

Structure and properties of fine metallic particles

I. D. Morokhov, V. I. Petinov, L. I. Trusov, and V. F. Petrunin

USSR State Committee on the Use of Atomic Energy, Institute of Chemical Physics, Academy of Sciences, USSR and Moscow Engineering Physics Institute
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This review considers the present status of theoretical and experimental investigations of fine metallic particles (FMP) with characteristic dimension from 100 to 1 nm. An analysis is made of the influence of the size of FMP on the structure, on the phonon spectra, the heat capacity, the Debye temperature, the behavior of the FMP in an electromagnetic field, the relaxation of the electronic spins, the magnetic susceptibility, and the optical properties. Changes in the structure and in the phonon spectrum are due chiefly to disintegration of the surface layers of atoms and to the large curvature of the surface of the FMP. The electronic states of FMP are treated with allowance for the pronounced discreteness of the levels. A comparison is made of theoretical and experimental results on the effect of the parity of the number of electrons in the particles on the paramagnetic susceptibility and on the Knight shift. Relaxation of electron spins in FMP of alkali metals is discussed with allowance for the effect of the surface and of impurities, and also of a possible contribution from the pronounced discreteness of phonon and electron states. Investigations of optical properties and of plasma oscillations indicate an important role of surface states in relation to electronic transitions in FMP.

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1. INTRODUCTION

During the last two decades, a new trend of investigations has originated at the junction between the physics of metals and colloidal chemistry: the physics of ultradispersed media (UDM). This trend is due to investigation of a special class of materials, consisting of macroscopic ensembles of fine metallic particles (FMP) or of semiconductor or dielectric particles whose dimensions lie in the range from 1 to 100 nm. The greatest development has so far occurred in investigations of metallic UDM, whose basic physical properties differ substantially from the properties of metals in the usual bulk state and in a number of cases are unique. These systems reveal interesting combinations of electrical, magnetic, thermal, superconducting, mechanical, and other properties, not encountered in bulk materials.

The majority of characteristics of UDM are determined by the properties of the individual fine particles of the ensemble. When the size of the particles becomes comparable with a characteristic correlation scale of one or another physical phenomenon or with a

characteristic distance of some transport process, then various dimensional effects occur in these systems. It is also in UDM that all the peculiarities of surface states show up most clearly, since in such systems the field of the surface atoms may attain several tens of percent. Furthermore, an extended surface exerts an influence on the lattice and electron subsystems of the UDM, sharply changing the spectra of the various elementary excitations, which are sensitive to a change of symmetry and of boundary conditions.

But a number of physical properties of UDM are due not solely to anomalies of the characteristics of individual particles, but also partly to their collective behavior in the ensemble in the presence of interaction between them. This relates primarily to transport processes in UDM: in particular, the conductivity, superconductivity, and thermal conductivity, manifestations of which are to a considerable degree determined by correlations between the electron and phonon states in ensembles of particles.

The presence in the ensembles of nonidentical particles and of interactions between them leads to a com-

plicated theoretical problem of statistical averaging of physical parameters. Within the domain of UDM theory, fruitful use has been made in recent years not only of the methods of solid-state physics, but also of various aspects of general thermodynamics and statistical physics, quantum physics, the theory of the atomic nucleus, etc. Experimental investigations of physical processes and phenomena in UDM are being carried out by use of the usual methods of experimental physics, including contemporary methods of studying surfaces: structural analysis with x-rays, electrons, and neutrons, Auger electron spectroscopy, photoelectronic spectroscopy, infrared spectroscopy, mass spectroscopy of secondary ions, nuclear and electronic magnetic resonance, nuclear gamma resonance, etc.

It has recently been shown that there exists a possibility, in principle, of obtaining the most variegated materials in an ultradispersed state: pure metals and alloys, intermetallic compounds, oxides, etc.¹ Methods used for this purpose are evaporation in a vacuum,^{2,7} condensation of metal vapors in an inert gas medium,^{3-5,178} thermal dissociation of various salts,^{1,177} precipitation from solutions, electrolytic precipitation plasmochemical synthesis,⁶ etc. For investigation of physical properties, and primarily of dimensional effects, the greatest interest lies in methods that insure obtaining particles with a narrow distribution of sizes. From this point of view, preference must at present be given to the various versions of the condensation method developed by M. Ya. Gen and his collaborators.³

A few words about terminology. Ultradisperse metallic media include all metallic systems whose disperse component is sufficiently small (less than 10^{-5} cm) if only in a single dimension. To this class of materials may be assigned amorphous metals, various filament and cluster formations in porous glasses and zeolites, insular and fine-grained films, finely dispersed powders, various disperse precipitations of phases in alloys, etc. Common to all these systems is the presence of ultra-disperse metallic formations.

This paper will consider the structure and physical properties of such isolated formations; more exactly, of fine metallic particles, sometimes called zero-dimensional metals. A discussion of physical properties and various phenomena in UDM that are modeled by ensembles of fine particles that interact and are in contact, including electrical conductivity, thermal conductivity, superconductivity, etc., will be given in another review.

2. STRUCTURE OF FINE PARTICLES

a) Structure of clusters of a few atoms

With respect to a number of features, the structure of FMP is qualitatively different from the structure of the corresponding bulk materials. At the lower limit of particle dimensions (~ 1 nm), the structure has been studied relatively little; but there is reason to suppose that it is similar to (though not identical with) the structure with short-range order that is characteristic of liquids and of amorphous solids.¹ For system with long-

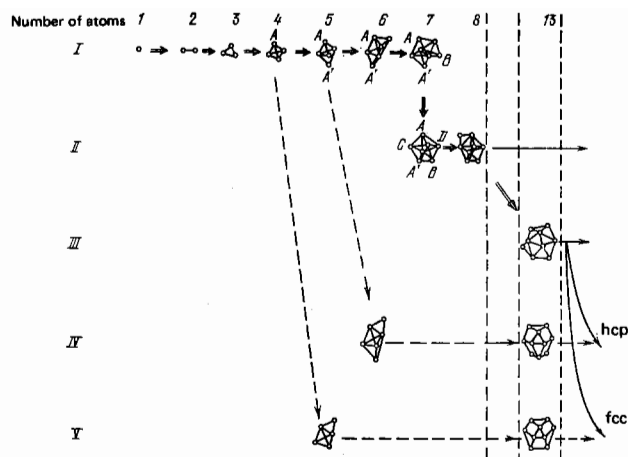


FIG. 1. Formation of dense cluster structures from single atoms. Lines IV and V correspond to the macrocrystalline hcp and fcc structures, respectively.

range, central forces of interatomic interaction, it may be expected that the stablest structures will be dense ones in which all the interatomic distances are approximately equal.

If we trace the picture of the formation of a particle by successive addition of single atoms,¹¹ then the densest configurations corresponding to the different numbers of atoms (Fig. 1) will be an isosceles triangle, a tetrahedron, a regular bipyramid, and a bipyramid with a tetrahedron on one of the faces. By adding a seventh atom (*B*), one can construct a second tetrahedron on a face of the preceding one (see Fig. 1). Then atom *B* is quite close to atom *A'* of the original bipyramid. The stablest configuration is obtained if the five atoms *AA'BCD* take the form of a regular pentagon. By a small elastic deformation (equal to several percent), all seven atoms can be located at equal relative distances, and such a configuration will have one more interatomic bond (14 instead of 13; that is, two bonds to each atom, line II in Fig. 1). By addition of subsequent atoms in such a way that tetrahedra are formed on the faces of the seven-atom cluster, one can obtain various cluster structures, containing 13, 147, 309, 561, etc. atoms (Fig. 2). Structural syntheses of fine particles were carried out in Refs. 8-11; for groups of a small number of atoms ($N \leq 13$), the authors carried out a repeated traversal of the configuration, prescribing a model potential energy of the interatomic interaction (of the Lennard-Jones or Morse type) and minimizing the energy of the FMP. Because the number of stable isomers increases sharply with increase of the number of atoms, for large particles ($N > 10^3$) one must be satisfied with trying to find the principal regions of configuration space that correspond to highly stable clusters.⁸ What criteria are used for such "construction" of particles? First, it is required that they shall be locally dense; and this in turn assumes that they must possess a high degree of tetrahedrality, i.e., they must be built up on the basis of elements that by themselves are known as stable. Second, they must be energetically stable, under the condition that the interatomic pair interaction is described by some realistic

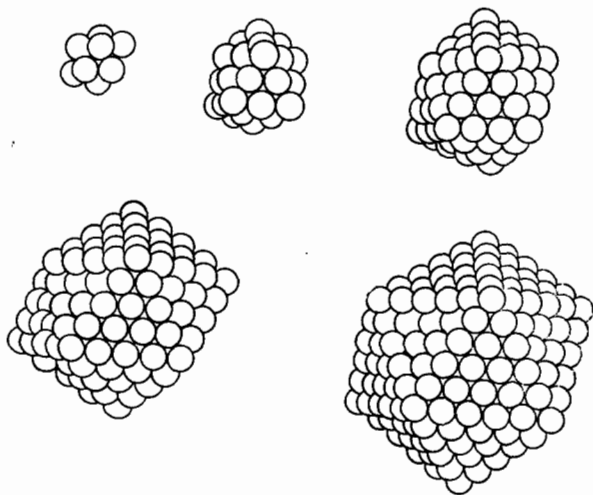


FIG. 2. Stable cluster structures of pentagonal symmetry.

potential energy. In minimization of the total potential energy, it is assumed that cooperative atomic shifts occur; that is, that structural relaxation is possible. The types of structure considered are both the usual crystalline types (cube, tetrahedron, octahedron, cube-octahedron, dodecahedron) and also noncrystalline types, containing, among the elements of symmetry, axes of the fifth order (icosahedron, pentagonal pyramid, etc.) (see Fig. 2). What are the reasons for consideration of structures of the latter type? First, the stablest seven-atom cluster has a fifth-order symmetry axis. Second, in many configurations of the icosahedral type (see, for example, Fig. 2), each of 12 surface atoms, again by a small elastic deformation, acquires five neighbors (instead of the four characteristic of the hcp and fcc structures); and such configurations, which have a fifth-order symmetry axis, are found to be very stable.

For each of the icosahedral particles, one can picture a particle-twin, with a structure of the undeformed fcc lattice type. But formation of fine particles with the fcc (or hcp) structure requires passage through the stages that are represented in Fig. 1, lines IV and V. In these stages, one of the atoms has only two bonds; and a configuration of such symmetry is by no means the stablest for the given number of atoms. Therefore the formation of particles of such small sizes with hcp or fcc symmetry is improbable.

Numerical calculations have shown, for example, that the energy of a 13-atom icosahedral cluster is 17% lower than the energy of the fcc cluster.^{8,10} Moreover, it has been found that these clusters are unstable both for a Lennard-Jones potential energy and for a Morse potential energy¹⁸¹; they spontaneously transform to the icosahedral form.

The icosahedral structure can be represented as a set of multiply twinned, slightly deformed fcc crystals,¹⁸² as a result of which the surface consists entirely of close-packed planes of the {111} type (line III in Fig. 1). On the other hand, the surface of fcc particles is faceted by {200} planes, with less dense packing, the atoms on which have smaller coordination

numbers, and this corresponds to a higher surface energy.

The energy of elastic deformation, which is initially very small but increases in proportion to the volume, will, for FMP of large size, exceed the gain in surface energy, and this will ultimately cause destabilization of the icosahedral structure. Since fifth-order symmetry is not permissible for macrocrystals, formation of large particles will inevitably be connected with occurrence of internal voids or internal elastic stresses. Obviously there is some critical size above which the pentagonal structures become less stable than the crystalline.

At the same time, with increase of the size of FMP the restoration of a cubic facet requires rearrangement of a larger and larger number of atoms. Thus there are significant kinetic obstacles; and these apparently explain the pentagonal shapes that are observed experimentally in many systems (inert gases,⁸ noble and transition metals^{182,183}) for relatively large (~100–300 Å) metallic particles.

Although pentagonal structures have also been observed experimentally in metals, the theoretical analysis based on the pair-interaction model is unacceptable for these systems. In this connection, investigations have been made¹⁸²⁻¹⁸⁸ on estimation of the bond energy and determination of the relative stability of structures on the basis of calculations of the density of states by the methods of electron theory. Without going into details here, we remark that such factors as the following were found to be important: the character of the filling of the strongly degenerate electronic energy levels, and also the instability of a structure with a degenerate ground state (the Jahn-Teller effect). Many papers have used, for calculations of the electronic structure of FMP, various versions of the traditional methods of quantum chemistry.^{181,186,188} One must distinguish Refs. 181 and 188, in which, for investigation of geometric relaxation in FMP, an iterative variant of the Hückel method, reminiscent of the method of the self-consistent field, was developed, with optimization of the geometry of the FMP. It was found that the electronic structure and the character of the interatomic bond change substantially with change of size and shape of FMP containing $\sim 10^3$ atoms.

