

Liquids in ultrathin channels (Filament and cluster crystals)

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1. INTRODUCTION

In connection with searches for ways to increase the critical parameters of superconductors, especially since 1964,^[1,2] an entire set of objects whose properties differ from those of three-dimensional bodies by virtue of an increased role of the surface, geometry, or size has been invented and studied. They are thin films (20–100 Å) in contact with a dielectric or with a semiconductor or films of the type of amorphous mixtures of substances that react weakly with one another.^[2,3] The critical temperatures T_c of such objects are higher than the T_c values of the original substances by factors of 2–5, but they do not exceed 5–10 °K. Analogous effects have been observed in metals in random channels of diameter 20–100 Å in porous glasses or in a ceramic. The critical magnetic fields H_c of such “synthetic” superconductors are 50–100 times as great as the H_c of the original materials.^[4] “Granular” superconductors have been proposed: metal particles in oxide films that insulate them from one another.^[5] A number of interesting physical results has been obtained with the artificial objects listed above. We can include among the artificial systems of more regular structure and with smaller characteristic dimensions the monomolecular films of fatty acids alternating with layers of atoms or ions, e.g., of metals.^[6] Crystalline regularity and atomic discreteness exist in a number of natural “chemical” crystals that we can consider as quasi-one-dimensional or quasi-two-dimensional. For example, they include organic conductors like the salts of tetracyanoquinodimethane, which have been intensively studied recently,^[7] superconductive layer systems like NbSe_2 ,^[8] Ag_2F ,^[9] the organometallic crystals TaS_2 (pyridine) $1/2$,^[10] and graphite compounds.^[11] In these substances the conducting filaments or layers have atomic dimensions and crystalline regularity. Yet their T_c values are low: 3–6 °K, though in a number of cases the H_{cII} along the layers is hundreds of times larger than H_{cI} , and exceeds the paramagnetic limit field.

The study of the physical properties of systems having separate conducting and nonconducting regions is also an interesting independent problem. We can apparently say of the majority of the listed natural objects that those of their components that “insulate” the conducting filaments or layers from one another interact chemically with these conducting regions. The chemical interaction that makes possible the stability of the system nevertheless restricts the number of possible compounds and structures. Forced combination of conducting and insulating regions can permit a study of a number of other combinations of substances. Such combinations have been made possible by filling, for example, the cavities and channels of dielectric matrices like zeolite crystals with liquid metals. Here the channels or cavities of 5–10 Å diameter form regular space lattices.

Introduction of non-wetting metallic liquids into the channels of dielectrics requires expending energy on dispersing the liquid, whereas chemical interaction in the formation of crystals involves the release of energy of the order of 10–100 kcal/mole. If the channels in the matrix are of atomic dimensions, then it should take energies of the order of the heats of vaporization, i.e., also of the order of 10–100 kcal/mole, to force non-wetting liquids into them. When we recalculate this in terms of pressure we get values of the order of 5–50 kbar, i.e., quite realistic ones. Apparently these systems differ from chemical systems not only in the sign of the energy of formation. They can be created not according to chemical rules. One can treat the monoatomic filaments in the channels of dielectric matrices or drops (clusters) in their cavities as individual objects under conditions of dimensional quantization, as being a sort of molecules from which a new physical object has been formed—filament or cluster crystals. The dielectric matrix serves as a container that confines the filaments or drops in space in a definite order. The lack of a chemical interaction with the matrix that affects the electronic structure of the atoms is compen-

