

## SECONDARY STRUCTURE OF CRYSTALS

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*Published experimental data on the dependence of the properties of crystal substances on crystal size are discussed. The dependence is of the same form for different properties and different crystal substances.*

*When the crystal diminishes in size, its properties remain constant until the size decreases to  $10^{-5} - 10^{-6}$  cm; smaller crystals considerably change their properties. It is shown that the currently available experimental data are sufficient to substantiate the notion of an "elementary unit of a solid crystal" ("crystal quantum").*

*The elementary unit of a crystal is regarded as a basis for the secondary structure (macrostructure) of a solid and an elementary carrier of its "crystal" properties. Due to this notion, we can interpret the vast experimental material on the real structures and properties of solids from a single viewpoint.*

The problem of the secondary structure of solids arose at an early stage of the development of modern crystallography. After the theory of X-ray diffraction in crystals had been proposed, the atomic structure of crystals was acknowledged as their primary structure. However, Darwin [1] noted that the experimental diffraction intensities may not be matched to theory without assuming that crystals consist of microregions — units about  $10^{-4}$  cm in size. Darwin's calculations were subsequently confirmed, and it was proven that crystals have a block structure. Real crystals are currently considered to consist of  $10^{-4}$ - $10^{-5}$  cm blocks.

There is more evidence of the secondary structure of real crystals, e.g., the results of observations of crystal growth (these data are reviewed in [2-4]). In the early 1930s, Zwicky [5] made an attempt to substantiate the secondary structure of crystals based on surface tension forces. However, these calculations proved to be erroneous [6]. Later, more attempts have been made. The most famous works are "Cooperative effects in crystals" by A. Goetz (1935) [2] and "Micellar theory of metals" by Yu. A. Klyachko (1933-1935) [3]. In the 1930s, these works stimulated an extensive discussion. Many famous scientists took part in the discussion (Bom, Bragg, Friedel, et al.). The discussion was of great importance for crystallography, since it gave impetus to the development of modern theory of real crystal structures. The key notion in the theory is a structure (point, linear, etc. [7]) defect.

These ideas, advanced in the 1930s, in fact revive the concepts of an earlier ("preatomistic") period of the development of crystallography. In the 19th century, the theory of crystal structure developed by R. J. Haüy was widespread. According to this theory, a crystal consists of minute parallelepipeds called "integrating" and "subtractive" molecules [8]. Similar ideas were suggested by E. S. Fedorov, who believed that a crystal consists of parallelepipeds (polyhedra). Each parallelepiped is regarded as a crystal molecule [9].

Recent developments in physics and chemistry of solids gave many new facts on the real structure and properties of crystals. In particular, ample evidence on the size effect (variation of the properties of crystal solids with decreasing size) was obtained. These data were systematized and reviewed in [10]. Based on the results of these studies, the notion of an elementary unit of a crystal solid (crystal quantum) was formulated and stated as indispensable for a unified and consistent explanation of the known experimental data. Later some other notions, theories, and consequences were formulated to develop the concept of the secondary crystal structure [33].

Currently the size effect in crystals is supported by reliable experimental data. Here we consider on particular examples how the properties of different substances change when the crystals diminish in size.

Figure 1a shows the dependence of the lattice parameter on the crystal size for silicon [11] and cerium dioxide [12]. It is seen that the lattice parameter deviates from that of a bulky sample in the size range  $10^{-5}$ - $10^{-6}$  cm.