The role of relaxation of "surface" atoms, and also the effect on the electronic structure of "point defects," have been estimated by model calculations for one-, two-, and three-dimensional FMP containing a finite number of atoms. It is interesting that in the range of small particle sizes (≤ 50 nm), the distinct face characteristic of crystals is unstable, and there is a tendency for the edges and vertices to become rounded off and for the face to become convex. This apparently means that there is a size limit of applicability of Wulff's theorem, which governs the laws of faceting of crystals.

b) Change of interatomic distances

In relatively coarse FMP ($\approx 10^2$ nm), the concepts of long-range order and crystalline structure have their

traditional meaning. But even in these particles, the field of "surface" atoms is very large, and therefore the structure of the particles has a number of differences from the structure of the corresponding bulk materials as regards the parameters and the type of symmetry. These differences manifest themselves in normal and tangential relaxation of FMP.¹¹ An atom in the surface layer has fewer neighbors than one in the interior, and they are all located on one side of it. This disturbs the equilibrium and symmetry in the distribution of forces and masses and leads to a change of the equilibrium interatomic distances as compared with their values in macrocrystals (normal relaxation), and also to shear deformations, a change of the reason for ordering of the atoms in the surface planes, and a "smoothing out" of vertices and edges by small angular deformations of the interatomic bonds (tangential relaxation).

We shall consider anomalies of the structure of FMP that manifest themselves in a change of the interatomic distances and of the root-mean-square static and dynamic displacements of atoms from the equilibrium positions, in stabilization of new (or high-temperature) phases and modifications, etc.

Under the action of the Laplace pressure exerted by the surface (as in a drop of liquid), in particles of small size one can expect a change of the mean interatomic distance, related to the relative change of volume¹²

$$\frac{\Delta V}{V} = \kappa \frac{2\sigma}{r}, \quad (1)$$

where r is the radius of the particle, κ is the coefficient of volume compressibility, and σ is the surface energy. The quantity $2\sigma/r$ represents the Laplace pressure (strictly speaking, for crystals one must consider the surface stress α). An estimate by formula (1) shows that for particle size 10^{-6} cm, $\sigma \approx 10^3$ erg/cm², and $\kappa \approx 10^{-12}$ cm³ erg⁻¹, the value of the change of volume amounts to $\sim 10^{-3}$, which corresponds to a relative change of interatomic distance $\sim 5 \cdot 10^{-4}$.

Changes of the interatomic distances corresponding to this estimate have been detected by various structural methods. Thus the presence of lattice deformation has been established with x-rays¹³ for particles of Cd with mean dimensions about 65 nm; a change of the lattice parameter has been noticed¹⁴ in small (10–100 nm) particles of titanium carbide. A decrease of the lattice parameter has been detected by electron diffraction¹⁵ in very small (2.5–14 nm) particles of gold. The authors of the present paper, by neutron-diffraction analysis, have detected a decrease of the lattice parameter in Al particles with mean dimensions 40 nm ($a = 0.402$ nm instead of the value 0.4049 nm for bulk specimens). Generalizing the data of several papers, the authors consider that the interatomic distance in fine particles decreases in inverse proportion to their size.

For fine particles of Co, the size dependence of the lattice parameter a has been determined¹⁶; its value decreases from 0.3533 to 0.3517 nm with decrease of the particle size from 12 to 150 nm; the behavior is

also nonlinear. In some cases, an anisotropic distortion of the lattice is observed in FMP. Such an effect was observed in Ref. 13, where it was established that the degree of deformation of Mg particles, with mean size 29.5 nm, was different along different directions. Anisotropic deformation of the lattice in FMP with anisotropic compressibility was investigated also by Komnik *et al.*¹²

A decrease of the lattice parameters has been detected not only in FMP of pure metals, but also in fine particles of alloys.^{18,19} Gen *et al.*^{18,19} showed that in fine particles of Fe-Co alloys, the lattice parameter is noticeably smaller than in bulk specimens, and the character of the dependence of the interatomic distance on the composition of the alloy is also different.

c) Structural transformations

In fine particles, just as in thin films and filamentary crystals, the thermodynamic conditions for phase equilibrium are changed because of the effect of surface energy. New phases can form in them that are not characteristic of the given material in the bulk state. And in those cases in which there is a polymorphic transformation in the bulk state, its temperature (and/or the composition corresponding to the existence boundary of the modification in the FMP) can change. With decrease of the specimen size from infinite to very small, the contribution of the surface ($F_S = \sigma S/V$) to the free energy $F = F_V + F_S$ (F_V is the volume contribution) increases. It may then turn out that if phase 1 is stable at a certain temperature in bulk specimens, i. e., $F_V^{(1)} < F_V^{(2)}$, then on decrease of the size, with allowance for F_S the condition

$$F_{V_2} + \frac{\sigma_2 S_2}{V_2} \leq F_{V_1} + \frac{\sigma_1 S_1}{V_1}, \quad (2)$$

may be satisfied, so that phase 2 will be stable for sufficiently small sizes.

From the condition (2) for phase equilibrium, one can obtain an expression for the relative change of the phase-transition temperature T_{12} in fine particles as compared with bulk specimens, T_{12}^∞ . Using the fact that

$$F_{V_2} - F_{V_1} = \lambda \left(1 - \frac{T_2}{T_{12}^\infty} \right), \quad (3)$$

where λ is the heat of the phase transition, we get

$$\frac{T_{12}^\infty - T_{12}}{T_{12}^\infty} = \frac{1}{\lambda} \left(\frac{\sigma_1 S_1}{V_1} - \frac{\sigma_2 S_2}{V_2} \right). \quad (4)$$

For more rigorous determination of the phase-transition temperature in fine FMP, it is necessary to take into account also the Laplacian pressure, which for size 10 to 1 nm is 10^3 to 10^5 atm, the effect of various defects and impurities contained in the particles, and electric and magnetic fields.

On the basis of the relation (4), changes of the boundaries of the regions of existence of the phases are to be expected in FMP. Supporting this deduction, there are experimental researches in which shifts were observed in the boundaries of the temperature intervals of the stable state of the various phases. Reference 20 gives results on detection of the cubic β phase in FMP

of manganese, in which the phase exists in the bulk state only at high temperatures, 727–1095°C; and also in FMP of cobalt, of which it is characteristic at temperatures from 400°C to the melting temperature 1495°C. A change of the temperature boundaries of existence of structural phases has been detected also in fine particles of a number of dielectric materials.²¹⁻²⁴

It follows from the equilibrium equations (2) and (3) that with decrease of the particle dimensions, formation of a phase with a smaller surface energy, i.e., with denser packing, will be advantageous.¹ For example, of the two crystalline lattices fcc and bcc that are common in metals, the first may turn out to be more advantageous, since its specific volume and surface energy are smaller. Therefore if the close-packed fcc phase is stable in the bulk state, then it will exist, upon decrease of the particle size until it transforms to the amorphous or liquid phase. But if the relatively friable bcc phase is stable in the bulk state at some temperature, then with decrease of particle size a phase transition is possible, with formation of the other crystal lattice. In fact, electron-diffraction data show that particles of Nb, Mo, W, and Ta with mean size 5–10 nm have the fcc or hcp lattice instead of the bcc of the bulk state,^{25,26} and particles of the rare-earth metals Y, Gd, Tb, Dy, Ho, Er, and Tm have the fcc instead of the hcp.²⁷ Gadolinium FMP have been investigated in the size range from 110 to 24 nm.²⁸ X-ray structural investigations showed that their structure depends on the size of the particles and differs sharply from the structure of bulk crystals. In bulk specimens of gadolinium, under normal conditions, the structure corresponds to the hcp lattice. Coarse particles of gadolinium, of size 110 nm and above, also have this same lattice. But analysis of x-ray photographs established that the specimens contain a noticeable fraction of the cubic phase (fcc), which increases with decrease of the particle size, while the fraction of the hcp phase decreases. In particles of size 24 nm, the hexagonal phase was not detected at all. It is characteristic that the cubic phase also undergoes changes on decrease of the particle size. It develops initially in the form of a denser modification, with lattice parameter $a = 0.5321 \pm 0.0008$ nm,¹ and then on decrease of the particle size it goes over to a new fcc phase with parameter $a = 0.5392$ nm. In particles with diameter 24 nm, the ratio of the last two phases is approximately 1:4.

Similar anomalies have been detected also in FMP of terbium and of holmium.²⁹ Earlier, a cubic modification of gadolinium and of other rare-earth elements was also detected by electron diffraction in thin films of thickness less than 15 nm. The structure of films of thickness greater than 20 nm was identified as a mixture of hcp and fcc phases. While the appearance of new phases in thin films could be connected somehow with the influence of the substrate,³⁰ in the case of fine particles it can be explained only as a manifestation of a size factor.

From the equilibrium condition (3), one can establish

the qualitative character of the state diagrams, free energy vs temperature, and the dependence of the phase-transition temperature on the particle size. References 1 and 26 describe various types of phase diagrams for single-component systems, as they depend on the character of the symmetry and on the ratio of the specific volumes of the initial and final phases. Phases appear on some of these that are characteristic solely of fine particles and not of the bulk state. The possibility of such a phenomenon is corroborated experimentally. For example, there is a report³¹ of detection of a cubic phase in fine particles of Be and Bi, for which the hcp lattice is characteristic in the bulk state, and of an amorphous phase in particles of Gd and Se. An amorphous phase has also been observed in fine particles of Fe and Cr.²⁰ Furthermore, for FMP of chromium³⁰ electron diffraction has established³² a new cubic phase, which has parameter $a = 0.4588$ nm and belongs to space group $Pm\bar{3}n$, with 2 atoms at (a) positions and 6 at (c) positions.

The stabilization of high-temperature phases in FMP is apparently explained by a significant contribution of the relatively "loose" surface layers to the free energy.^{7,17} This, together with an increase of the rms displacement and a lowering of the translational symmetry, which decreases the degree of ordering, causes an increase of the specific entropy in FMP. Analysis within the framework of a model that takes account of these facts³³ shows that in general, the stability boundary of the high-temperature phase shifts toward lower temperatures. These regularities, as well as other size-dependent structural anomalies, have been observed in FMP of various metals, alloys, and compounds and are probably of fundamental nature.

d) Root-mean-square displacements

Change of the dynamic characteristics of FMP is due to peculiarities of their structure and of the interatomic interactions. The large ratio of surface to volume in FMP finds expression in the spectrum of oscillations, in the mean-square amplitudes (\bar{u}^2) and velocities of the atomic oscillations, in the degree of isotropy of the displacements, etc. These peculiarities are important in many phenomena, for example, in scattering of charge carriers, optical absorption, diffusion of impurities, generation of point defects, and others. They make a contribution to the heat capacity and thermal conductivity of UDM. It is known that the root-mean-square amplitude of thermal oscillations of atoms located on the surface of a bulk crystal is appreciably larger than for atoms in the interior. This has been noticed both in theoretical works³⁴ and in precision experiments by diffraction of slow electrons.^{35,36} But in FMP, when a substantial fraction of the atoms are located on the surface or in surface layers, the mean displacement of the atoms increases still more and shows up noticeably in the properties and characteristics of the material; this makes it possible to detect them experimentally.

A whole series of investigators consider that on transition from a bulk specimen to FMP, there occurs a

change of the amplitude of oscillation of the atoms and, accordingly, a softening of the phonon spectrum. The basis for this was experimental data for FMP of tungsten,³⁷ gold,³³ and lead,³⁹⁻⁴¹ obtained in investigation of the Mössbauer effect, and also direct measurements of the phonon spectrum of magnesium oxide⁴² by inelastic scattering of neutrons.

Experimental data⁴³ on the decrease of the electrical resistivity and increase of the temperature of transition to the superconducting state in particles of aluminum and silver, with decrease of their size from 15 to 3 nm, and on the increase of the specific heat of fine particles of palladium (6.6 and 3.3 nm) as compared with bulk specimens, are also interpreted on the assumption of a softening of the spectrum of oscillations of the lattice. The same phenomenon is used to explain the lowering of the Debye temperature for particles of silver,⁴⁴ aluminum,⁴⁴⁻⁴⁶ indium and lead,⁴⁶ gold,⁴⁷ vanadium,⁴⁸ and palladium.⁴⁹

In a fine particle, which behaves essentially as an acoustic resonator, only waves of length less than the particle dimension can be excited. But in a bulk specimen, there is no low-frequency limit to the oscillations. Therefore it may be supposed that diminution of the particle size must not necessarily lead to softening of the phonon spectrum; rather, on the contrary, it should shift the phonon spectrum toward the short-wavelength region. It should be noted that so far, information about the phonon spectrum of ultradisperse systems is obtained principally from indirect data, which cannot be interpreted uniquely. For example, at present it is an established fact that there is a sharp increase of the critical temperature for superconductivity upon decrease of the grain-size in thin films of a number of metals. This also is explained by a change, more accurately a softening, of the phonon spectrum. Special investigations,¹⁷⁹ however, have shown that this is not so. It was found that in tin particles insulated from each other, the critical temperature was independent of the particle size and corresponded to the critical temperature of bulk specimens of tin. And only when there are contacts between the particles and collective current states is an increase of T_c observed. At the same time, it may be assumed that the phonon spectrum of insulated particles differs from the phonon spectrum of a bulk specimen more sharply than does that of particles in contact.

Direct data on the increase of the root-mean-square displacements of the atoms in particles of small volume have been obtained by diffraction methods: with x-rays for gold and copper,⁴⁹ with electrons for silver and chromium, with neutrons for vanadium nitride (by the authors of the present review) and for particles of lead dispersed in glass.⁴⁹ In x-ray study of the structure of FMP of zirconium carbide, it was noted that the value of the root-mean-square displacement increases with decrease of the size of the blocks.⁵² For the smallest value of the block size attained in the specimens investigated (20 nm along directions $\langle 111 \rangle$ and $\langle 100 \rangle$ and 14 nm along direction $\langle 110 \rangle$), the largest values of the root-mean-square displacement were determined.