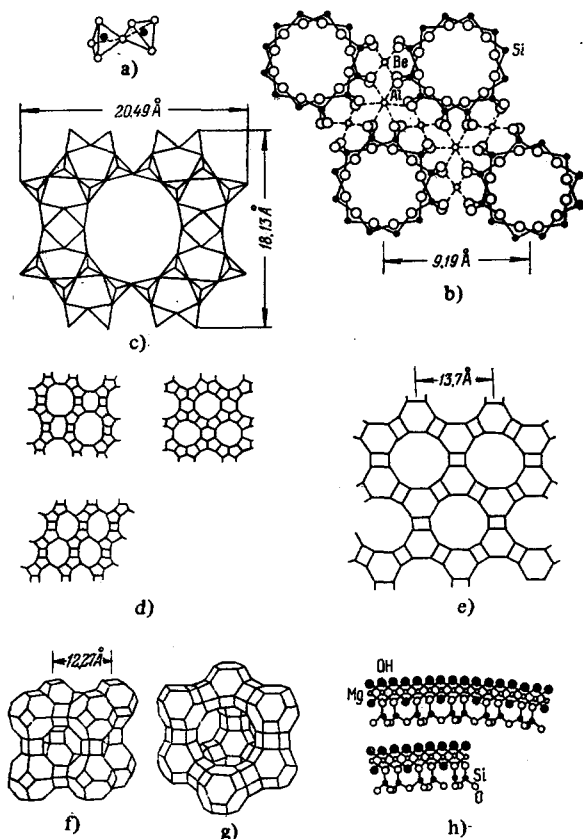


FIG. 1. Structures of skeletal aluminosilicates and chrysotile-asbestos. a) Linking of AlO_4 - SiO_4 tetrahedra. The structures of: b) beryl, c) mordenite, d) mordenite, ferrierite, dachiardite, e) gmelinite in a plane perpendicular to the axes of the large parallel channels. Shape of the cavities of zeolites: f) NaA, g) NaX, h) monocrystalline layers that form the structure of chrysotile fibers.

sated by the "physical" interaction of the filaments or clusters with the matrix and through it with each other. It has proved possible in synthesizing these crystals by forcing non-wetting liquids into capillaries of atomic dimensions also to make certain assertions concerning the microscopic aspects of non-wettability and surface tension.

2. CHANNEL MATRICES—ZEOLITES AND ASBESTOS MINERALS

A rigorously periodic system of identical channels and cavities of atomic diameter exists in zeolites, which are widely used as adsorbents, molecular sieves, and catalysts.^[12] Zeolites are skeletal aluminosilicates whose structure is formed by linking AlO_4 and SiO_4 tetrahedra by common vertices as in Fig. 1.^[13] Since aluminum and silicon do not have the same valence, cations (potassium, sodium, etc.) enter into the composition of the zeolites which are situated not within the zeolite lattice, but on the inner surface of the channels and cavities (near the aluminum-oxygen tetrahedra), and can migrate along them and play an important role in adsorption, catalysis, and ion exchange. The channels in a zeolite are usually filled with water that wets their walls. The structural formula of the unit cell of a zeo-

lite is: $M_{x/n}[(\text{AlO}_2)_x(\text{SiO}_2)_y]\text{NH}_2\text{O}$, where y/x is usually from 1 to 5 for different zeolites, and M is a cation of valence n . The number N of molecules of zeolitic water is determined by the volume of the cavities or channels. The water in zeolites commonly occupies up to 50% of the volume of the crystal and it can be removed by heating to 200–500°C. The skeleton of the zeolites is strong (hardness of 4–5 on the Mohs scale), and they can withstand temperatures up to 800°C or compression up to 100 kbar. Some zeolites are alkali-stable (NaA, NaX), and others acid-stable (mordenite). The commercial zeolites NaX (faujasite), NaA, and mordenite possess the largest channel diameters. The entrances into the channels of these zeolites are formed of rings of tetrahedra (Fig. 1). Table I gives the free diameters of the plane rings (with allowance for the dimensions of the tetrahedra).

A. The zeolite $\text{NaX}-\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 32\text{H}_2\text{O}$

The system of cavities between the cubooctahedra (Fig. 1g) forms a diamond lattice with the lattice constant 25.4 Å. The density of the zeolite containing water is 1.91 g/cm³ and without water is 1.41 g/cm³. The diameter of the cavities is ~13 Å, while that of the entrances into them (windows) is 7–8 Å. The volume of the large cavities is ~42% of the volume of the crystal (with 27 water molecules per cavity). For every large cavity, there is one small cavity inside a cubooctahedron with windows ~2.5 Å. The volume of the small cavities is ~8% of the volume of the crystal (5 water molecules per cavity).

B. The zeolite $\text{NaA}-\text{Na}_{12}[(\text{AlO}_2)_{12}(\text{SiO}_2)_{12}] \cdot 29\text{H}_2\text{O}$

The system of cavities in Fig. 1f forms a cubic lattice of lattice constant 12.27 Å. The density of the zeolite containing water is 1.96 g/cm³ and without water it is 1.49 g/cm³. The diameter of the cavities is 11.4 Å, and that of the entrances into them is 4.2 Å. The volume of the large cavities is ~40% of the volume of the crystal, and that of the small cavities is 7%.