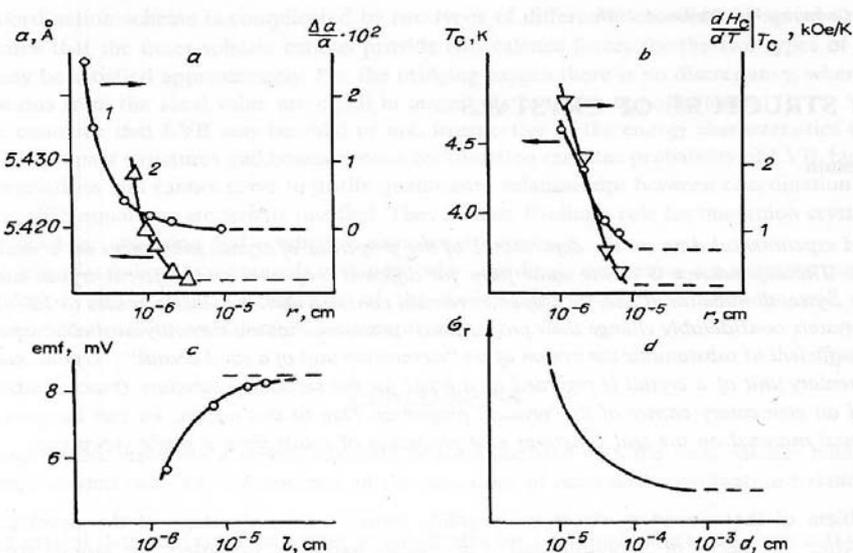


Fig. 1. Size dependences of the properties of different substances:  $r$  is the crystal size,  $l$  is the film thickness, and  $d$  is the sample thickness. *a*) Lattice parameter for silicon [11] (curve 1) and cerium dioxide [12] (curve 2); *b*) Critical temperature for the superconductive-state transition and the derivative of the critical magnetic field for tin films on glass support [16]; *c*) thermal electromotive force of the copper-constantan film thermocouple as a function of the thickness of a copper film at a constant thickness of the constantan film [18]; *d*) tensile strength (modulus of rupture, schematically) vs crystal thickness [15, 20]. For bulky samples, the values of properties are shown by dashed lines.

These data were obtained by X-ray diffraction; electron diffraction data are less exact and may be affected by uncontrollable heating of the sample [13]. Similar dependences were obtained for tin [14], magnesium oxide [15], and some other substances.

The dependences of the critical-temperature for the superconductive-state transition and of the derivative of the critical magnetic field on the crystallite size in tin films [16] are represented in Fig. 1b. Deviations of the values from those of a bulky sample start in the range  $10^{-5}$ - $10^{-6}$  cm. The dependences are typical for finely divided superconductors [17].

The size dependence of the thermal electromotive force of a copper-constantan film thermocouple [18] also deviates from the values of a bulky sample near  $10^{-5}$  cm (Fig. 1c).

Figure 1d shows the size dependence of tensile strength of various crystalline samples - whisker crystals of metals and salts, thin single crystals of alkali halides, polycrystalline metal films, and wire samples [19, 20]. Tensile strength starts to grow relative to the values of bulky samples around  $10^{-4}$  cm, i.e., at larger thicknesses of the sample. This is probably due to the low tensile strength of bulky samples in the presence of cracks, defects, etc.

It is interesting to compare the size dependences of several properties of the same sample. Figure 2 gives the data obtained in [21] for  $\text{EuBa}_2\text{Cu}_3\text{O}_y$  (high-temperature superconductor) films. It is seen that the size dependences of different properties are identical. The value of a property quickly deviates from the value of a bulky sample at film thicknesses of  $10^{-5}$ - $10^{-6}$  cm. Interesting examples are furnished by the studies of the structure transformations of finely divided samples. Figure 3a shows how the crystal structure of aerosol particles of silver iodide

changes with decreasing size of the particles. Almost all particles larger than  $7 \times 10^{-6}$  cm are cubic. Near  $5 \times 10^{-6}$  cm the compound undergoes a phase transformation, so that all particles of smaller size have a hexagonal structure [22]. It is interesting that, according to