Increase of the root-mean-square displacement has

been detected also in FMP of TiN.⁵³ But in addition to a size effect, in this case there may be an effect from the high rate of cooling of the particles in the plasma reactor, which causes quenching of the nonequilibrium defects of the structure.

It should be mentioned that in the majority of the papers cited above, the results were obtained by diffraction methods from measurements of the angular dependence of the intensity of Bragg reflections at constant temperature, most frequently room temperature. Therefore, strictly speaking, what were determined in these experiments was the values of the total displacements, which are produced not solely by the increase of the amplitude of the thermal oscillations of the atoms, but also partly by static deformation of the particle. In order to separate the dynamic root-mean-square displacement from the static, investigations were made at different temperatures.

X-ray investigation⁵⁴ of fine particles (~15 nm) of silver at two temperatures, 294 and 104 K, made it possible to determine by two methods—from the angular and from the temperature dependence of the total intensity of the diffraction maxima—the Debye-Waller factor, the root-mean-square displacement of the atoms, and the Debye temperature. And although values are obtained that are close to each other (the Debye temperature θ_D is 161 ± 7 K and 156 ± 3 K), the experimental data on the angular dependence of the intensity of the Bragg reflections at 109 K show that in the specimen investigated, in addition to an increase of the dynamic displacement as compared with a bulk specimen of silver (by a factor of about 2, which is close to the values observed for the surface of a single crystal), a static deformation shows up noticeably.

By means of electron diffraction on very fine particles of gold (uniform in size within the range 20–2 nm), measurement of the Debye-Waller factor has been carried out over the wide range of temperature from 300 to 1100 K.⁵⁵ The size and temperature dependence of the Debye-Waller factor has been constructed and expressed in the form of a parameter α , which determines the intensity of the diffraction maximum at temperature T as $I(T) = I(T_0) \exp(-\alpha T)$ and is equal to

$$\alpha = 16\pi^2 \frac{\langle u^2 \rangle}{T} \left(\frac{\sin \theta}{\lambda} \right)^2 = 12 \frac{h^2}{km\theta_D} \left(\frac{\sin \theta}{\lambda} \right)^2. \quad (5)$$

From the experimental data for FMP of size greater than 2 nm, an expression was obtained for $\alpha = \alpha_\infty + q/r$, where r is the particle dimension, $\alpha_\infty = (4.8 \pm 1) \cdot 10^{-4} \text{ K}^{-1}$ is the value for bulk specimens, and $q = (1.5 \pm 0.5) \cdot 10^2 \text{ \AA K}^{-1}$. These results also show that in fine particles the effect of softening of the modes of the phonon spectrum dominates, and that the root-mean-square displacement here is significantly larger than in the bulk metal.

The relation of the mean-square displacements \bar{u}^2 to the atomic force constants can be conveniently demonstrated in the example of the simplest model, which represents the body as a set of harmonic oscillators. At high temperatures, it follows from the equality of the kinetic and potential energies of an oscillator that

$$m\omega^2\bar{u}^2 = kT, \quad (6)$$

where m and ω are the mass and the frequency of oscillation of an atom, k is Boltzmann's constant, T is the temperature, and $\omega^2 = \beta/m$, where β is the quasielastic force constant ($F = -\beta u$, where u is the displacement of the atom). Thus measurements of \bar{u}^2 enable us to judge the changes of the potential barriers and of the rigidity of the interatomic bonds on transition from a bulk crystal to FMP. For example, during changes of the crystalline structure of FMP or during adsorption of impurities, often accompanied by formation of surface compounds, there may occur a weakening of the interatomic bonds, which is accompanied by an increase of \bar{u}^2 . Furthermore, decrease of the values of β on the surface means lowering of branches of the potential-energy curve for a surface atom, i. e., lowering of the activation energy of surface processes.

3. OSCILLATIONS OF ATOMS IN ULTRA-DISPERSED PARTICLES

a) Spectral density of states

The role of the surface in the transformation of the distribution function $D(\omega)$ has been graphically demonstrated in an investigation of silicon particles⁵⁶ by the methods of inelastic scattering of slow neutrons. The specimen was a powder prepared by grinding of monocrystalline silicon.

The form of the function $D(\hbar\omega)$ for a fine powder has changed noticeably (Fig. 3) as compared with bulk material. Thus the amplitudes of the maxima at $\Delta E \approx 19.5, 26.5$, and 64 MeV have decreased, whereas the density of oscillations in the range $\Delta E \approx 31-55$ MeV has increased. It is very probable that these changes are caused by the increased role of the surface in the formation of curve 2, since particles are formed during the

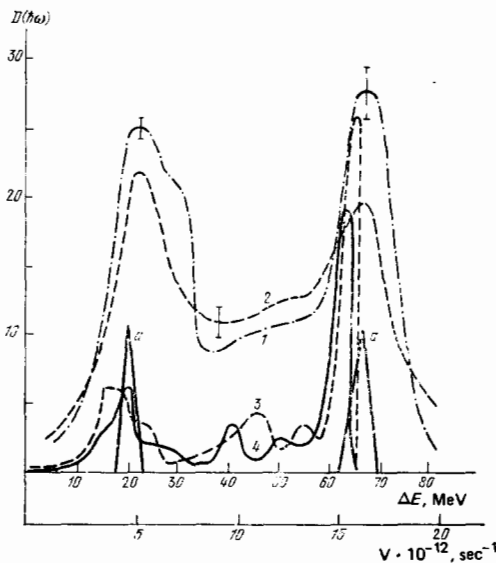


FIG. 3. Distribution functions for coarse (1) and fine (2) particles of silicon.⁵⁶ Curves (3) and (4) are calculated. The theoretical and experimental curves are not normalized in relation to each other. The statistical accuracy and the resolution with respect to energy (a) are shown.

grinding of the coarse powder that have large roughness and a considerable number of microcracks. The total number of surface atoms may then reach tens of percent.⁵⁷ Also in favor of such a supposition is the lowering of the maxima with energies 19.5, 26.5, and 64 MeV. These maxima are due to the high-symmetry points of the Brillouin zone, and the lowering of their amplitude can be explained by the increased role of the surface, whose symmetry is lower than that of the interior of the crystal.

The types of elastic waves and the spectrum of atomic oscillations in FMP have been studied relatively slightly. Over the last 30 years, many different approaches have been proposed to the so far unsolved problem of calculating the exact density of states $D(\epsilon)$ of a bounded elastic medium with a free surface. Oscillations of a semi-infinite continuum⁵⁸ and of a medium bounded by two parallel planes⁵⁹ have been studied. Maradudin and Wallis⁶⁰ calculated the low-temperature specific heat of a crystal also bounded in one dimension. All these authors were dealing with surface phenomena in thin films rather than with size effects in fine particles; thus it is impossible, for example, to use such models to investigate the effect of the shape of the particle on its thermodynamic characteristics.

For fine particles, numerical methods and modeling have been applied^{1,61}; but they are applicable only to particles containing a small number ($N \leq 150$) of atoms, because of the rapid increase of the amount of calculations. Use of a scalar-medium model has proved fruitful; here the unknown density of states $D(\epsilon)$ of an elastic medium is determined as the density of states of scalar waves.⁶²⁻⁶⁴ True, this model does not take into account, for example, the presence of longitudinal and transverse oscillations. Therefore the phase velocity must be interpreted as an effective velocity of sound c , a useful empirical parameter whose value cannot be assigned *a priori* but must be chosen from considerations of best agreement with experiment. It turns out that c in fact has the order of magnitude of the velocity of sound in solids. The exact density of oscillatory states for a body of finite dimensions (L_1, L_2, L_3) was first determined by Baltes,⁶⁶ although, as is mentioned by the authors of Ref. 64, the corresponding mathematical aspects of the problem were already contained in papers of Walfisz⁶⁵ fifty years earlier.

Thus for a particle in the form of a cube of edge-length L , the value of $D(\epsilon)$ is

$$D(\epsilon) = \frac{V}{2\pi^2 (c\hbar)^3} \epsilon^2 \pm \frac{3L^2}{4\pi (c\hbar)^2} \epsilon + \frac{3L}{4\pi c\hbar} \pm \frac{1}{8} \delta(\epsilon) + \frac{V\epsilon}{2\pi^2 (c\hbar)^3} \times \sum_{m_1, m_2, m_3=-\infty}^{+\infty} \frac{\sin(y\epsilon)}{y} = \pm \frac{3L^2\epsilon}{4\pi (c\hbar)^2} \sum_{m_1, m_2=-\infty}^{+\infty} J_0(y\epsilon) + \frac{3L}{2\pi c\hbar} \sum_{m_1=1}^{\infty} \cos(y_1\epsilon), \quad (7)$$

where

$$y_i = \frac{2}{c\hbar} m_i L_i, \quad y = \left(\sum_{i=1}^3 y_i^2 \right)^{1/2},$$

m are integers, $2\pi\hbar$ is Planck's constant, and J_0 is the Bessel function of order zero. The upper sign in

the equation corresponds to the Dirichlet boundary conditions (fixed surface, $u=0$), the lower to the Neumann boundary conditions (free surface, $\partial u/\partial a=0$). This expression clearly contains terms corresponding to contributions of the surface ($\sim L^2$), of the edges ($\sim L$), and of the vertices ($\sim L^0$).

By using the expression for $D(\varepsilon)$, we can find the free energy of a fine particle,

$$F = -kT \int_0^{\varepsilon_M} D(\varepsilon) \ln(1 - e^{-\varepsilon/kT}) d\varepsilon, \quad (8)$$

and determine all the temperature-dependent thermodynamic properties of FMP, the van der Waals forces, etc. (ε_M is the limiting Debye energy). In similar manner, one obtains a generalized Debye interpolation formula for particles of small dimensions⁶⁴ and determines the range of sizes and of temperatures within which one can expect fulfilment of a " T^3 " law for the specific heat. [We note that a relation similar to (7) can also be obtained for fermions; it has been found fruitful in the study of the behavior of electrons in thin films and in FMP.]

The problems considered here are intimately related to the general problem of Weyl (see Ref. 60), by which is understood the problem of calculating the distribution of characteristic values of wave equations and the problem of determining their dependence on the type of boundary conditions. Weyl considered three types of boundary problems: for scalar and for vector fields, and also for the displacement field (within the framework of elasticity theory). For fine particles, the influence of the boundary (in the case of the boundary conditions of Dirichlet, of Neumann, and of mixed type) leads to a mixture of longitudinal modes and also of Rayleigh modes, localized in the surface region. As Weyl's theorem states, only on passage to large volumes do the boundary conditions become unimportant; as $V \rightarrow \infty$, independently of the shape of the particle.

$$D(\omega) \sim \frac{V\omega^3}{2\pi^2} (2v_t^{-3} + v_l^{-3}). \quad (9)$$

Since the time when Weyl proved his theorem, a cornerstone in the description of acoustic phonons in solids, significant efforts have been made to obtain asymptotic expressions for the density of states. While this problem is basically solved for scalar and electromagnetic fields, only first-order corrections are so far known for an elastic displacement field [see formula (7)]. We emphasize that these corrections are connected with a more accurate calculation of the modes in FMP, not with allowance for localized surface modes, and that they are caused physically by constructive and destructive interference of oscillations perturbed by opposite free boundaries of the FMP.

It is immediately evident from the relation (7) that for FMP with a free surface ($\partial u/\partial a=0$), the density of states is higher than in a bulk crystal, for which $D(\omega)$ is given by the first term in the sum (7). Hence, one obviously must expect an increase of the low-temperature specific heat and a decrease of the Debye temperature (θ_D). This has in fact been observed in experiments carried out by the methods of neutron diffraction,

calorimetry,⁶⁸ and Mössbauer spectroscopy.⁴² For example, the relative decrease of the Debye temperature is proportional to the value of $SN^{-1/3}$ (where S is the area of the surface of the FMP).

In his time Montroll,⁶⁹ neglecting oscillation effects, obtained a relation for $D(\omega)$ valid for not too small FMP,

$$D(\omega) = \frac{V\omega^3}{2\pi^2} v_s^{-3} + \frac{S\omega}{8\pi} v_s^{-2} + \frac{\Lambda\omega}{4\pi} v_s^{-1}; \quad (10)$$

v_t are the effective velocities of sound, and Λ is an effective distance related to the curvature of the surface of the particles. Within the framework of elasticity theory, only the value of $v_s^{-3} = 2v_t^{-3} + v_l^{-3}$ is precisely defined physically (v_t and v_l are the velocities of transverse and of longitudinal waves).

The correct expression for v_s^{-2} , found in Refs. 62 and 64 with allowance for the exact boundary conditions $\sum [\delta_{\alpha i} (A - B) \text{div} u + B(\partial_i u_\alpha + \partial_\alpha u_i)] = 0$ ($B = v_t^2$; $A + B = v_l^2$), has the form

$$v_s^{-2} = \frac{2v_t^4 - 3v_t^2 v_l^2 + 3v_l^4}{v_t^2 v_l^2 (v_t^2 - v_l^2)}. \quad (11)$$

This result reflects the effect of intermixture of the modes, caused by the finiteness of the particle dimensions. A similar relation has been obtained for spherical particles with free surfaces, and also for particles with pinned surface atoms.

