ser.(USA), **46** (1982) 78

LAMBERT R.M., PACCHIONI G. (Eds.): Chemisorption and Reactivity on Supported Clusters and Thin Films, NATO ASI Ser.E, **331**, Kluwer Academic Publishers, Dordrecht 1997

LANG J.M., DUBOST B., ANDIER M., SAINFORT P.: J.Cryst.Growth, **83** (1987) 456

LEE J.W., STEIN J.D.: J.Phys.Chem., **91** (1987) 2450

LURJE A.I.: Theory of elasticity, Nauka, Moscow 1970 (in Russian)

MACKAY A.L.: Acta Cryst., **15** (1962) 916

MAISSEL L.I., GLANG R. (Eds.): Handbook of Thin Film Technology, McGraw-Hill Book Company, New York-St.Louis-San Francisco-Düsseldorf-London-Mexico-Panama-Sydney-Toronto 1970

MARKS L.D., SMITH D. J.: J.Cryst.Growth **54** (1981) 425

MARKS L.D., SMITH D. J.: J.Microsc.(Gr.Brit.), **130** (1983) 249

MARKS L.D.: Phil.Mag.A, **49** (1984) 81

MARKS L.D.: Ultramicroscopy, **18** (1985) 445

MARKS L.D.: Surf.Sci., **150** (1985) 302

MARKS L.D.: Structure and dynamics of surfaces, Eds. W.Schommers, P.von Blankenhagen, Springer-Verlag, Berlin 1986 (p.71)

MARKS L.D., AJAYAN P.M., DUNDURS J.: Ultramicroscopy, **20** (1986) 77

MATSUMOTO S., SAITO Y., KAMO K., SETAKA N.: Jap.J.Appl.Phys., **21** (1982) L183

MELMED A.J., HAYWARD D.O.: J.Chem.Phys., **31** (1959) 545

MELMED A.J., GOMER R.: J.Chem.Phys., **34** (1961) 1802

MIAO B., YANG G., WANG S.: Phys.Lett.A, **121** (1987) 283

MIHAMA K., YASUDA Y.: J.Phys.Soc.Jap., **21** (1966) 1166

MIKHAJLIN A.I., ROMANOV A.E.: Fiz.Tverd.Tela, **28** (1986) 601 (in Russian)

MONOSMITH W.B., COWLEY J.M.: Ultramicroscopy, **21** (1988) 177

MONTANO P.A., SHENOY G.K., ALP E.E., SCHULZE W., URBAN J.: Phys.Rev.Lett, **56** (1986) 2076

MOROKHOV I.D., TRUSOV L.I., CHIZHIK S.P.: Highly dispersed metallic media, Energoatomizdat, Moscow 1977 (in Russian)

MOROKHOV I.D., TRUSOV L.I., LAPOVOK V.I.: Physical phenomena in highly dispersed media, Energoatomizdat, Moscow 1984 (in Russian)

NARA S.: phys.stat.sol.(b), **49** (1988) 555

NATSIK V.D., SMIRNOV S.N.: Low Temp. Phys. (USA), **21** (1995) 518

NELSON D.R.: Phys.Rev.B, **28** (1983) 5515

NEPIJKO S.A., STYOPKIN V.I.: Bull.Acad.Sci.USSR, Phys.Ser.(USA), **46** (1982) 144

NEPIJKO S.A., STYOPKIN V.I., HOFMEISTER H., SCHOLZ R.: Ultradispersiv particles and its ensembles, Ed. P.G.Borziak, Naukova Dumka, Kiev 1982 (p.3) (in Russian)

NEPIJKO S.A., STYOPKIN V.I., SCHOLZ R.: Poverkhnost.Fiz.Chim.Mech., No.4 (1984) 116 (in Russian).

NEPIJKO S.A.: Physical properties of the small metal particles, Naukova Dumka, Kiev 1985 (in Russian)

NEPIJKO S.A., BONDARENKO T.N., HOFMEISTER H.: J.Cryst.Growth, **71** (1985) 735

NEPIJKO S.A., STYOPKIN V.I.: Bull.Acad.Sci.USSR, Phys.Ser.(USA), **49** (1985) 50

NEPIJKO S.A., STYOPKIN V.I., HOFMEISTER H., SCHOLZ R.: J.Cryst.Growth, **76** (1986) 501

NEPIJKO S.A., GORBAN´ S.A., VIDUTA L.V., FEDOROVICH R.D.: Int.J.Electronics, **73** (1992) 1011