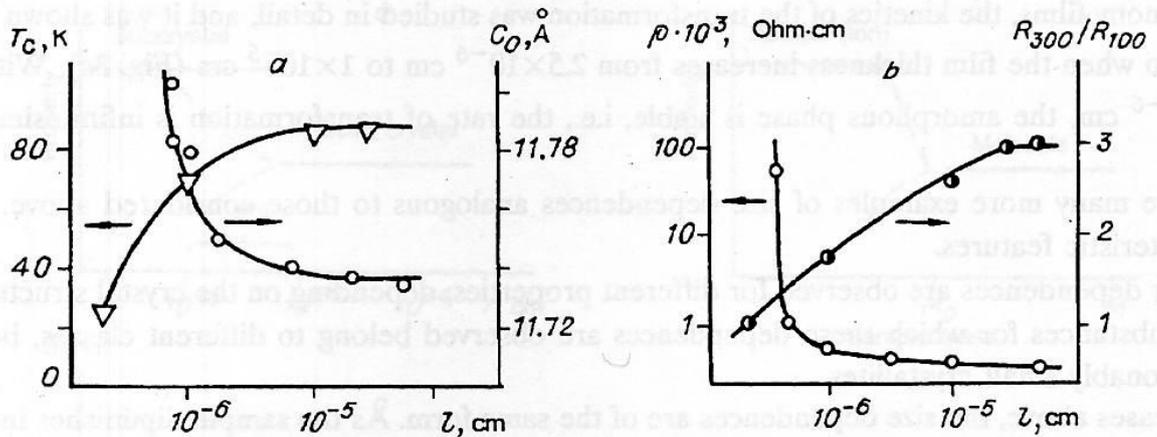


Fig. 2. Size dependences of the properties of the high-temperature superconductor  $\text{EuBa}_2\text{Cu}_3\text{O}_y$  on the film thickness [21]. a) Critical temperature for the superconductive-state transition  $T_c$  and the lattice parameter  $C_0$ , b) resistivity and the ratio of resistances at 300 and 100 K.

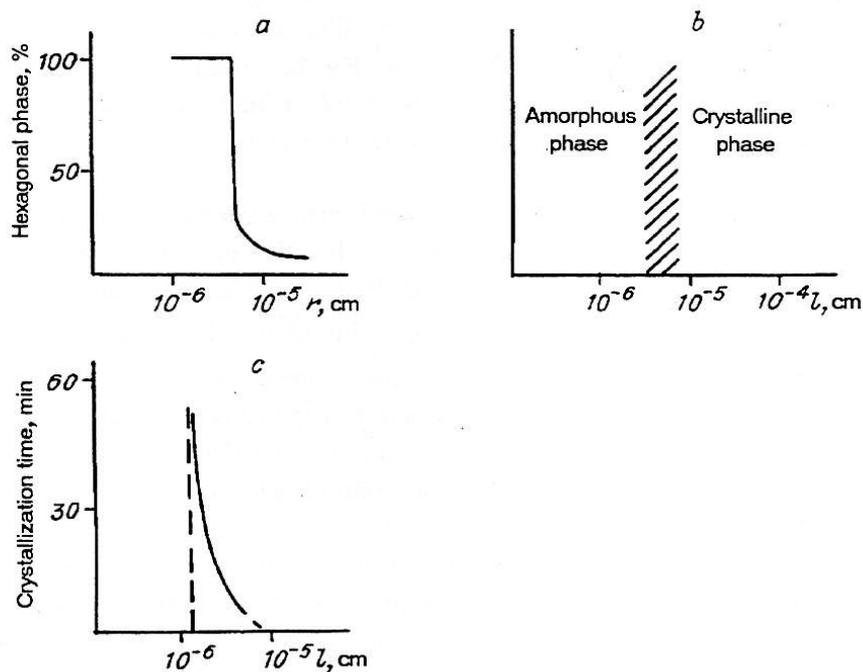


Fig. 3. Size dependences of phase transformations, a) Content of the hexagonal phase in aerosol particles of silver iodide [22]; b) amorphous phase-crystalline phase transition in films of different substances as a function of film thickness [23-25]; c) crystallization time of amorphous antimony vs film thickness [25].

[22], aerosol particles of cubic silver iodide consist of separate blocks  $3.6 \times 10^{-6}$  cm in size, with the sizes of particles exceeding  $7 \times 10^{-6}$  cm.

Thin films of different substances also exhibit size dependences of structural transformations that are similar in character [23]. Along with crystal modifications, thin films

often show amorphous phase-crystalline phase transformations. The size dependences of these transformations were investigated for different substances. Amorphous phase is often observed at room temperatures in the range of small thicknesses. After the critical thickness is achieved in the course of deposition, spontaneous crystallization occurs. The critical thickness is usually within  $10^{-5}$ - $10^{-6}$  cm (Fig. 3*b*). These results were obtained for antimony, bismuth, germanium telluride, ytterbium, and other substances [23, 24]. For antimony films, the kinetics of the transformation was studied in detail, and it was shown that the transition time tends to zero when the film thickness increases from  $2.5 \times 10^{-6}$  cm to  $1 \times 10^{-5}$  cm (Fig. 3*c*). With film thicknesses less than  $2.5 \times 10^{-6}$  cm, the amorphous phase is stable, i.e., the rate of transformation is infinitesimal (dashed line in Fig. 3*c*) [25].

There are many more examples of size dependences analogous to those considered above. It is necessary to note their characteristic features.

1. Similar dependences are observed for different properties, depending on the crystal structure of a substance.

2. The substances for which these dependences are observed belong to different classes, but all of them are crystals with reasonably small crystallites.