A quantum approach to the calculation of $D(\omega)$,^{62,70} developed in the spirit of Montroll's theorem,⁶⁹ is based on the expression

$$D(\omega) = \sum_{is} \delta(\omega - \omega_{is}),$$

where for spherical FMP of radius R , $\omega_{is} = v a'_{is}$; a'_{is} is the s th zero of the derivative of the spherical Bessel function of order l , with weight $(2l+1)$, and v is the effective velocity of sound, which is actually an adjustable parameter. On the basis of this approach it has been shown that the spectrum of elastic oscillations in FMP is quantized; the minimum frequency ω_0 is of order $\pi v/2R$. The energy interval δ between successive allowed states is practically constant for linear chains and decreases as ω^{-1} and ω^{-2} respectively for two- and three-dimensional fine particles.

b) Heat capacity; Debye temperature

The peculiarities of the oscillatory spectrum should lead to anomalies of various physical properties, primarily of the heat capacity. For such low temperatures and such small dimensions of the FMP that only the fundamental mode is excited, the specific heat changes according to the law $C_V \sim T^2 \exp(-\hbar\omega_1/kT)$. This occurs at temperatures $0 < T \ll \theta_0$; $\hbar\omega_2/k = \theta/(3N)^{1/3}$, where ω_1 is the frequency of the first excited mode. Estimation shows that this is possible in clusters with a small number ($N \leq 50$) of atoms. In the range $\theta_0 < T \ll \theta_D$ (when $10^2 \leq N \leq 10^6$), there occurs a state intermediate between the single-mode and the Debye, for which the corrections to the law $C_V \sim T^3$ may be substantial. In the analysis of this situation, two approaches are possible. The first, which takes account of quantum size effects, leads to a value of the

specific heat proportional to

$$\frac{d}{dT} \sum_{n=1}^{3N-3} \hbar \omega_n (e^{\hbar \omega_n / kT} - 1)^{-1}. \quad (12)$$

The second approach, based on the continuum approximation, is correct for not too small FMP; in it, the specific heat is determined by the expression

$$\frac{d}{dT} \int d\omega D(\omega) \hbar \omega (e^{\hbar \omega / kT} - 1)^{-1}, \quad (13)$$

where $D(\omega)$ is the density of states, determined with allowance for surface and size effects, and also with allowance for the shape of the particle (see above).

Treating the FMP as an oscillating elastic medium with free surfaces, Baltes and Hilf⁶² found the specific heat of a fine particle, with allowance for quantum size effects:

$$C_{osc}(TR) = V_m \sum_l \sum_s \frac{3(2l+1) k_B^2 \xi^2}{4\pi R^3 (e^{\xi} - 1)^2}, \quad (14)$$

where $\xi = \hbar c a_l' / kTR$; V_m is the molar volume. The upper limit of the summation over l is determined by the condition

$$\sum_{l=0}^{l_{max}} (2l+1) \leq N.$$

It can be shown that for bulk materials ($R \rightarrow \infty$), the relation (14) goes over to the classical Debye formula for the specific heat C_B . Analysis of these two expressions for the specific heat shows that C_p is higher for FMP and that this difference decreases with increase of size.

Attempts at experimental observation of the size effect of the specific heat are known.^{48,71,72} Comsa and coauthors⁷² made measurements of C_p for FMP of palladium, where the oscillatory contribution to the total specific heat is large as compared with other metals. The method of evaporation and condensation made it possible to prepare FMP of well separated fractions, with mean particle dimensions 3 and 6.6 nm. As the measurements showed (Fig. 4), the specific heat is considerably larger for FMP, and the increase of C_p is larger for the relatively finer particles. For $T > 20$ K, the law $C \sim T^3$ is obeyed for particles of all sizes.

In the comparison of theory with experiment, the effective velocity of sound c was an adjustable param-

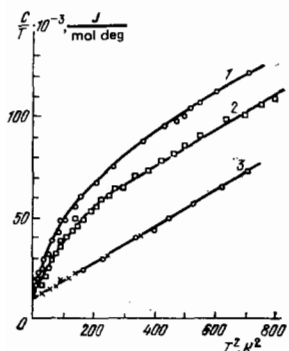


FIG. 4. Temperature variation of the specific heat of FMP of palladium. Dimensions of the particles (nm): 3.0 (1) and 6.6 (2); 3, bulk specimen.⁷²

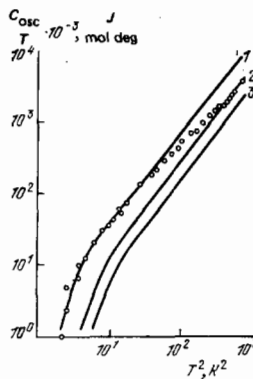


FIG. 5. Temperature variation of the oscillational specific heat of FMP of palladium. Theoretical relations with value of the velocity of sound (m/sec) 10^3 (1), $1.3 \cdot 10^3$ (2), and $1.565 \cdot 10^3$ (3). Points, experimental data.⁷³

eter. The value of c for bulk material ($c = c_B = 1.56 \cdot 10^5$ cm/sec) was determined from measurements of θ_D , which for FMP of palladium was 274 K. It was found (Fig. 5) that over the temperature interval investigated, quantitative agreement of theory with experiment could not be achieved by use of this value of c_B . Only in the temperature range 1.4–4.4 K was fair agreement observed between the theoretical and experimental data, with $c = 10^5$ cm/sec $< c_B$. Over the interval 4.4–24 K the effective velocity of sound increases to $1.3 \cdot 10^5$ cm/sec. The size and temperature dependences of c for FMP of palladium are shown in Fig. 6. For comparison, the function $c_B(T)$ is shown in the same figure. It is evident that the S-shaped type of dependence $c_B(T)$ that is characteristic of bulk Pd occurs also in FMP, but that there is a general shift toward low temperatures.

From a comparison of the data from measurement of the specific heat and, on the other hand, of the Debye frequency (θ_D), it can be concluded that there is a correlation between the temperature and size dependences of θ_D and C_p in FMP. The corresponding relation can be found from formula (14):

$$\theta_{D,p}(R, T) = \frac{\hbar}{k_B} \omega_{max} = \frac{\hbar}{k_B} a_{max} R^{-1} u_p(R, T), \quad (15)$$

where ω_{max} is the maximum frequency of oscillation of the particle. Remembering that θ_D in FMP of most materials is smaller than its value θ_B in the corresponding bulk bodies, one can conclude that the effective velocity of sound in FMP decreases with decrease of

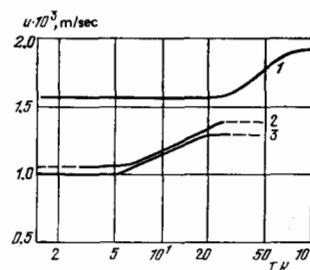


FIG. 6. Temperature variation of the effective velocity of sound in palladium.⁷² 1, bulk specimen; 2 and 3, FMP with dimensions 6.6 and 3.0 nm respectively.

size, and according to a law that is stronger than a linear one. Intuitively, this result should not be regarded as unexpected, if we recall (see Sec. 2) that in FMP, on the average, the atoms have a smaller number of neighbors and a different type of structure as compared with macrocrystals, and that the peculiar loosening up of the surface layers is accompanied by a lowering of the atomic density and by effective weakening of the forces of interatomic interaction.

In the same approximation, by considering elastic oscillations of FMP whose density of states contains the corrections (7) caused by the presence of surface, one can find the size dependence of θ_D .⁷³ For a spherical FMP containing N atoms, the limiting wave vector is determined by the relation

$$N = \frac{2}{3\pi} R^3 k_c^3 + \frac{1}{4} R^2 k_c^2 + \frac{2}{3\pi} R k_c, \quad (16)$$

where the terms on the right side take account of volume, surface, and linear contributions (for a spherical particle, the last is dependent on the curvature of the surface). If $k_0 = (6\pi^2/v)^{1/3}$ is the limiting wave vector in bulk material (v is the atomic volume), then the relation (7) can be written in the form

$$k_0^3 R^3 = R^3 k_c^3 + \frac{3\pi}{8} R k_c^2 + 3k_c, \quad (17)$$

or if, to the first order, $k_c = k_0(1 + \Delta k/k_0)$,

$$\frac{k}{k_0} = \frac{\theta_D}{\theta_0} \approx \frac{3R^3 k_0^3 + (9\pi/8) R k_0}{3R^3 k_0^3 + (9\pi/4) R k_0 + 3}, \quad (18)$$

where θ_D is the Debye temperature of a macrocrystal. Another, less accurate relation is obtained if one neglects the Rk_c term in (16) for fine particles:

$$\frac{\theta_D}{\theta_0} \approx \frac{1 + (3\pi/8) R k_0}{1 + (3\pi/4) R k_0}. \quad (19)$$

Finally, to within terms of order R^{-2} ,

$$\frac{\theta_D}{\theta_0} \approx 1 - \frac{3\pi}{8Rk_0}. \quad (20)$$

for FMP of arbitrary shape, with surface area S and volume V , the relation analogous to (19) has the form

$$\frac{\theta_D}{\theta_0} \approx \frac{1 + (\pi S/8V) k_0}{1 + (\pi S/4V) k_0}. \quad (21)$$

The phenomena of softening of the oscillations in FMP, lowering of the Debye temperature, and, accordingly, increase of the root-mean-square dynamic displacements of the atoms have been observed for many metals (see Table I).

It is interesting to note that the existence of these

TABLE I. Ratio of Debye temperatures in FMP and in bulk material for several metals.

Metal	Particle dimension, nm	θ_{DP}/θ_{D0}
Ag ⁷⁴	20	0.75
Ag ⁴³	10-20	0.75-0.83
Al ⁴³	15-20	0.50-0.67
In ⁷¹	2.2	0.8
Pb ⁷¹	2.2	0.87
	3.7	0.90
	6.0	0.92
V ⁴⁴	3.8	0.83
	6.5	0.86
Pd ⁷²	3.0	0.64-0.83
	6.6	0.67-0.89

effects makes it possible, by use of Lindemann's criterion, to explain directly the significant lowering of the melting temperature of FMP⁷⁵ as compared with the melting temperature of the corresponding metals.

The reason mentioned for the change of the Debye temperature in FMP is not unique. Study of the structure of FMP (see Sec. 2) shows that along with the relative loosening up of the surface region, there is a compression of the central part of the volume of a fine particle. Estimation of the influence of this effect on θ_D is possible by introduction of the Laplace pressure due to the effective curvature of the surface. The Debye temperature is connected with the value of the volume V of the FMP by the relation

$$\frac{\partial \ln \theta_D}{\partial \ln V} = -\gamma_G, \quad (22)$$

where γ_G is Grüneisen's constant. Considering the change of volume of the FMP under the influence of the Laplace pressure, we find under the condition that the isothermal compressibility $\beta = -(\partial \ln V / \partial p)_T$ is independent of pressure,⁷¹

$$\ln \left(\frac{\theta_D}{\theta_0} \right) = \gamma_G \beta f \left(\frac{1}{R_1} + \frac{1}{R_2} \right). \quad (23)$$

In first approximation, the change of θ_D is

$$\Delta \theta \approx \frac{2\gamma_G \beta f \theta_0}{R}. \quad (24)$$

On combining the expressions (20) and (24), we find

$$\frac{\theta_D}{\theta_0} \approx 1 + \left(-\frac{3\pi}{8k_0} + 2\gamma_G \beta f \right) \frac{1}{R}. \quad (25)$$

It is evident that in FMP of radius R , the Debye temperature changes both as a result of the renormalization of the oscillation spectrum caused by the finite size of the particle, and because of the influence of the hydrostatic pressure caused by the curvature of the surface. Since β , γ , and σ are positive as a rule, the effects of the two factors mentioned are opposite in sign. A numerical calculation made with the relation (24) for FMP of gold showed that these factors make comparable contributions to the size dependence of θ_D (Fig. 7).

It seems that noticeable anharmonicity is inherent in FMP, which are characterized by anomalously large values of the root-mean-square displacement. Anharmonic effects in FMP remain practically uninvestigated. It can be expected, in particular, that FMP will be characterized by larger coefficients of thermal ex-

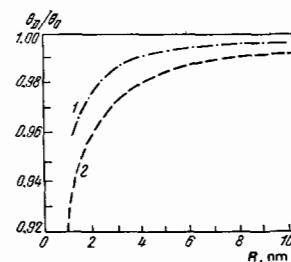


FIG. 7. Dependence of relative Debye temperature on size of gold FMP.⁷¹ 1, calculation by formula (19); 2, calculation by formula (14).

pansion than are macrocrystals. Various anomalies are also predicted in such processes as diffusion,¹ heat conduction,⁷⁶ and other surface-activation processes.^{189,191-193}

These factors are also important in the analysis of the interaction of FMP with external acoustic fields.¹⁹⁹⁻²⁰¹

4. ELECTRONIC STATES IN FINE METALLIC PARTICLES

a) Energy spectrum

In a metal of finite size, the spectrum of the electrons is discrete. The system of levels in a large volume can be obtained by considering the electrons contained in a large cube and using periodic boundary conditions. The discreteness of the levels in this case can be estimated by means of the Heisenberg relation $\Delta p \cdot a \sim \hbar$. This enables us to find the distance between levels $\delta = \hbar p_0 / 2ma$, where p_0 is the limiting Fermi momentum, a is the dimension of the system, and m is the effective mass of the electrons.