NEPIJKO S.A., WIESENDANGER R.: Europhys.Lett., **31** (1995) 567

NEPIJKO S., KLIMENKOV M., KUHLENBECK H., ZEMLYANOV D., HEREIN D., SCHLÖGL R., FREUND H.-J.: Surf.Sci., **412**/**413** (1998) 192

NEPIJKO S., SCHULZE W., RABIN I., VIDUTA L.: Ann.Physik, **7** (1998) 101

NIHOUL G.: Microsc.Microanal.Microstruct., **2** (1991) 637

NIKITIN L.V., NAKASHIDZE O.M., NEPIJKO S.A., OSTRANITSA A.P.: Bull.Acad.Sci.USSR, Phys.Ser.(USA), **50** (1986) 194

NIKITIN L.V., NAKASHIDZE O.M., AKHMEDOV M.Z., NEPIJKO S.A., OSTRANITSA A.P.: J.Magn.Magn.Mat., **148** (1995) 279

Nissen H.-U., Wessiken R., Beeli C., Csanadi A.: Phil.Mag.B, **57** (1988) 587

Nohara A., Imura T.: J.Phys.Soc.Jap., **27** (1969) 793

Novikov V.I., Repin I.A., Semenikchin I.A., Svirida S.F., Trusov L.I.: Fiz.Tverd.Tela, **27** (1985) 2179 (in Russian)

Ogawa S., Ino S.: J.Cryst.Growth, **13**/**14** (1972) 48

Ogburn F., Paretzkin B., Peiser H.S.: Acta Cryst., **17** (1964) 774

Persson B., Liebich A.: Phys.Rev.B, **28** (1983) 4274

Peterford-Long A.K., Long N.J., Smith D.J., Wallenberg L.R., Bovin J.-O.: Physics and chemistry of small clusters, NATO ASI Ser.B, **158**, Plenum Press, New York-London 1987 (p.127)

Peterford-Long A.K., Smith D.J., Wallenberg L.R., Bovin J.-O.: J.Cryst.Growth, **80** (1987) 218

Petrov A., Kudrenitskis I., Belogurov S., Nepijko S.: Ann.Physik, **5** (1996) 627

Petrov Yu.I.: Clusters and small particles, Nauka, Moscow 1986 (in Russian)

Polukhin R.A., Vatolin N.A.: Rasplavy, **1** (1987) 29 (in Russian)

Renou A., Gillet M.: Thin Solid Films, **41** (1977) 15

Renou A., Rudra A.: Surf.Sci., **156** (1985) 69

Renou A., Penisson J.M.: J.Cryst.Growth, **78** (1986) 357

Richter A., Romanov A.E., Pompe W., Vladimirov V.I.: phys.stat.sol.(b), **143** (1987) 43

Romanov A.E.: Disclinations-theory and experiment, Fiz.Tekhn.Inst., Leningrad 1984 (in Russian)

Romanowski R.: Highly dispersed metals, John Wiley&Sons, New York 1987

Saito Y.: J.Cryst.Growth, **47** (1979) 61

Saito Y., Mihama K., Chen M.S.: Phys.Rev.B, **35** (1987) 4085

Sato H., Shinozaki S., Cicotte L.S.: J.Vac.Sci. and Technol., **6** (1969) 62

Sato H., Shinozaki S.: J.Vac.Sci. and Technol., **8** (1971) 159

Schmid G. (Ed.): Clusters and Colloids, VCH, Weinheim 1994

Segall J.: Metals **9** (1957) 50

Shabes-Retchkiman P.S., Yacamán M.J.: Appl.Surf.Sci., **11**/**12** (1982) 149

Shiozawa T., Kobayashi T.: phys.stat.sol.(a), **104** (1987) 649

Smith J., Ogburn F., Bechtold C.: J.Electrochem.Soc., **115** (1968) 371

Smith D.J., Marks L.D.: J.Cryst.Growth, **54** (1981) 433

Smith D.J., Marks L.D.: Phil.Mag.A, **44** (1981) 735

Smith D.J., Peterford-Long A.K., Wallenberg L.R., Bovin J.-O.: Science, **233** (1986) 872

Solliard C.: Surf.Sci., **106** (1981) 58

Solliard C., Borel J.-P.: Helv.Phys.Acta, **61** (1988) 712

Ugarte D.: Electron Microscopy, vol.2: Material Sciences, Eds. López-Galindo, M.I.Rodriguez-Garcia, Granada 1992 (p.677)

Uppenbrink J., Wales D.J., Kirkland A.I., Jefferson D.A., Urban J.: Phil.Mag.B, **65** (1992) 1079