C. Mordenite $\text{NaM}-\text{Na}_{8.7}[(\text{AlO}_2)_{8.7}(\text{SiO}_2)_{39.3}] \cdot 24\text{H}_2\text{O}$

The structure contains parallel channels 6.7–7 Å in diameter whose axes are separated by 13–14 Å (Fig. 1c, d). The density of mordenite containing water is 2.13 g/cm³. The volume of the large channels is ~20% of the volume of the crystal. A number of zeolites has a system of parallel channels formed, as in mordenite, of the 12-membered rings of Fig. 1e.^[12] No zeolites with channels of 18-membered rings have yet been found.

The maximum dimensions of the crystallites of synthetic zeolites are ~0.1 mm.^[14] The natural crystals of mordenite are found in the form of needles 0.03 × 0.04 × 1 mm. The natural zeolites also include large crystals of volumes up to several mm³. The entrances into their channels are formed by 8-membered rings, but

TABLE I.

Number of tetrahedra in the ring	4	5	6	8	10	12	18
Free diameter, Å	1.1	2.1	2.8	4.3	6.3	8	15

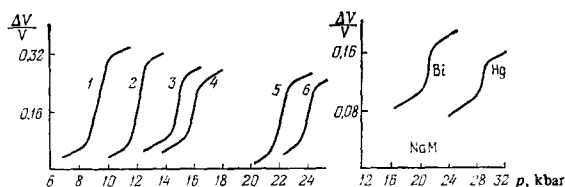


FIG. 2. Pressure-dependence of the volume of the zeolite-liquid metal system. 1-NaX-Bi, 2-NaX-Hg, 3-NaA-Hg, 4-NaA-Sn, 5-NaX-Ga, 6-NaA-Ga.

we have not succeeded in our attempts to introduce metals into these channels under pressure.

Regular channels of diameter 15–100 Å exist in the fibrous mineral chrysotile-asbestos (chrysotile) $Mg_3Si_2O_5(OH)_4$.^[13,15,16] The monocrystalline layers of the mineral of Fig. 1h have a natural curvature of 88 Å, and they bend in and out during growth, as one can see well in electron micrographs.^[16] Bundles of fibers of diameter 200–300 Å form transparent crystals of lengths up to several centimeters. Depending on their site of origin, the channels in the asbestos minerals are filled either with amorphous matter or water, which is removed by heating to 100–150 °C, whereupon one can introduce, for example, metals into the channels.

3. FILLING OF CHANNELS OF ATOMIC DIAMETERS WITH MATERIALS

Wetting liquids or adsorbable vapors enter the channels of zeolites spontaneously if the diameters of the molecules match the diameters of the channels. For example, sulfur has been introduced from the vapor into NaA with 16 atoms per cavity.^[17] Introduction of several atom percent of mercury or cadmium from the vapor into zeolites has been described.^[18] The ion-exchange properties of the zeolites are used for deposition within the cavities of metal atoms, which were present on the walls of the cavities in the form of ions. These ions are replaced, for example, by hydrogen ions. In this manner atoms of nickel, silver, and a number of other metals have been introduced into the cavities of zeolites.^[12] The method has been employed of introducing iron by decomposing its compounds in the channels of zeolites.^[19] One can introduce the maximum amount of metal (20–25% of the volume of the crystal) from a liquid under high pressure.^[20] Introduction of atoms of diameter about 3 Å into channels composed of 4- and 5-membered rings is impossible. They can arrive there only in the form of ions and migrate by diffusion. Practically one-dimensional diffusion of impurities and defects has been observed in the 4-membered channels of rutile along the *c* axis.^[20] However, the solubility of the ions is small and the conductivity proved to be almost isotropic. Water molecules can be situated in the 6-membered channels of beryl (Fig. 1b). We have not succeeded in attempts to introduce non-wetting liquid metals into the channels of beryl under pressures up to 70 kbar. We also did not succeed in introducing the liquid metals Hg, Ga, In, Bi, Cd, Sn, Pb, and alloys under pressures up to 40 kbar into the 8-membered

channels of zeolites of the chabazite type. At the same time, experiments to fill the channels in the zeolites NaX, NaA, and mordenite with metals proved successful.