In a bulk metal, the energy spectrum is considered quasicontinuous because of the smallness of the distances between levels; in the calculation of the partition function, the sum is usually replaced by an integral over a definite density of states, which is independent of the boundary conditions. In the case of fine particles, this procedure is not always justified. First, the smallness of the volume leads to a pronounced discreteness of the electronic levels. When the distances between them are comparable with the energy parameters of the physical phenomenon under consideration, the discreteness of the levels may lead to anomalous properties of fine particles as compared with the properties of the bulk metal. Second, it is not permissible to neglect the special character of electronic states of the surface in fine particles; the contribution of these states may become important and even decisive.

It was Fröhlich⁷⁷ who first turned his attention to the special character of electronic states in FMP. He represented the electronic states of particles as equidistant levels and calculated the electronic specific heat. It turned out that at low temperatures the specific heat C_V of FMP falls exponentially with lowering of the temperature, whereas for macroscopic specimens this relation is linear.

Somewhat later, a low-temperature anomaly of the magnetic susceptibility was predicted theoretically.⁷⁸ But the properties of FMP were analyzed in the greatest detail by Kubo^{79,80} and by Gor'kov and Éliashberg.⁸¹ Kubo assumed initially that the distribution of electronic levels in particles is purely random, and he introduced a phenomenological probability density for their distribution. This approach is based on the fact that the spread of the particles with respect to size, the difference in shape, and the uncontrollable imperfections, including atomic-scale roughness of their surfaces, make the distribution of levels in an ensemble of FMP completely random. Therefore the mean distance between electronic levels in a particle can be found by use of the usual density of states $dn/d\varepsilon$ at the

Fermi level for bulk metals,

$$\Delta = \left(\frac{dn}{d\varepsilon} \right)^{-1} = \frac{2\pi^2 \hbar^3}{mp_0 V} \quad (26)$$

(V is the volume of a particle).

Gor'kov and Éliashberg,⁸¹ in contrast to Kubo, used, for description of the system of levels in an ensemble of FMP, the statistics of the distribution of levels in a system of highly excited nuclei, the mathematical apparatus for which had at that time been developed in Refs. 82-84. Application of this statistical approach made it possible to predict theoretically a number of interesting properties of FMP.^{79-80,85-88} We shall discuss some properties of particles that are due to the peculiarities of their electronic states. We shall consider the case of fine particles in which the discreteness of the levels does not manifest itself ($\Delta \ll kT$), and also the case of finer particles, when the pronounced discreteness of the electronic levels should play an important role ($\Delta > kT$).

b) Behavior in an electromagnetic field ($\omega \ll \omega_p$)

According to classical ideas,⁸⁹ the electric moment p and magnetic moment M of metallic particles can be written in the form

$$M = \alpha_m^* HV, \quad \alpha_m^* = \alpha_m + i\alpha_m', \quad (27)$$

$$p = \alpha_e^* EV, \quad \alpha_e^* = \alpha_e + i\alpha_e', \quad (28)$$

here α_m^* and α_e^* are the complex magnetic and electric polarizabilities. Usually one sets $p = \alpha_e E$, $M = \alpha_m H$. Here for convenience the electric and magnetic polarizabilities are represented in the form of ratios α_e/V , α_m/V . The values of α_m' and α_e'' depend on the particle dimension a and conductivity σ and on the frequency ω , and for spherical particles⁸⁹

$$\alpha_m' = \frac{4\pi}{105} \frac{a^4 \sigma^2 \omega^2}{c^4}, \quad (29)$$

$$\alpha_e'' = \frac{a^2 \sigma \omega}{10c^2}, \quad (30)$$

where c is the velocity of light. The relations (29) and (30) are valid for particles of size $a \ll \delta$, where δ is the skin depth,

$$\delta = c\sqrt{2\pi\sigma\omega}. \quad (31)$$

The electric polarizability of spherical particles in general can be expressed in terms of the complex dielectric constant⁹⁰:

$$\alpha_e' = \frac{3}{4\pi} \frac{(\varepsilon' - 1)(\varepsilon'' + 2) + \varepsilon'^2}{(\varepsilon' + 2)^2 + \varepsilon''^2}, \quad (32)$$

$$\alpha_e'' = \frac{9}{4\pi} \frac{3\varepsilon''}{(\varepsilon' + 2)^2 + \varepsilon''^2}. \quad (33)$$

In the frequency range $\omega \ll \omega_p$, in metals with a high conductivity, $\varepsilon'' \gg \varepsilon'$ and $\varepsilon'' = 4\pi\sigma/\omega$. Therefore to a good approximation, we may suppose that for spherical metallic particles

$$\alpha_e' = \frac{3}{4\pi}, \quad (34)$$

$$\alpha_e'' = \frac{9}{(4\pi)^2} \frac{\omega}{\sigma}. \quad (35)$$

As is evident from (34), the value $\alpha_e' = 3/4\pi$ is the largest possible for any reasonable values of ε' and ε'' , and the ratio $\alpha_e''/\omega' \ll 1$ for all values $\omega \ll \omega_p$ (that is, the electrical losses of high-conductivity particles are negligibly small).

It might be supposed that the relations (29), (30) and (34), (35) could change when the discreteness of the electronic states in FMP became important ($\Delta < kT$, $\omega < \Delta/\hbar$). According to the results of Ref. 81, quantization of the levels leads to a large change of the polarizability of the particles. As long as the field frequency $\omega \ll V_E/a$ (the reciprocal time of flight of an electron from wall to wall of the particle) and the field intensity E is small in comparison with the internal fields,

$$eEa \ll \Delta; \quad (36)$$

then for sufficiently high temperatures, but ones satisfying the condition

$$kT \ll \sqrt{\Delta \cdot eE}, \quad (37)$$

the interaction of a particle with the field can be treated like the interaction with this field of a giant atom with a certain polarizability. In this case the particles does not manifest its metallic properties. Its polarizability can be represented⁸¹ in the form $\alpha_e^* = \alpha_e^0 + \alpha_e^\omega$, where

$$\alpha_e^0 = \frac{e^2 a^3 m^3 v_E^{1/2}}{5\pi^2 \hbar^2}, \quad (38)$$

$$\alpha_e^\omega = \frac{139}{1200} \frac{e^2}{\pi^2 v_E \hbar} A(z), \quad z = \frac{\pi \hbar \omega}{\Delta}. \quad (39)$$

The function $A(z)$ is complex, and its oscillatory character shows up principally for FMP of heavy metals.⁵ It follows from the conditions (36) and (37) that FMP of size 10 nm at $T < 10^4$ K and in fields $E < 10$ V/cm have a polarizability exceeding by 2 to 3 orders of magnitude the polarizability of an ordinary metallic bead of the same size. At the same time, in strong fields $\alpha_e = 3/4\pi$. Such an anomalously large polarizability of FMP is contrary to the relations (32) and (33). Despite the discreteness of the electronic states, the dielectric formalism can be used to describe the electromagnetic properties of FMP. Then by substituting arbitrary values of ϵ' and ϵ'' in the relations (32) and (33), one can show that α_e cannot exceed the value $3/4\pi$. This result was arrived at by the authors of Ref. 91, who showed that the relations (38) and (39) had been obtained without allowance for the depolarizing field of the particles.

We shall consider the experimental results on the electric and magnetic polarizability of fine particles in alternating fields. It is of course impossible to measure experimentally the polarizability of a fine particle taken individually. Usually⁹²⁻⁹⁴ specimens are prepared in the form of a suspension of particles in a dielectric matrix. At small concentrations, there is a simple relation between the dielectric and magnetic permittivities and the volume concentration of the particles:

$$\epsilon^* = \epsilon_0 (1 + 4\pi\alpha_e^* \theta), \quad (40)$$

$$\mu^* = \mu_0 (1 + 4\pi\alpha_m^* \theta), \quad (41)$$

where ϵ_0 and μ_0 are the dielectric and magnetic permittivities of the matrix. The expressions (40) and (41) are linear approximations to the well-known Clausius-Mossotti relation and are valid when $|4\pi\alpha_m^* \theta| \ll 1$ and $|4\pi\alpha_e^* \theta| \ll 1$. Experimental investigations on the effect of quantization of the electronic states on the polariza-

bility of particles of beryllium, copper, and aluminum were first made by Petinov and Naumenko over a wide range of frequencies (10^3 – 10^{10} Hz), electric fields (10^3 – 10^4 V/cm), and temperatures (1.8–300 K). The particles were obtained by evaporation of the metals in a flow of inert gases⁹⁴; they had spherical form and a comparatively small spread of sizes.

Measurement of ϵ' at frequency 10^3 was done by a bridge method with a plane condenser, and at frequencies 10^7 Hz with a cylindrical condenser, connected in the circuit of a threshold generator. The relative error in ϵ' in a change of the intensity E at frequency 10^3 Hz did not exceed 1%; at frequency 10^7 Hz, 0.1%. The greatest relative accuracy of ϵ' and μ' was achieved with microwaves and was 0.05%. The measurements of ϵ' and μ' with microwaves were made by a resonance method.⁹⁵

As a result it was possible to establish that over the frequency range 10^3 – 10^{10} Hz, for particles of copper, aluminum, and beryllium with dimensions 10–100 nm, the values of α_e^* and α_m^* are completely determined by the relations (29), (30), (34) and (35) and are independent of the electric field intensity E . The linear relations (40)–(41) are satisfactorily fulfilled for $\theta < 2 \cdot 10^{-2}$. For larger values, or when the homogeneity of the suspension is disturbed, the relation of ϵ^* and μ^* to α_e^* and α_m^* becomes nonlinear.

No anomalies of the electrical polarizability have been observed in fine particles of gold⁹² in the size range 2.5–6.0 nm and in the particles of silver⁹³ of size 4.0 nm. Thus it may be considered that quantization of the levels in FMP does not change their behavior in an electric field. At the same time, experimental results⁹⁶⁻⁹⁸ on investigation of the absorption of electromagnetic radiation in the far infrared region (10^{11} – 10^{13} Hz) by FMP of aluminum differ sharply from theory.^{81,99-103}

By using formula (73.2) of Ref. 89 and the expressions (30) and (35) for α_e^* and α_m^* , we shall first find the coefficient of absorption of spherical particles without allowance for the discreteness of their electronic states:

$$\beta = \theta \left(\frac{9}{4\pi} \frac{1}{\sigma_c} + \frac{4\pi a^3 \sigma}{10c^3} \right) \omega^2. \quad (42)$$

Thus in the classical case, the coefficient of absorption of an electromagnetic field by particles $\sim \omega^2$.

For FMP with pronounced quantization of the levels, the function $\beta(\omega)$ should have an oscillatory character.⁸¹ The absorption coefficient β for such particles can be represented in the following form¹⁰³:

$$\beta = A\theta \frac{a\omega^3}{v_{pc}} \Phi(\chi); \quad (43)$$

here A is a constant dependent on the material of the particles, and $\chi = \pi \hbar \omega / \Delta$. The function $\Phi(\chi)$ varies with χ in a complicated manner and for heavy metals oscillates with increase of χ , but for light metals goes over smoothly to a constant value (Fig. 8). Experimental values of β have been determined from the results of measurement of the transmission ratio I_1/I_2 of specimens with two different thicknesses l_1 and l_2 of the lay-

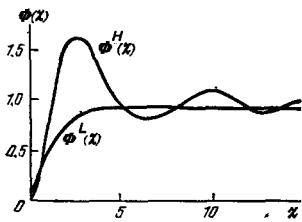


FIG. 8. Form of the function $\Phi(\chi)$. $\Phi^H(\chi)$, characteristic variation for FMP of heavy metals; $\Phi^L(\chi)$, of light metals.

ers of particles, by the formula

$$\beta_{\text{exp}} = (I_1 - I_2)^{-1} \ln \frac{I_1}{I_2}, \quad (44)$$

where I is the intensity of the radiation transmitted through the specimen.⁹⁷⁻⁹⁹

Figure 9 shows the experimental functions β_{exp} for particles of aluminum of size 4.8 and 15 nm. Both curves are approximated well by the expression

$$\beta_{\text{exp}} = \gamma \omega^2, \quad (45)$$

which agrees qualitatively with (42) and (43). But actually there is not quantitative agreement between the theoretical and experimental values of β , and the reason for the ambiguities that arise consists in the fact that the absolute values of β_{exp} exceed the theoretical by several orders of magnitude. It may be assumed that the anomalously large coefficients of absorption are caused by effects of interaction between particles; more exactly, by current states, which occur in an ensemble of fine particles in contact because of exchange of electrons between them.

c) Behavior in a magnetic field

The peculiarities of fine metal particles show up also when they are magnetized in a constant field. Here several aspects due to the smallness of their size are

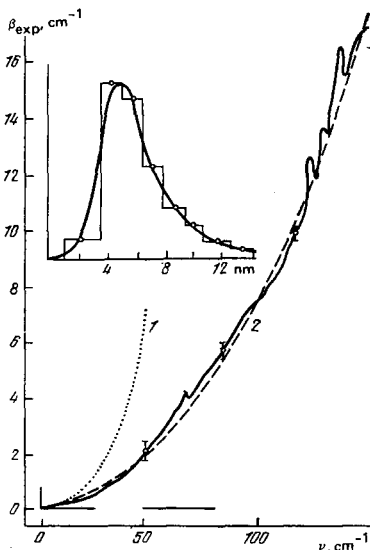


FIG. 9. Spectral variation of absorption coefficient for FMP of aluminum.¹⁵⁰ Dimensions: 1, 15 nm; 2, 4.8 nm; $\gamma_{\text{exp}} = 9 \cdot 10^{-4}$ cm. The inset shows the size distribution function of the particles ($\bar{x} = 4.8$ nm, dispersion $\sigma = 1.60$).

important. First, the relaxation of spins in fine particles is determined principally by the scattering of electrons by the surface. Second, the discreteness of the electron and phonon states may change the relaxation mechanism itself noticeably. Finally, the particles become so small that their Pauli paramagnetism may be obscured by Curie paramagnetism, produced by particles with an odd number of electrons.