Urban J., Sack-Kongel H., Weiss K.: High Temperature and Materials Science, **36** (1996) 155

Urban J., Sack-Kongel H., Weiss K.: Catal.Lett., **49** (1997) 101

Uyeda N., Nishino M., Suito E.: J.Coll.Int.Sci., **43** (1973) 264

Uyeda R.: J.Cryst.Growth, **45** (1978) 405

Vainshtein B.K.: Usp.Fiz.Nauk, **152** (1987) 75 (in Russian)

Valkealahti S., Manninen M.: Phys.Rev.B, **54** (1992) 9459

Vladimirov V.I., Romanov A.E.: Disclinations in crystals, Nauka, Leningrad 1986 (in Russian)

Vladimirov V.I, Polonskii I.A., Romanov A.E.: Zh.Tekh.Fiz., **58** (1988) 1473 (in Russian)

Vladimirov V.V., Gorban´ S.A., Nepijko S.A.: Sov.J.Commun.Electron.(USA), **36** (1991) 135

Wallenberg L.R., Bovin J.-O.: Surf.Sci., **156** (1985) 256

Wallenberg L.R., Bovin J.-O., Peterford-Long A.K., Smith D.J.: Ultramicroscopy, **20** (1986) 71

Wang T., Lee C., Schmidt L.D.: Surf.Sci., **163** (1985) 181

Washecheck D.M., Wucherer E.J., Dahl L.F., Ceriotti A., Longoni G., Manasser M., Sansoni M., Chini P.: J.Am.Chem.Soc., **101** (1979) 6110

Wayman C.M., Darby T.P.: J.Cryst.Growth, **28** (1975) 53

Wentorf(jr) R.H.: The art and science of growing crystals, John Wiley&Sons, New York 1963 (p.176)

Westmacott K.H., Dahmen H.: Rev.Phys.Appl., **21** (1986) 757

White D., Baird T., Fryer J.R., Smith D.J.: Electron Microscopy and Analysis 1981, Inst.Phys.Conf.Ser. No.61, London, Bristol 1982

WOLTERSDORF J., NEPIJKO S.A., PIPPEL E.: Surf.Sci., **106** (1981) 64
YACAMÁN M.J., OCANA T.: phys.stat.sol.(a), **42** (1977) 571
YACAMÁN M.J., HEINEMANN K., YANG C.Y., POPPA H.: J.Cryst.Growth, **47** (1979) 187
YACAMÁN M.J., ROMEN L.D., GOMEZ A., MUMIR Z.A.: Phil.Mag.A, **40** (1979) 645
YACAMÁN M.J., FUENTES S., DOMINGUES J.M.: Surf.Sci., **106** (1981) 472
YAGI K., TAKAYANAGI K., KOBAYASHI K., HONJO G.: J.Cryst.Growth, **28** (1975) 117
YANG C.Y.: J.Cryst.Growth, **47** (1979) 274
YANG C.Y., YACAMÁN M.Y., HEINEMANN K.: J.Cryst.Growth, **47** (1979) 283
YU-ZHANG K.: Mater.Sci.Forum, **22/24** (1987) 627
YU-ZHANG K., BIGOT J., CHEVALIER J.-P., GRATIAS D., MARTIN G., PORTIER R.: Phil.Mag.B, **58**(1988)1
ZHIGILEJ L.V., MIKHAJLIN A.I., ROMANOV A.E.: Fiz.Met.Metalloved., **66** (1988) 65 (in Russian)

(Received January 6, 1999; Accepted March 1, 1999)

Authors' addresses:

V. G. GRYAZNOV, A. M. KAPRELOV
Institute for High Pressure Physics of the Russian Academy of Sciences
Academgorodok, Troitsk
Moscow Region, 142092
C.I.S./Russia

J. HEYDENREICH
Max Planck Institute of Microstructure Physics
Weinberg 2
D-06120 Halle (Saale)
Germany

S. NEPIJKO*
Institute of Physics
Ukrainian Academy of Sciences
Prospect Nauki 46
252022 Kiev, C.I.S./Ukraine

A. E. ROMANOV
A.F.Yoffe Physico-Technical Institute of the Russian Academy of Sciences
Polytechnical Street 26
St. Petersburg, 194021
C.I.S./Russia

J.URBAN
Fritz-Haber-Institute of the Max-Planck-Society
Faradayweg 4-6
D-14195 Berlin
Germany

*corresponding author
e-mail: nepijko@yahoo.com