A powder of the zeolite (5–10 μm crystals) was compressed at 8–10 kbar pressure into cylindrical ampoules of mild steel, dehydrated at 300–400 °C in vacuo, had liquid metal poured over it and the ampoule was closed with a stopper and lid. Mordenite was dehydrated under a layer of liquid metal until the water had boiled away. The ampoule was placed in a chamber of the compression-mold type, was compressed from above and below in the heated state by pistons, and the decrease in volume of the ampoule with increasing pressure was measured. Figure 2 shows typical pressure dependences of the volume of the zeolite-liquid metal system. A sharp decline in volume that amounts to 15–25% of the volume of the zeolite crystals occurs at some critical pressure p_c . Measurements of the electric conductivity under pressure showed that the crystals of the zeolites NaX and NaA, whose skeletons are dielectrics, acquire a conductivity of the order of that characteristic of a metal. The conductivity vanishes if the pressure is removed. Measurements of the density of such crystals lead one to conclude that here certain metals (Ga, Sn, Bi) remain in the cavities with 10–15 atoms in each, in spite of the disappearance of metallic conductivity, and this number does not vary appreciably with time. Others (Cd, Hg) leak out of the channels immediately after the pressure is removed, and one can again introduce 15–20 atoms of metal per cavity into this same zeolite under pressure. This behavior strongly depends on the degree of dehydration of the zeolite. There are no analogous data on mordenite. X-ray analysis showed that stresses arise in the skeleton of the zeolite that disappear upon removing the metal from the cavities. The structure of the zeolite is preserved, but it has not been possible to observe the droplet lattices.^[21] Sulfur and selenium^[22] have also been introduced into zeolites under a pressure of 1–2 kbar. X-ray studies of single crystals of NaA of 50 μm size containing sulfur have established that each cavity contains two parallel S_8 rings oriented with respect to the entrances into the cavity.^[17]

The zeolite powder can be freed of metal by dissolving the metal, for example, in mercury or in an etching agent that does not act on the zeolite. The zeolite is freed of mercury by water. The pressure at which a metal enters the channels of chrysotile is smaller than for the zeolites. An asbestos fiber 10–15 mm long is cemented at its middle into a tube made of a dielectric, is dehydrated at 120–150 °C, is cut off at the ends, and metal is poured onto these ends from both sides in the tube. With increasing pressure, the metal penetrates into the channels of the asbestos from both ends, as is established from the appearance of conductivity in the fiber. If one decreases the pressure to 50–100 atm, the contacts are broken. The pressure-dependence of the conductivity is diffuse, in line with the scatter in the diameters of the channels.

TABLE II.

	Be	Mg	Ca	Mn	Zn	Sr	Pd	Cd	Ba	Yb
Q , kJ/g-atom	309	128	172	225	115	141	390	100	175	166
σ_{cal} , dyne/cm	3300	666	590	1760	815	403	2760	600	490	585
$\sigma_{cal}/\sigma_{exp}$	2.9	1.2	—	1.0	1.1	1.1	1.7	1.0	1.5	1.3
	Re	Hg	Ra	Zu	He	Ne	Ar	Kr	Xe	
Q , kJ/g-atom	783	60	147	173	0.08	1.74	6.45	9.40	12.6	
σ_{cal} , dyne/cm	5500	355	400	575	0.02	6.3	16.3	19.0	23.9	
$\sigma_{cal}/\sigma_{exp}$	2.0	0.9	—	—	1.6	0.9	1.0	1.0	1.0	

4. BEHAVIOR OF NON-WETTING LIQUIDS IN CAPILLARIES OF ATOMIC DIAMETERS. SURFACE TENSION AND HEAT OF VAPORIZATION

Experiments with capillaries of atomic diameters allow one to draw a number of conclusions regarding the microscopic aspects of the non-wettability and surface tension. For a number of liquid metals, data analogous to those given in Fig. 2 imply that non-wetting liquids do not completely fill the cavities of zeolites as water does, but only about halfway. This ratio is even worse for mordenite: one-quarter. If we assume that the metal in the cavities exists as compact droplets, we can compare their diameter with that of the cavity. In all cases one finds a difference of 2.5–3.5 Å that can be associated with the fact that these liquids do not wet the walls of the cavities. In the present case the presence of a gap of ~1.5 Å is manifested on a macroscopic scale. Evidently it would be very complicated to measure such a unit gap, for example, between a drop of mercury and some surface.