We shall first consider the role of the surface in the relaxation of the electron spins. The EPR lines of fine particles whose size is less than the skin depth have the usual Lorentz form¹⁰⁵

$$P = \frac{\gamma^2 H_0^2 \tau_c \chi_0 H_1}{1 + \gamma^2 \tau_c^2 (H_0 - H)^2}, \quad (46)$$

where H_0 is the resonance field, χ is the statistical susceptibility, H_1 is the amplitude of the high-frequency field, τ_c is the effective relaxation time of the spins of the conduction electrons, and γ is the gyromagnetic ratio. Electron spins may change their orientation during an interaction with lattice oscillations, impurity atoms, and defects and during a collision with the surface. On taking it into account that all these mechanisms are independent, one can express τ_c in the form¹⁰⁵

$$\tau_c^{-1} = \tau_v^{-1} + \tau_s^{-1}, \quad (47)$$

$$\tau_v^{-1} = \tau_r^{-1} + \tau_i^{-1}, \quad (48)$$

τ_r , τ_i , and τ_s are the relaxation times in interaction of the spins with the lattice, impurities, and the surface, respectively.

The surface relaxation time τ_s for spherical particles of diameter a is determined by the expression¹⁰⁵

$$\tau_s = \frac{2}{3} \frac{a}{\epsilon v_F}, \quad (49)$$

where a is the diameter of the particle, and where ϵ is the probability of turnover of an electron spin at the surface. The value of ϵ gives some information about the character of the surface; in principle, it can be used to study the anomalies of structure of the surface of metals.

For particles containing a large number of impurities ($\lambda < a$), the function $\tau_s(a)$ should have¹⁰⁵⁻¹⁰⁹ quadratic character:

$$\tau_s = \frac{2a^2}{\epsilon v_F \lambda}. \quad (50)$$

It has been shown theoretically,¹¹⁰ however, that the relation (50) is practically never satisfied for fine particles. This can also be seen by consideration of the dynamics of turnover of spins polarized by a field, with allowance for diffusion of them to the surface of the particles. When a field is turned on, the concentration n of such electron spins at a point r changes in accordance with the equation

$$\frac{\partial n}{\partial t} = D \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial n}{\partial r} \right) + \frac{n}{\tau_v}, \quad (51)$$

with the boundary condition

$$D \frac{\partial n}{\partial r} \Big|_{r=a} = -\frac{\epsilon n v_F}{4}, \quad (52)$$

which corresponds to spin reversal at the surface of

particles with probability c . In general, $n = n(r, t)$. But if the time τ_D of diffusion of spins between the walls ($\tau_D \sim a^2/D$) is small in comparison with τ_V and τ_S , then one may suppose that $n(r, t) = n(t)$. Then (51) and (52) lead to the relation (49). Usually¹⁰⁶ $\tau_V, \tau_S > 10^{-9}$ sec. We shall estimate τ_D for particles of size 100 nm, starting from the fact that $D \approx (1/3)\lambda v_F$. If $v_F \sim 10^8$ cm/sec and $\lambda \sim 1$ nm (the case of a very "dirty" metal), then $\tau_D \sim 10^{-11}$ sec. Thus the relation (49) remains valid even for very "dirty" particles.

Before passing on to a presentation of the experimental data, we shall first analyze the basic theoretical predictions about the influence of a pronounced discreteness of the electron states on the magnetic susceptibility and spin relaxation of FMP. The magnetic susceptibility of such particles was investigated earlier with allowance for the parity of the number of electrons in the particles.⁷⁹⁻⁸¹ It was found that in small magnetic fields, when the Zeeman energy is less than the mean distance between levels, $\mu H \ll \Delta$, the electron spin paramagnetism of FMP with an even number of electrons (even FMP) is suppressed to zero at low temperatures ($kT \ll \Delta$). In particles with an odd number of electrons (odd FMP), on the contrary, the paramagnetism is enhanced with lowering of temperature according to the Curie law.⁸⁵ But this paramagnetism is very weak, since its contribution corresponds to only a single Bohr magneton per particle, and it can be isolated only at very low temperatures.⁸¹ A rigorous mathematical basis for this phenomenon was given in Ref. 85. But this paper did not consider the effect of mixing of the wave functions of electrons with different spin directions through spin-orbit interaction. This was studied later,¹¹¹⁻¹¹³ and it was found that even as a result of weak spin-orbit interaction the paramagnetism of even particles does not disappear on decrease of the temperature to zero, but approaches a certain value. The paramagnetism of odd particles in this case varies according to a modified Curie law. Figure 10 shows the theoretical variation of the relative spin susceptibility of "even" and "odd" particles with the ratio of kT/Δ , calculated in Ref. 111. The parameter p characterizes the degree of mixture of the spin states and is expressed in terms of the effective energy of this

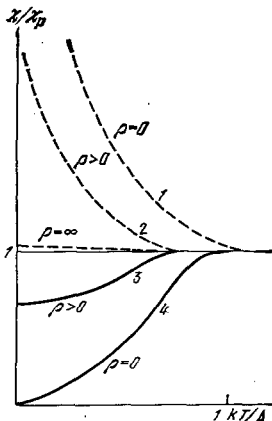


FIG. 10. Spin susceptibility of FMP. 1 and 2, odd particles; 3 and 4, even particles.

interaction¹¹¹:

$$p = 2\pi \left(\frac{H_{S0}}{\Delta} \right)^2. \quad (53)$$

When $\Delta < kT$ or $p = 1$ (the case of strong spin-orbit coupling), the paramagnetism of even and odd particles tends toward the Pauli paramagnetism.

A peculiarity of the magnetism of fine particles is the dependence of their susceptibility and of the shape of the EPR line on the value of the magnetic field intensity.^{81,85} For metal particles with weak spin-orbit interaction ($H_{S0} \approx 00$), the paramagnetic susceptibility experiences small oscillations,⁸¹

$$\chi_{||} = \chi_{\infty} \left[1 - \frac{\Delta}{(2\pi\mu H)^2} + \frac{1 + \cos^2(2\pi\mu H/\Delta)}{(2\pi\mu H/\Delta)^4} \right]. \quad (54)$$

For particles of light metals, the intensity of the EPR signal as a function of H is determined by the expression⁸¹

$$\chi_{\perp} \approx \frac{H_0}{H_0^2 - H^2} \int_0^H \chi_{||} dH. \quad (55)$$

Thus in the experiment, the intensity of the EPR line should show a quantum change with the value of the magnetic field. Of course this can be observed only under the conditions $kT < \Delta$ and $\mu H < \Delta$. When these inequalities are violated, the shape of the EPR line is described by the relation (45). The discreteness of the electronic levels should also affect the relaxation processes in FMP. In a bulk metal, the change of Zeeman energy during relaxation of the electron spins is usually compensated by kinetic energy of electrons. But in the presence of discreteness of the levels, such a transfer of energy becomes difficult. Discreteness of the phonon spectrum is also an obstacle to relaxation ($\Delta \varepsilon \approx \hbar u/a$, where u is the velocity of sound and a is the particle dimension).

The chief process of spin relaxation in particles at low temperatures is dependent on spin-orbit interaction. The corresponding relaxation time can be estimated with the well-known Elliott relation

$$\frac{1}{\tau} = \frac{v_F}{a} (\Delta g)^2. \quad (56)$$

The value of $\Delta g = g_0 - g$ depends on the effective energy E of the spin-orbit interaction and of the corresponding forbidden bandwidth:

$$\Delta g \sim \frac{H_{S0}}{E}. \quad (57)$$

The relation (56) determines the relaxation time until the particle size becomes such that $a \cdot \Delta \sim \hbar v_F$. In this range of dimensional effects, τ loses the meaning of a relaxation time and, rather, gives the value of the spin-orbit interaction.¹¹⁴ In this case, τ can be written in the form⁸⁰

$$\frac{1}{\tau} = \frac{1}{\hbar} \frac{H_{S0}^2}{\Delta}. \quad (58)$$

On taking into account that $\Delta \sim a^{-3}$ and comparing (58) with (56), we get $H_{S0} \sim a^{-2}$. Thus for coarse particles, in which the electron spectrum is quasicontinuous, spin-orbit interaction is a cause of spin relaxation. On the other hand, for very fine particles it can be expected that the inequality $\Delta > H_{S0}$ will be satisfied. In the latter case, spin-orbit interaction constitutes weak

perturbation of the discrete one-electron states in the particle. For each specific metal, there may exist a definite range of particle sizes within which the discreteness is clearly manifested, and at the same time the interaction H_{S0} is comparable with the distance Δ between levels or even exceeds it. In this case, naturally, the effectiveness of the relaxation process increases sharply, and the anomaly of the magnetic susceptibility is suppressed.

Kawabata⁸⁶ calculated the residual EPR linewidth $\delta\omega_e$ and the amount of the shift of resonance $\Delta\omega_e$ at low temperatures:

$$\delta\omega_e \sim \frac{\hbar\omega_z}{\tau\Delta}, \quad (59)$$

$$\Delta\omega_e = -\frac{\hbar\omega_z}{\tau\Delta}. \quad (60)$$

These estimates are correct when

$$\tau\Delta \gg \hbar \text{ and } \hbar\omega_z \ll \Delta \quad (61)$$

(ω_e is the resonance frequency). On decrease of particle size ($a \rightarrow 0$), as is seen from (59) and (60), $\delta\omega_e \sim a^2$ and $\Delta\omega_e \sim a^2$. For pure metals with a small value of the spin-orbit interaction, when the condition (61) is satisfied, one can expect an extremely small EPR linewidth.

Investigations of the spin states of the conduction electrons, by the EPR method, have been made on particles of lithium,^{94,109,116-121} sodium,¹²²⁻¹²⁵ silver,^{126,127} platinum,¹²⁶⁻¹²⁸ and gold.^{129,130} A characteristic peculiarity of the EPR lines of sufficiently fine particles is the presence of wings that distort their Lorentzian shape.^{94,124} Such broadening is probably due to the fact that in actual specimens there is always some spread of sizes. Since the spin relaxation time depends on the particle size [see the relation (47)], the experimental curves represent a superposition of EPR lines of particles of different sizes. The observed shape of the EPR lines can evidently be described by means of the relation (46) and the size-distribution function of the particles:

$$\frac{dP}{dH} \approx 2\gamma^2 H_0^2 H_1 \chi_0 \sum V(r_i) v_c^2(r_i) \frac{H_0 - H}{[1 + \gamma^2 \tau_c^2(r_i) (H_0 - H)^2]^2}; \quad (62)$$

here H_0 is the resonance field, $V(r_i)$ is the volume fraction of particles of radius r_i , and $\tau_c(r_i)$ is given by the expression (46).

The effect of particle size on EPR linewidth has been investigated in greatest detail in lithium and sodium.

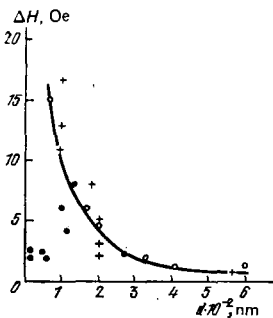


FIG. 11. Variation of EPR linewidth with size of FMP of lithium.

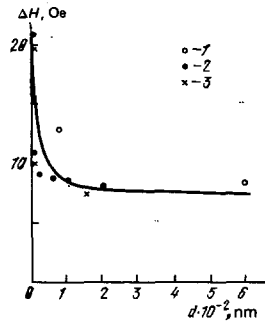


FIG. 12. Variation of EPR linewidth with size of sodium particles. 1, according to Ref. 122; 2, according to Ref. 123; 3, according to Ref. 124.

Figures 11 and 12 show the variation of ΔH with particle size, obtained at room temperature and plotted on the basis of data taken from various papers. These variations clearly demonstrate the connection of the linewidth with the particle size. It is characteristic that the data of all the papers on sodium particles indicate a steady increase of EPR linewidth with decrease of particle size. But for lithium particles, Ref. 119 reported an abrupt drop of ΔH on decrease of the particle size from 100 nm to 10 nm. The authors¹¹⁹ attribute this phenomenon to the discreteness of the electronic states. It is assumed that when the condition

$$\mu_B H \ll \Delta \quad (63)$$

is satisfied, conversion of Zeeman energy to phonon energy is impeded, and this leads to a lowering of the probability of spin turnover during collision with the surface. No important peculiarities in the intensity, shape, and position of EPR lines were observed on cooling to 1.5 K.¹¹⁹ But the drop of ΔH on decrease of the size of lithium particles, observed in Ref. 119, is difficult to relate to quantization of the levels.

As follows from Refs. 78 and 81, quantization of the levels can manifest itself in any physical phenomena only under the condition that the energy factors capable of mixing the system of levels are smaller than the discreteness of these levels. For detection of the effect of quantization in a magnetic field, of course, it is necessary that $\mu H < \Delta$ and $kT < \Delta$. For the particle sizes represented in Figs. 11 and 12, the second condition is not satisfied at $T = 297$ K. By use of these inequalities and of the relation (26), it can be shown that for manifestation of the quantization of levels, the physical size of the particles must be less than a_H and a_T , defined by the formulas

$$a_H \approx \left(\frac{2\pi\hbar^3}{m^3 v_F \mu_B H} \right)^{1/3}, \quad (64)$$

$$a_T \approx \left(\frac{2\pi\hbar^3}{m^3 v_F kT} \right)^{1/3}. \quad (65)$$

Setting $m \sim 10^{-27}$ g and $v_F \sim 10^8$ cm/sec, we find that at field $H = 3000$ G, $a_H \sim 12$ nm; and that at $T = 300$ K, $a_T \sim 2$ nm.