3. In all cases above, the size dependences are of the same form. As the sample diminishes in size, the property at first stays invariable or changes insignificantly. Dramatic changes in the properties start from crystallite sizes of  $10^{-5}$ - $10^{-6}$  cm.

4. Clearly, the observed uniformity of the size dependences must be due to a reason common to all substances and properties. It is generally agreed that changes in the properties of finely divided samples are explained by an increase in specific surface or in the portion of atoms lying on the surface of particles. Experimental data presented in Figs. 1-3 suggest that an increase in specific surface may not be the reason for the observed changes in the properties of crystals in the  $10^{-5}$ - $10^{-6}$  cm range (e.g., electric properties, including superconductivity, strength [26], and some other properties). The changes in the structure of particles and films as depicted in Fig. 3 may not be explained by surface effects either. The same is true of the lattice parameter (Fig. 1*a*). With the surface effect the lattice parameter would change only in several surface layers. Experiments show, however, that the lattice parameter changes throughout the volume of the particles (tens and hundreds of atomic layers). These changes are usually attributed to other effects, for example, to "internal pressure" [12].

5. Structure defects evidently cannot cause the observed changes in the properties near the critical size.

Based on items 1-3, we can formulate the notion of a size function of a crystal, which is common to all crystals and their properties (*r*-function). The generalized *r*-function of a crystal has the form shown in Fig. 4*a*. When the crystal decreases in size, the value of the property remains constant to the critical size  $r_q = 10^{-5}$ - $10^{-6}$  cm.

Earlier, it was noted [10] that the form of the function represented in Fig. 4*a* is characteristic of a sample consisting of molecules (atoms) if some intramolecular (atomic) property is being measured (Fig. 4*b*). The value of the property changes when the size (mass) of the sample becomes smaller than the size (mass) of a separate molecule (atom). The critical size in this case is the size of a molecule (atom). This analogy allows us to introduce the notion of an elementary unit of a crystal [10].

An elementary unit of a crystalline solid ("crystal quantum" or minimal crystal) is defined as follows. A minimal crystal (mic) is a minimal quantity of a crystalline solid that preserves normal (limiting) properties characteristic of a bulky sample of the given substance. A smaller crystal loses (or changes significantly) these properties. For different substances, the sizes of mics are within  $10^{-5}$ - $10^{-6}$  cm. Some experimental data [11, 12, 22, 28] suggest that  $r_q = (3-4) \times 10^{-6}$  cm. A mic of this size contains  $10^6$ - $10^8$  atoms (molecules), and its form and symmetry must be determined by the character and symmetry of interatomic (intermolecular) interactions.

The size function of the crystal represented in Fig. 4*a* is an essential condition for introducing the notion of an "elementary unit of crystal." If the unit exists in reality, the size

function should be of the form shown in Fig. 4s, unless there are some other effects explaining the form of the  $r$ -function in the general case with consideration of particular properties. Using this notion one can explain the size dependence of any property for any crystal substance, although the mechanisms underlying such dependences may differ. The critical factor in the size of a crystallite. For films and whisker samples, the critical size must be thickness equal to the size of the elementary unit (mic). The comparatively smooth changes of the properties near the critical size may be explained by the polydispersive character of the samples.

An essential thermodynamic condition of stability of an elementary unit is the presence of a free energy minimum in the vicinity of  $r_q$ . This is equivalent to the presence of a minimum for a certain number  $N_q$  of structural units (atoms or molecules) per crystal particle (Fig. 4c). The presence of the minimum indicates increased stability of the particles of this size (e.g., under mechanical action). This conclusion is in agreement with the known experimental data of minimal size of crystals subjected to mechanical action? E/g/, mechanochemical treatment [27] or ultimate mechanical deformation [28].