In the case of mordenite, the amount of metal that enters the channels of 6.7 Å diameter (about 4% and 6% of the volume of the crystal for Hg and Bi; Fig. 2) corresponds to monatomic filaments of these metals of diameters 3.2 and 3.7 Å.^[23] From these data the size of the gap due to non-wetting also turns out to be ~1.5 Å. The difference in the macroscopic amounts of mercury and bismuth that enter mordenite under pressure directly depends on the difference in diameters of their atoms.

By using the data of Fig. 2 for mordenite, we can estimate the work done by the press in dispersing the metal into monatomic chains. If we assume that the surface energy of the atoms is spherically symmetrical, the work done by the press against the forces of surface tension can be correlated with the heat of vaporization Q of the liquid. For mercury, which has a filled electron shell, these energies coincide (15 and 14.6 kcal/g-atom), while for bismuth with an unfilled shell, the heat of vaporization is greater by a factor of almost three (15 and 41 kcal/g-atom). This implies that for mercury the surface tension σ can be defined in terms of the atomic heat of vaporization Q/N (N is Avogadro's number) per unit surface: $\sigma = Q/Nd^2$. For metals like bismuth, the surface energy of the atom is not spherically symmetric, and no such simple relationship exists between σ and Q . Here liquefaction does not affect the strongest bond, which does not participate in surface tension, but makes the major contribution to the heat of

vaporization. In liquid form metals like bismuth must consist of chains, while liquids like mercury are apparently isotropic to a high degree. Table II gives the group of elements with filled electron shells together with the values of σ_{cal} as calculated by the simple formula introduced above. The diameters of the atoms are taken from Ref. 24, and the experimental values σ_{exp} from Ref. 25. The temperature at which the σ_{exp} were measured is usually lower than T_b for metals with high boiling point T_b . This can yield an appreciable discrepancy between the experimental and calculated data. For the liquefied noble gases the heat of vaporization and σ_{exp} are known at the same temperature, and a calculation of σ from Q gives the best results; if we take as the elementary surface the surface of the atomic volume V in the liquid we obtain: $\sigma = Q/6NV^{2/3}$ (see Table II). The relationship between the heat of vaporization and the surface tension was noted even in the past century,^[26] when the microscope nature of surface tension was widely discussed in the literature,^[27] but nothing was known of the electronic structure of atoms.

The experiments with capillaries of atomic diameters confirm the simple ideas used to explain this relation, and they also allow one to understand the reason for the discrepancy between σ_{cal} and σ_{exp} in absolute value for a large group of elements.

If all the foregoing is true, then it will not seem remarkable that one can apply to capillaries of atomic diameters the well-known formula relating the diameter D of the capillary and the pressure p_c at which a non-wetting liquid enters the channel: $p_c = 0.4\sigma/D$ (kbar, dynes/cm, Å). A calculation of p_c for the case of the three zeolites indicated in Fig. 2 and metals having the most varied surface tensions gives pressure values that differ from the experimental only by 10–20%. However, one must include in the diameter of the channel also the gap due to non-wettability (in the case of mordenite this doubles the diameter of the column of metal in the channel) (Fig. 3a), and also ignore the narrow diaphragms and take the diameter of the channel equal to its maximum value assuming that diaphragms of atomic extent exert no appreciable resistance to the liquid (Fig. 3b)

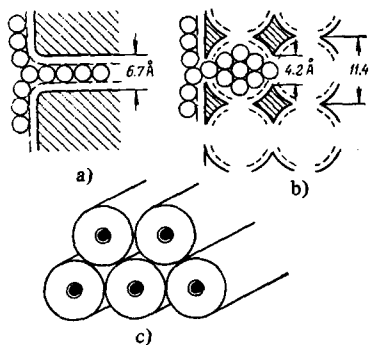


FIG. 3. Schematic diagram of the filling by metal atoms (a) of a channel in mordenite and (b) of the cavities in the zeolite NaA. The walls of the channels and the cavities are indicated arbitrarily; c) schematic diagram of a bundle of fibers of chrysotile-asbestos containing a metal in the channels.

(in the case of the zeolite NaA this is 4.2 Å as compared with 11.4 Å).

When one introduces alloys into zeolites, one observes filtration of the atoms of lower surface tension. Zeolites behave like energy atomic sieves when solutions of non-wetting liquids are forced in.