A narrow line in the EPR spectrum of lithium particles ($a \sim 60$ nm) was also observed in Ref. 94. The intensity of this line increased with lowering of temperature. In particles of lithium of the same size containing impurity atoms of sodium, the narrow line was

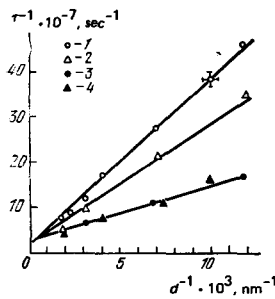


FIG. 13. Variation of τ^{-1} with size of FMP of lithium with sodium content.

absent. Before explaining the nature of this line, we shall consider the effect of impurities on the relaxation of electron spins in fine particles. In Ref. 117, a study was made of the contribution of impurity atoms of sodium to the relaxation of spins in fine particles of lithium. Figure 13 shows the variation of τ^{-1} with d^{-1} for such particles. It is evident from the figure that the experimental results fall well on straight lines differing in slope, but practically converging to a single point on the axis of ordinates, which according to the expression (47) corresponds to τ_V . Thus impurity atoms of sodium have practically no effect on τ_V in small particles of lithium, but they noticeably decrease the probability of spin reversal during collision of electrons with the surface. This could occur only because sodium atoms go to the surface of the particle, i. e., because fine particles have a fundamental tendency to cleanse themselves of impurities and defects.^{117 1)} The surface is always an effective trap for impurities and defects; and in fine particles, because of diffusion processes, the impurities, even at comparatively low temperatures, rapidly leave the interior ($\tau \sim a^2/D$) and become concentrated on the surface. This in turn causes a change of the probability ε of spin turnover at the surface. It is characteristic that in particles of pure lithium, $\varepsilon \approx 5 \cdot 10^{-6}$ sec, while in "dirty," $\varepsilon \approx 2 \cdot 10^{-6}$ sec.⁹⁴ The latter value is nearly equal to the probability of spin turnover during scattering of electrons by the surface of sodium particles,¹²² where $\varepsilon \approx 2 \cdot 10^{-6}$ sec. Very similar values of ε have been found for particles of lithium in Refs. 109 and 119, and for particles of sodium in Refs. 123 and 124. The reasons for the occurrence of a narrow line in lithium particles⁹⁴ are perhaps related to paramagnetic impurities on the surface. The absence of such a line in the EPR spectrum of sodium particles and of "dirty" lithium particles with sodium impurity may be due to the fact that sodium does not form such paramagnetic impurities.

There is an alternative explanation of the observed effect, dependent on "cutting off" of the phonon spectrum in fine particles.¹²² A fine particle may be regarded as

¹⁾ A general property characteristic of two-component FMP is their tendency toward concentration stratification, as a result of which the surface layers become enriched and the internal regions depleted with respect to the second component. This effect, first predicted in Ref. 17, and confirmed experimentally in Ref. 90, is possible even when the components are soluble without limit in the bulk state.

an acoustical resonator, whose minimum frequency is set by the size, $v_{\text{min}} = u/2d$ (u is the velocity of sound). Thus phonons smaller than $h\nu_{\text{min}}$ cannot be excited in an isolated particle.⁷⁹ This relates both to volume and to surface oscillations. Since the relaxation of the spins of the conduction electrons is dependent primarily on interactions with phonons and on transfer of the Zeeman energy to the lattice as a result of direct and Raman processes, the rate of relaxation will decrease when $\mu H < h\nu_{\text{min}}$. This also enables us to explain the observed effect qualitatively, especially if we take into account that $v_{\text{min}} \sim 10^{10}$ Hz already corresponds to particle sizes $a \sim 50$ nm. We must emphasize an interesting peculiarity in the relaxation of electron spins both in FMP of lithium and in bulk specimens, which has so far not received a sufficiently clear theoretical interpretation. It is connected with the temperature independence of the relaxation mechanism of the conduction electrons in this metal. It is usually assumed that in lithium, a dominant role in the relaxation of the electron spins is played by impurity atoms. But experimental investigations on specimens with different impurity contents, including FMP, have so far not shown any dependence of the linewidth on temperature. Here the contribution of the surface is easily traced, despite the small probability of spin reversal on it. Furthermore, in sodium the temperature dependence of the linewidth shows up very well even in particles of size 20 nm. Figure 14 shows results of experimental investigations on the effect of temperature on ΔH for particles of sodium.^{122, 123} Although in particles of size ~ 2 nm almost 75% of the total number of atoms take part in the formation of the surface (and therefore may be regarded as "impurity" atoms), the effect of the temperature on the relaxation of electron spins is clearly evident. Incidentally, we note that in Ref. 123, even in particles of size 2 nm, no effect of quantization of the electronic levels and of the "evenness" or "oddness" of the number of electrons in the particles upon the EPR spectrum was detected.

References 116, 118, 120, and 124 are also devoted to investigations of the effect of quantization of the electronic levels in fine particles of lithium and sodium. Christiane Taupin¹¹⁶ studied the paramagnetic resonance of fine particles of lithium in irradiated crystals of LiF. She observed that when the irradiated specimens are annealed, the EPR spectrum has a very nar-

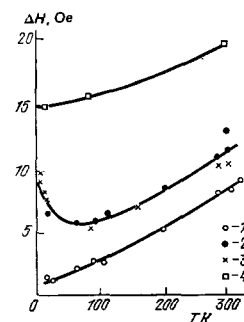


FIG. 14. Variation of EPR linewidth with temperature for FMP of sodium. Sizes (nm): 600 (1), 70 (2),¹²² 15 (3), and 2 (4).¹²⁴

row line. The intensity of this line increased with lowering of temperature. Furthermore, the nuclear magnetic-resonance spectrum in such particles showed the presence of a comparatively narrow line, not shifted with respect to the matrix. The results of this work are interpreted as follows. During the annealing of the irradiated specimens there are formed, along with coarse particles, fine lamellar formations of lithium, whose thickness is less than 1 nm. In these formations, also, quantization of electronic states develops. Then the oddness of the number of electrons in some formations leads to the occurrence of a temperature-dependent paramagnetism, and the evenness of the number of electrons in others to a falling of the paramagnetism to zero. The latter also causes the appearance of an NMR line with zero Knight shift. Here it is appropriate to mention that investigations of similar specimens by the EPR method^{109,131-133} revealed no effects of quantization of the electronic states in lithium particles formed after annealing.

Interesting results have been obtained in investigation of fine particles of lithium in a matrix of CO₂¹¹⁸ and of xenon.¹²⁰ Particles of lithium in a matrix of CO₂ revealed a decrease of the spin-lattice relaxation time with decrease of the temperature and of the particle size. But in this matrix it was not possible to avoid the presence of solitary lithium atoms. In a xenon matrix, the EPR line had a normal shape, and its intensity depended on the temperature (Fig. 15). In the high-temperature range, the paramagnetic susceptibility of the particles corresponds to Pauli paramagnetism; in the low-temperature range, it varies in accordance with Curie's law. Curie paramagnetism was also observed in finer particles of lithium, of size only 1 nm¹²⁶; in particles of platinum of diameter 2.2 nm, suspended in gelatine¹²⁸; and in particles of aluminum with $a \sim 2$ nm, in an inert matrix.¹²⁷

A number of papers¹²²⁻¹²⁴ report a noticeable broadening of the EPR lines in fine particles of sodium in the temperature range below 100 K (see Fig. 14). The authors of these papers established that this broadening was due to the effect of saturation of the EPR line because of decrease of the spin-lattice relaxation time. In the opinion of Gordon,¹²⁴ this peculiarity of fine particles of sodium is due to the discreteness of the electronic levels; but other authors¹²² attribute it to the discreteness of the phonon spectrum. At present it is difficult to give preference to one mechanism or the other.

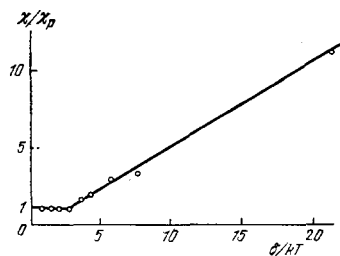


FIG. 15. Variation of χ/χ_0 with the ratio δ/kT for FMP of lithium of size 3.2 nm.

The anomalies of the magnetic susceptibility of fine particles show up very definitely also in NMR investigations, in particular in the Knight shift.¹³⁴⁻¹⁴⁰ It is known that in consequence of the hyperfine interaction of the conduction electrons with the nucleus, the NMR lines are shifted with respect to dielectric materials containing similar nuclei. The amount of this Knight shift is determined by the following expression:

$$K = \frac{8\pi}{3} \frac{\chi_p}{N_0} |\chi_F(0)|^2; \quad (66)$$

here N_0 is the number of nuclei in unit volume, and $|\chi_F(0)|^2$ is the mean probability density of all electronic states on the Fermi sphere at the position of the nucleus. As follows from (36), the Knight shift is directly proportional to the paramagnetic susceptibility of the conduction electrons. It must be emphasized that in the investigation, the EPR and the measurements of magnetic susceptibility χ may be masked by impurity paramagnetism. The Knight shift enables us to separate out only the paramagnetism of the conduction electrons.

As has already been mentioned above, Taupin first discovered, in an investigation of fine particles of lithium, a line in the NMR spectrum with zero Knight shift.¹¹⁶ The observed line can be explained by the presence in the specimen of ultra-small particles of lithium with an even number of electrons, for which, according to the results of Ref. 88, χ should be zero. A similar result was also obtained at very low temperatures in even particles of aluminum.¹³⁴ In fine particles of tin¹³⁸ and copper,^{136,137} the paramagnetism retained a residual value. Figure 16 shows the experimental variations, relative to the shift at $T=0$, for tin^{138,141,142} and for copper.¹³⁷ It follows from the data presented that with decrease of particle size and rise of temperature, χ drops but retains residual values at $T=0$. This behavior of $\chi(T)$ can be explained by allowing for the shift of the levels corresponding to the ground singlet state and an excited triplet state. This leads to incomplete pairing and, of course, to retention of a paramagnetic susceptibility at $T=0$. Here it is appropriate to mention that in ensembles of fine particles, the probabilities of formation of particles with even and with odd numbers of electrons are evidently equal. But the effect of oddness of the particles on the Knight shift, practically, does not show up experimentally. The presence of oddness of the particles should increase the Knight shift on lowering of the tem-

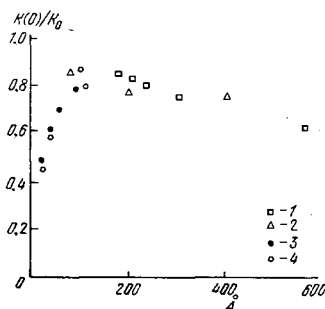


FIG. 16. Variation of Knight shift with size of FMP of tin (1, according to Ref. 138; 2, according to Ref. 141; 3, according to Ref. 142) and copper (4, according to Ref. 137).

perature. This would lead to the appearance of a doublet of NMR lines, one of which would shift in one direction and the other in the other on lowering of the temperature. Such an inconsistency has so far not received adequate explanation. It is possible that all the particles are even. This may be a consequence of the higher chemical activity of odd particles, which are essentially radicals. They may enter, more effectively than even particles, into a chemical bond with any molecule that falls on the surface, and thereby a single unpaired electron, by forming a valence bond, will leave the conduction band. For any conditions for obtaining particles, there is always one molecule per particle that is capable of forming a chemical bond.

It is also possible that disturbance of the parity of the particles and their residual paramagnetism at zero temperature are dependent on electronic exchange between particles by tunneling of the electrons through dielectric barriers.¹⁴⁷

5. OPTICAL AND EMISSION PROPERTIES

a) Absorption of radiation

The optical properties of particles, in particular of noble metals, have already been under investigation for a long time. Particles for such investigations are prepared in the form of colloidal suspensions,¹⁴⁴⁻¹⁴⁶ in photosensitive glasses,¹⁴⁴ by growth of insular metallic^{7,147-149} or metallo-ceramic films of Au-SiO₂, and also by evaporation in a gas.⁴

The character of the absorption of light by FMP is well demonstrated by Fig. 17, which shows the variation of the transmission of light by gold particles of size 4 nm.¹⁵⁰ The specimens were prepared by spraying the particles on to glass and differed with respect to the thickness of the layer. In the range from 560 to 600 nm, there is a clear minimum of the transmission in all cases that is absent in bulk specimens. To interpret the variations obtained, the authors¹⁵⁰ used various theoretical models¹⁵¹⁻¹⁵⁵ that allow for the effects of interaction between the particles and for the influence of the particle shape. For this purpose, the concept of effective dielectric constant of the medium was introduced, and it was estimated theoretically with

the aid of data on the polarizability of the particles and on their packing density. The effect of quantization of the electronic states was not taken into account.