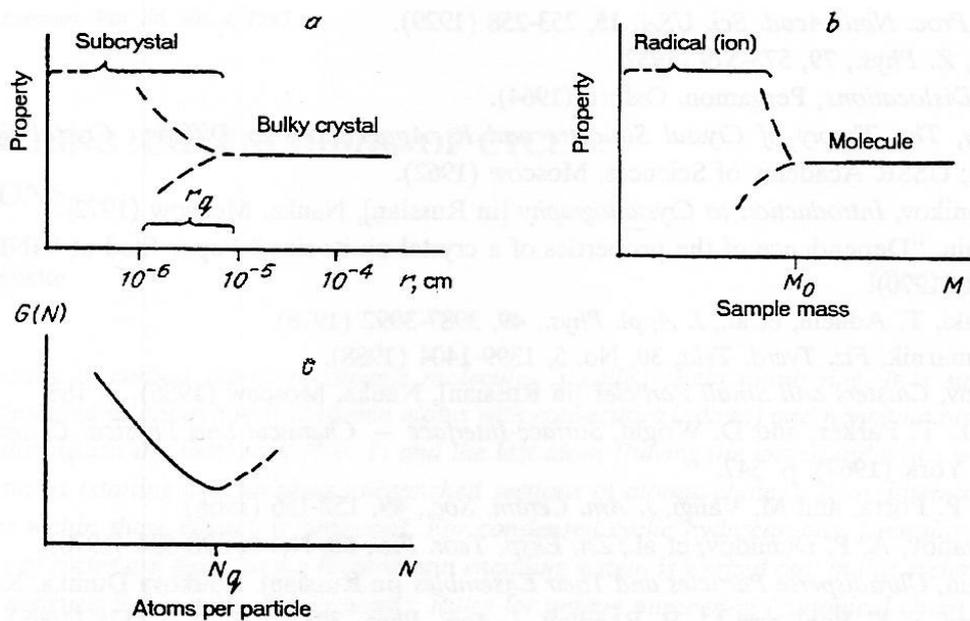


Fig 4. Generalized size function of a crystal [10] (a), general dependence of a “molecular” property on the mass of a sample consisting of molecules (b), and dependence of the free energy of a crystal particle on the number of atoms (molecules) in it (thermodynamic condition of stability of an elementary crystal unit (c)).

The free energy minimum (Fig. 4c) is equivalent to a minimum on the size function of potential energy of interaction between atoms or molecules comprising the crystal. The potential energy can change only as a result of changes in the interatomic distances of the crystal. Hence it follows that at  $r < r_q$  ( $N < N_q$ ) for small parties the interatomic distances (lattice parameter) should change (Fig. 1a). Also, the free energy minimum (Fig. 4c) indicates that at  $N < N_q$  crystal particles should have increased specific energies due to a deficiency in the particle mass. Specific energy is evidently a factor responsible for the known properties of nanophase particles and materials.

Thus the concept of an elementary unit of a crystal agrees well with the available experimental data. Moreover, this concept provides a natural solution to the problem of secondary structure of crystal. It is assumed that in normal. (equilibrium) conditions a crystals consist of elementary units (mics). The problem of an interface between these units is of special interest. The available experimental data suggest that the boundaries between mics may serve as sources and sites of dislocations. Probably it is not accidental that the maximal density of dislocations ( $10^{-11}$ - $10^{12}$  per  $\text{cm}^2$ ) is nearly coincident with the number of elementary units per  $\text{cm}^2$

of crystal cross section with the linear size of a mic  $3 \times 10^{-6}$  cm. Some experimental data [29-30] suggest that the real boundaries between mics are channels for transporting substances (diffusion) and charges (current) through the crystal.

The concept of an elementary unit of a solid ("supermolecule") has been successfully developed by V. B. Aleskovskii et al. [31, 32]. These works proved the practical value of the approaches using the notion of an "elementary unit of a crystal" and showed that current knowledge on the secondary structure of crystals serves as a reliable basis for experimental solid state chemistry.

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Dear colleagues!

In the problem of the secondary crystal structure (SCS) it is necessary to consider one circumstance. Crystals and their properties are subjects of the SCS theory. Though the main thing here is a purely chemical approach. The main subject of chemistry is a molecule. And in the SCS an elementary crystal unit is a giant molecule (with the size of 300 angstroms). Before joining to a crystal, atoms or small molecules of substance are bound to giant molecules named micromolecules passing through an intermediate stage of subcrystal (an analogue of radical molecule). This process was observed repeatedly in electron microscopy (see "Secondary structure and properties of crystals", p. 74, Fig. 21).

Then the micromolecules are combined into blocks and embedded as a whole into an existing crystal. When the molecules have been combined into the crystal, it could be difficult to distinguish them. Here the size effect can help, when the inverse process – successive disintegration of the crystal – is used. Properties of the sample are changed at destruction of the molecule. All of this is described in the monograph. In this way any molecule can be identified in principle.

Instead of conclusion: an important stage in structural organization of substance was missed earlier – a condensed state molecule. The particular cases of liquid and amorphous solid are discussed in Theorem 14 of the monograph.