If all the foregoing correctly reflects the situation at least in general terms, then apparently curvature of the order of the radius of the atomic shells corresponds to a pressure of 70–100 kbar. Such pressures suffice to cause many phase transitions in particles of small dimensions in the region of scratches or sharp corners.^[3]

5. PHYSICAL PROPERTIES OF SYSTEMS OF CLUSTERS AND FILAMENTS

The physical properties of cluster or filament crystals or of filaments of atomic diameter in a dielectric medium are of quite definite interest for a number of problems of solid state physics and practical applications. Yet there is extremely little information on the properties of such systems. Their study is in its initial stage and is greatly complicated by the need to carry out the investigations using powders (5–70 μm), which in addition must be recovered from melts of metals, or as in the case of the asbestos minerals, one must select among the natural fibers those whose channels are not sealed with solid materials. Since zeolites *per se* constitute an extremely important tool of chemical technology, the problem of getting large crystals will certainly be solved.

A. Cluster crystals (zeolites NaX, NaA)

The skeletons of the zeolites are good dielectrics like quartz. The ionic conductivity can be high, and takes place along the channels or their surface which can attain values of 1500 m²/cm³. At pressures above the critical, liquid metals penetrate the channels of the zeolites and form regular lattices that reproduce the configuration of the channels and cavities of the skeleton. In this case the interaction between 10–20 atomic clusters suffices to form a system having a conductivity of the order of a metal, as is found in measuring the conductivity under pressure. When one cools gallium and mercury in zeolites to 80–100° below the melting points of the massive metal under pressure, one observes a stepwise increase in conductivity that can be ascribed to solidification of the zeolite metal. The arrangement of the 10–20 atoms in the droplet in the spherical cavity (Fig. 3b) substantially differs from their arrangement in the crystalline massive metal. Nevertheless, the configuration of the droplets is apparently the same in all the cavities, as is governed by the strict identity of the cavities of the zeolite and is confirmed by the sharpness of the transitions at the melting and freezing points. Yet it is not clear of what does the melting of these droplets or clusters fixed in the cavities of the matrix consist, and how is it reflected in the conductivity. The existence of supercooling by 30–40° also indicates the existence of interaction between the clusters. If one reduces the external pressure, the zeolite crys-

tals become insulators. Here part of the metal leaves the cavities, the distance between the clusters increases, and this apparently leads to disappearance of the metallic state. The density data indicate that here droplets of 10–15 atoms still remain in the cavities of the zeolite. One observes sharp peaks in the thermal conductivity at temperatures corresponding to the melting of the zeolitic metal in such a dielectric system of clusters fixed in space by the cavities of the zeolite skeleton. The thermal-conductivity peaks shift to lower temperatures as the metal leaks out of the zeolite.^[29] All this indicates the existence of a sufficiently organizing interaction between the clusters in the cavities of the zeolites, apparently through the dielectric, which quenches the fluctuations and allows one to treat such a system as a cluster crystal. The electronic properties of such crystals depend sharply on the dimensions of the clusters. It has not been possible to detect a Mössbauer effect in a system of tin clusters. From this we can conclude that tin does not enter into chemical reaction with the oxygen of the skeleton, while the interaction of the clusters with the walls of the cavities is relatively weak.

The decline in the melting temperatures of individual particles as they become smaller has been traced down to diameters of the order of 20 Å (300–400 atoms)^[29] and can be described by the formula $T_d/T_\infty = (1 - d_0/d)$, where d is the diameter of a particle, and d_0 is a parameter that has a different form in the different theories of melting, ranging from 10–20 Å to 3–5 Å (theory of surface-layer melting).^[30] For clusters of Hg, Ga, and Sn of diameter 8–9 Å in the cavities of zeolites, the value is $d_0 = 2-3$ Å. This also allows us to identify the phase transitions observed in such systems with melting. It is assumed that the reason for the lowering of the melting temperature of small particles consists of the competition of the heat of melting with the gain in surface energy upon transition from the solid to the liquid state. For particles of atomic diameter, one must evidently take into account the concrete geometry of the cluster in the "solid" and "liquid" phases.

Thus the lack of broadening of the phase transition and the lowering of its temperature apparently indicate that both the collective and the individual properties of particles of 10–20 atoms are manifested in these properties of cluster crystals. Since the width of the thermal conductivity peaks (1–2°) essentially does not depend on the metal content in the zeolite (the number of atoms per cluster), this can serve as an argument in favor of a uniform distribution of the atoms over the cavities, even when their number is smaller than the maximum possible one.