According to the phenomenological theory of Mie, in which the absorption and scattering spectra of FMP are calculated by means of the complex dielectric constant, there should be no optical size effects for particles in the size range $0 < R \leq 10$ nm, provided ϵ ($\epsilon = \epsilon_1 + i\epsilon_2$) has the form characteristic of bulk material. But the value of ϵ for particles in which the energy spectrum is discrete depends on the size, and furthermore it does not vary monotonically with frequency but oscillates in consequence of transitions between electronic states.¹⁵⁶ True, it is a complicated problem in practice to prepare 10^{10} - 10^{13} particles of identical sizes and shapes, as is necessary for experimental investigations, and therefore these oscillations are smoothed out for an ensemble of particles. But the value of ϵ averaged over the ensemble carries traces of the discreteness of the spectrum and differs from the value of the dielectric constant of bulk material. The size dependence of the imaginary part of the mean value of ϵ has the form^{156,157}

$$\epsilon_2(\omega) = \epsilon_0(\omega) + \frac{A(\omega)}{R}. \quad (67)$$

For the function $A(\omega)$, several different expressions have been obtained within the framework of various models.^{156,157} Optical absorption by conduction electrons is important in bulk metals over the frequency range from zero to the plasma frequency. In FMP, the corresponding absorption peaks are concentrated in a narrow frequency band, specific for surface and volume plasmons of various types.¹⁵⁸⁻¹⁶⁰ Experimental measurements have been made of the temperature and frequency dependence of the optical absorption of FMP of gold¹⁶¹ over a size range corresponding to 10^2 to 10^5 atoms. The measurements were made at temperatures 300 and 1.5 K, over the spectral range from 0.5 to 4.2 eV. Figure 18 shows the absorption spectra of FMP of gold.¹⁶¹ With increase of the particle dimensions, the peak corresponding to plasma absorption becomes narrower and more clearly expressed. The spectral variations $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$, calculated from the data on the absorption spectrum, have different characters.

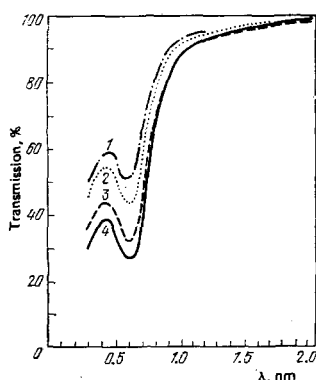


FIG. 17. Wavelength dependence of transmission of light through a layer of FMP of gold of thickness 0.29 (1), 0.32 (2), 0.36 (3), and 0.55 g/m² (4).

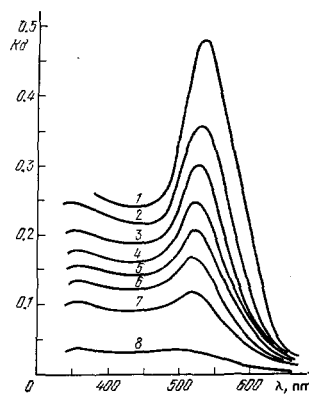


FIG. 18. Experimental absorption spectra of FMP of gold of various sizes. Sizes (nm): 5.6 (1), 5.4 (2), 5.15 (3), 4.9 (4), 4.7 (5), 4.4 (6), 4.0 (7), 2.9 (8); $T = 300$ K.

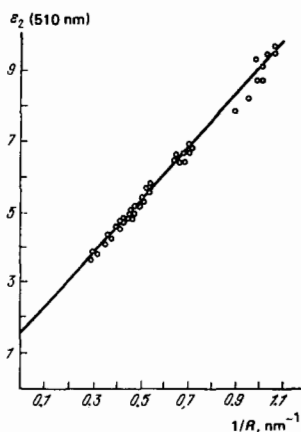


FIG. 19. Variation of imaginary part of dielectric constant for gold particles with reciprocal radius ($\lambda = 510$ nm).¹⁶²

With decrease of the particle size, $\epsilon_1(\omega)$ decreases, but $\epsilon_2(\omega)$ increases.

From the absorption spectra obtained at 300 and 1.5 K for particles of different sizes, it was established that the temperature dependence of the position of the absorption maximum becomes weaker with decrease of the particle size; this may be due to suppression of the interaction of the electrons with the thermal oscillations because of quantum size effects. Figure 19 shows the variation of the imaginary part of the dielectric constant for particles of Au with the value of their reciprocal radius, at constant wavelength ($\lambda = 510$ nm). Obviously the results agree very well with those predicted theoretically [see the relation (67)].

Starting from the assumption that the size dependence of the change of the imaginary part of the dielectric constant $\sim 1/R$, one can calculate the size dependence of the linewidth of the plasma absorption. The linear variation of the width of this line with $1/R$ is corroborated experimentally by data of Kreibig.¹⁶¹ The relation (67) takes into account only size-dependent changes of the electronic spectrum and disregards reorganization of the phonon spectrum, change of the type and the parameters of the atomic structure, and other factors that manifest themselves in the same range of particle sizes. We note that with decrease of the sizes of the particles, there is a change of shape of the edge of the absorption band in the low-frequency region. The spectral variation becomes smoother, in comparison with the theoretically predicted variation $\epsilon_2^{(i)}(\omega)$ due to intraband transitions.¹⁶² In particles containing 10^4 atoms, these transitions begin at photon energy 2.3 eV, whereas in finer particles, containing $5 \cdot 10^2$ atoms, they begin at energy 1.8 eV. Thus the absorption edge in FMP is shifted toward the longwave part of the spectrum as compared with its position in bulk gold (Fig. 20). The explanation of the change in the spectral variation $\epsilon_2^{(i)}$ must be sought in an increase of the role of surface atoms and in a change of the electronic structure of the particles, in consequence of a decrease of the coordination number and a difference of the lattice potential at the surface from its value in the interior.

An important role may be played by a change of gen-

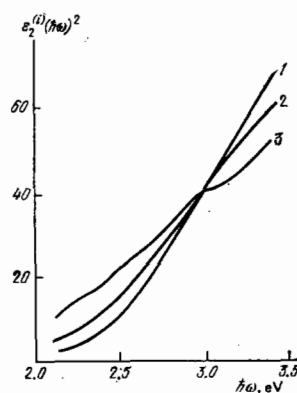


FIG. 20. Variation with particle size of the position of the band edge for intraband transitions in FMP of gold.¹⁶² Sizes (nm), 7.6 (1), 3.1 (2), and 2.2 (3).¹⁶²

eral character in the interatomic distances in FMP as compared with their values in bulk materials. Christensen and Seraphin¹⁶³ calculated the effect of changes of the interatomic distance on the character of the bond and on the dielectric constant. They established that the threshold energy for intraband transitions changes by 0.2 eV on compression of the particle by 2%. If the decrease of interatomic distance were the only reason for the change of shape of the edge of the absorption band, then for agreement with experiment it would be necessary to assume that the strain of compression is about 5%, which is quite realistic. Here the threshold energy changes on passage from the center of the particle to its surface; this indicates in addition, though in an indirect manner, a nonuniform character of the strain in FMP.

In addition to this, there is an effect that causes a shift of the opposite sign of the edge of the absorption band, because of intraband transition. Measurements made by the method of x-ray photoelectronic spectroscopy of small clusters of silver (containing ~ 10 atoms) show that the *d* band in them narrows and shifts as compared with the parameters characteristic of bulk silver; this is explained qualitatively by the decrease of the mean number of neighbor atoms in such particles.

Along with changes of the energy structure of the particles, it is necessary to take into account the possibility of the appearance of new types of electronic transitions, as a result of the fact that the symmetry in the surface region of FMP does not coincide with the symmetry of a bulk crystal. One of the properties of FMP that is evidently most important, especially for their optical and catalytic properties, is a decrease of the ability of the electrons to shield electrostatic fields.¹⁶⁴⁻¹⁶⁷ A consequence of this fact is an increase of the radius of interaction between electrons, which must affect the chemisorption properties,¹⁹⁰ especially when they have to do with redistribution of the electrons between the particle and an adsorbed atom.

b) Plasma oscillations; emission

Size effects in the excitation of plasmons, which are a coherent superposition of electron-hole pairs, are

due to an increase of the static and dynamic polarizability and to the appearance of a dependence of the position of the plasma peak on the size of the particle. The width of this peak is dependent on nonconservation of momentum and on disintegration of the collective level to single-electron levels.

Two basic theoretical approaches, a hydrodynamic^{165,168} and a quantum-mechanical,¹⁶⁹⁻¹⁷² predict different types of change of the plasma frequency ω_p in FMP with change of size. According to the first ω_p should decrease with decrease of size, while according to the second the plasma frequency should increase.

In the hydrodynamic approximation, the magnitude and sign of the size-determined shift of the plasma frequency depend on the degree of roughness of the surface of the FMP on an atomic scale. When a smeared-out surface, depleted with respect to free charge carriers, makes an appreciable contribution to the formation of a plasmon, a shift of the plasma peak toward the low-frequency region is possible.¹⁶⁵

But quantum-mechanical analysis¹⁷⁰ shows that it is of great importance that on decrease of the size of FMP, the Fermi electron gas acquires an additional rigidity, which leads to increase of the plasma frequency. An increase of the plasma resonance frequency has been observed experimentally by Kulyupin and coauthors¹⁷¹ and also by Kreibig¹⁶¹ and other investigators.¹⁷³ Figure 21 shows the dependence of the absorption peak on the size of the FMP for gold. A shift of ω_p in the high-frequency region has been observed by investigating the radiative disintegration of collective excitations in FMP of silver when they are irradiated with slow electrons.¹⁷⁴ Increase of the dynamic polarizability of individual FMP may be due to peculiarities of structure of their surfaces.¹⁷¹ No less a role may be played by the mutual influence of the particles of an ensemble on each other, which causes the appearance of collective polarizability and strong fluctuations of the refractive index of the medium.¹⁶¹ An interesting topic is the effect of the size of FMP on the emission phenomena in metals. Of importance here are both the change of structure of the FMP surface and its adsorptive properties, as compared with the faces of a single crystal, as well as its considerably larger degree of

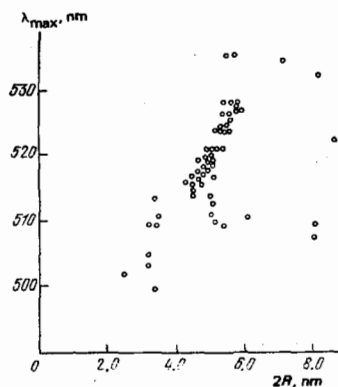


FIG. 21. Position of the maximum of the plasma peak in FMP of gold of various sizes.¹⁶²

geometric branching. Photoemission measurements have shown a decrease of the work function with decrease of the size of FMP of gold.^{174,175} This is explained by the significant change of the energy structure of FMP, in particular the decrease of the density of S states near the Fermi level.¹⁷⁴ Important also is the dependence of the chemical potential of the electron gas on the size of the FMP, which is dependent on the small compressibility of the Fermi gas.¹

In a phenomenological analysis,¹⁷⁵ account is taken of the work against electrostatic image forces in the FMP and the work against the Coulomb forces of interaction between an emitted electron and the positive charge remaining in the FMP. With decrease of particle size, the first component decreases, while the second (which is important for nonconducting UDM) increases. A quantum-mechanical treatment¹⁷⁶ also leads to the conclusion that the work function increases in FMP.

Thus although the existence of a size effect in the work function is beyond doubt, the character of this effect (decrease or increase of ϕ in FMP) depends on a number of parameters of the UDM: the type of material, the state of the surface, the conductivity, the type of adsorbed impurities, etc. Obviously by using these factors, one can change the sign of the size effect in the work function at will.

6. CONCLUSION

In this review we have considered the present status of investigations primarily of the structure, lattice dynamics, and electronic properties of fine metallic particles. In view of the limitation on the extent of the article, we have left aside a number of interesting problems, including magnetic ordering and superconductivity in a small ensemble of atoms. For study of these phenomena, fine metallic particles are a very interesting subject. In them, which are essentially zero-dimensional metals, the size and the surface for the first time enter as strong perturbing factors, capable of disturbing the magnetic and structural order and the superconductivity.

Also not touched upon in the review were phenomena connected with interactions between particles. These interactions are usually brought about through regions of contact, which can be regarded as potential barriers. They have a broad energy spectrum and are therefore of considerable interest for the study of tunneling and activation processes and of correlation of electron and phonon states for a large ensemble of particles. All this is at present extremely timely, since it opens up new possibilities for investigation of transport processes in disordered media.

The physics of fine metallic particles is a new and promising field of investigation. It is developing at the junction of a number of important scientific and practical fields of knowledge, among them surface physics and chemistry, colloidal chemistry and heterogeneous catalysis, powder metallurgy, and metallic glasses.

At present, there have already occurred two international conferences devoted to fine metallic particles

(Grenoble, 1977; Lausanne, 1980) and two all-union (Kiev, 1976, and L'vov, 1980). Participating in these conferences were specialists in the fields of physics, chemistry, and metallurgy.

The authors are sincerely grateful to A. P. Aleksandrov for his deep and interested discussion of a number of questions touched upon in the review, and also of the general prospects for development of this scientific trend. The authors are grateful to E. P. Velikhov, who supported the idea of writing this review and gave valuable encouragement.

Systematic investigations of ultradispersed media began in our country more than 30 years ago, and it is proper for us to mention here the pioneers in this direction of science, I. K. Kikoin, M. Ya. Gen, Yu. L. Golin, V. N. Lapovok, M. V. Yakutovich, and others, whose friendly criticism and advice were of constant help to the authors both during the writing of the review and in the research.

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