The study of the conductivity of cluster crystals in the metallic state for $p > p_c$ is complicated by the presence of the pressure-transmitting liquid metal between the crystals in the pressed powders. In the zeolite NaX containing mercury, one observes at $p > p_c$ a rapid rise in conductivity at 6–9°K and metallic magnetoresistance at 78°K. However, in view of the foregoing, the interpretation of these data is difficult.

At atmospheric pressure the crystals, which have made the transition to the nonconducting state, can be separated from the external metal. Density measurements indicate that they contain metal up to 10–20% of the volume of the crystal. Here the dielectric constant remains of the same order as for the empty zeolite (approximately 2). Very considerable changes occur in the optical properties. Depending on the filling material, the crystals acquire some particular tint or shade. If the clusters are large enough, as in the case of Se or S (16 atoms), then the absorbance spectra exhibit a region of sharp growth that reaches saturation, as is characteristic of the absorption spectra of ordinary crystals in the region of an optical absorption edge. For the cubic cluster lattice of selenium in the cavities of the zeolite NaA, the absorption edge lies at 3 eV, while for the diamond-type selenium cluster lattice in the zeolite NaX it lies at 2 eV.^[22] Apparently this difference involves the fact that in the former case the clusters are separated by 1–2 Å more (Fig. 1g, f). The long-wavelength regions of the spectra in both cases have a step-like form. One can consider each cluster as some sort of molecule with its own system of levels. However, the structure of such a molecule is as yet known only for the case of sulfur introduced from the vapor into the zeolite NaA.^[17] Introduction of materials under pressure can give a different filling of the cavities and a different structure of the clusters.

B. Metallic filaments in mordenite and asbestos minerals

An estimate of the binding energy of the mercury atoms in the monatomic chains in the channels of mordenite gives a value about 5 kcal/g-atom, i. e., the same as in massive mercury per bond. For bismuth this energy is about 30 kcal/g-atom, which is even larger than the energy of the two other bonds. All this allows us to hope that in the absence of external pressure these chains will prove continuous. There is as yet no information on the properties of these filament lattices. The distance between the filaments is about 10 Å, which is not so small that we should expect an interaction between them that would be certainly sufficient to produce a conducting system.

One can get conducting metal filaments of diameter 70–15 Å separated from one another by a 200–500 Å layer of dielectric by filling the channels of the chrysotile asbestos minerals with metals (Fig. 3c). The specimen usually is a crystal of 0.1–0.2 mm diameter and 10–15 mm length. Such a crystal contains up to 10^7 channels, while the penetrating conducting filaments are formed in only about one in 100 channels. The resistance of the specimens is usually from 10 to 1000 ohms. The diameters of the channels in the natural asbestos minerals can show a considerable scatter, as is manifested by the diffuseness of the dependence of the conductivity of the filaments on the pressure at which the metal is forced into the channels, although sometimes one can select specimens and pressures such that the scatter in the diameters of the obtained metallic filaments is small (for example, 23 ± 1 Å).^[20, 31] People have detected in these fine mercury filaments a

decrease in the melting point of the metal, diffuseness of this transition, supercooling, and a limitation of the mean free path of electrons by the walls of the channels. The transition to the superconducting state becomes diffuse with decreasing diameter of the filaments, and the diffuseness reaches 100% of T_c for filaments of 5-atomic diameter. The volt-ampere characteristics show a stepwise shape. Below the transition down to $0.5T_c$, the resistance falls exponentially and does not vanish. An appreciable increase in resistance appears before T_c in the thinnest filaments. The critical magnetic fields increase with decreasing diameter of the filaments, and reach 220 kOe at $T=0$ (from measurements up to 150 kOe). This is three times larger than the paramagnetic limit field for mercury.^[32] There is a heat-capacity peak in the transition region that is narrower than the transition in terms of resistance. Filaments of gallium, indium, and a number of alloys exhibit analogous behavior. There is no substantial increase in T_c . The interaction between the electronic systems of the individual metallic filaments in the asbestos minerals is non-zero only at the common contacts, the distance between which is 5–6 orders of magnitude larger than the distance between the filaments. Apart from the electrostatic and electrodynamic interactions in a system of such thin conductors when a current flows along them, we can apparently consider these filaments to be independent. The role of fluctuations in these non-interacting filaments begins to be manifested especially appreciably when the number of atoms per cross-section of the filament falls to 20–30. The width of the transition increases rapidly. Yet apparently there is no shift of the transition temperature toward zero, and the superconducting transition simply becomes ever less noticeable against the rising background of other phenomena.

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