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STRUCTURAL PROPERTIES OF SURFACE LAYERS OF DISPERSED SYSTEMS BY THE METHOD OF ESTIMATING THE DEFORMATIONS OF THE CRYSTAL LATTICE OF THE SOLID PHASE AND THE DENSITY OF THE DISPERSED MEDIUM. I

P. P. Olodovskii and L. A. Malkova

UDC 541.182.3

The distribution of the number of molecules of the dispersed medium in surface layers of the solid phase as a function of the concentration of water molecules, adsorbed on montmorillonite, is estimated.

The effect of adsorbed water and organic compounds on the change in the parameters and volume of the unit crystalline cell of kaolinite is demonstrated in [1, 2]. Calculations of the deformation of the lattice are performed.

In this work, the object of the investigation was the agrillaceous fraction of montmorillonite, separated from natural Crimean kill. The technique and the procedure used in the measurements remained essentially the same. The method of x-ray diffractometry using a DRON-2 was used.

Powder (3 g) was pressed into a special cell, whose reflecting surface was covered with beryllium foil, which was almost transparent to x rays. The moisture content of the sample was varied by drying in a vacuum dryer and by moistening with water in the dryer. Water vapor was added or removed through an opening in the cell, tightly covered with a threaded seal. The moisture content was determined by weighing.

The organic compounds used consisted of nitrobenzene and toluene. For adsorption of molecules of these compounds on the powder, the sample in the cell with an established moisture content was placed into the system with the air removed beforehand and saturated with nitrobenzene or toluene vapors.

A picture of the specimen in reflection was made in the discrete regime with Cu  $K_{\alpha}$  radiation. The current in the tube was 16 mA, the voltage was 36 kV, and the gaps equal 0.5, 1, and 0.25 mm. The vertical divergence of the Soller slits was  $1.5^{\circ}$ . An  $N_i$  filter was used. The limit of the measurements was 1000 counts/sec,  $R_c = 5$ . The angle  $2\theta$  for specific moisture contents of montmorillonite was recorded on a digital printer from the maximum intensity of reflections with an error of  $2\theta = 0.005^{\circ}$  (with a step size of  $0.01^{\circ}$ ). The reflections at (220), (222), and (400) of cerium dioxide, which was mixed with montmorillonite in a ratio of 1:20, were used as standards.

The parameters and the volume of the crystal lattice were calculated from four reflections of montmorillonite (200), (005), (060), and (331) with the help of formulas for the monoclinic syngony and computer programs that we wrote in FORTRAN.

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Central Scientific-Research Institute for Complex Utilization of Water Resources, Minvodkhoza SSSR, Minsk. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 46, No. 5, pp. 746-754, May, 1984. Original article submitted February 3, 1983.

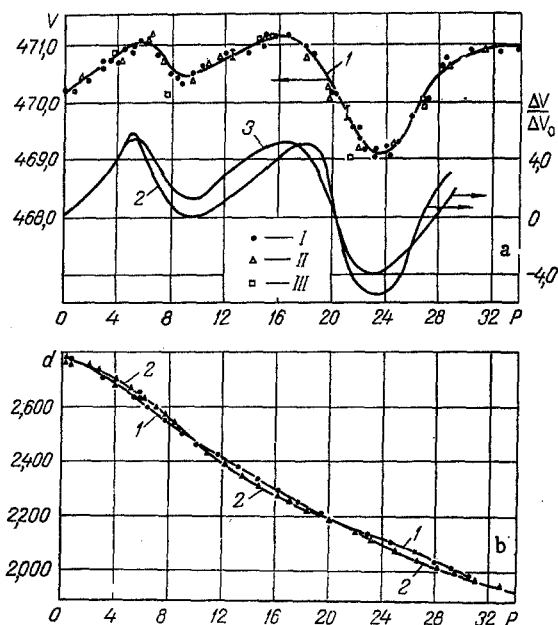


Fig. 1. Dependences: a) volume of unit cell (1) of montmorillonite with adsorption of water (I), water and nitrobenzene (II), water and toluene (III), 2) relative changes in the volume of the unit cell of montmorillonite, obtained from experimental curves and based on the calculation (3) with adsorption of water and nitrobenzene, and b) densities of montmorillonite (Crimean kill), measured in nitrobenzene, as a function of the adsorbed water P(%) for different values of the ratio m/V: 1) m/V = 0.0131 g/cm<sup>3</sup>; 2) 0.133. V, Å<sup>3</sup>; d, g/cm<sup>3</sup>. P at 1% equals 0.56 μmole/g.

It should be noted that the values of the parameters obtained in our experiments differ somewhat from those established for montmorillonite, due to the constant distortion of the reflection angles  $2\theta$ , caused by the presence of the beryllium barrier in front of the x-ray inlet. But, since we are interested in the changes in the parameters, the distortion itself is not of fundamental significance.

All of the experimental results are presented in Fig. 1. And, as is evident from the figure, both an expansion and compression of the volume of the unit cell of montmorillonite during hydration is observed, there is practically no additional contribution to deformation from adsorbed molecules of nitrobenzene, and toluene molecules give rise at different stages of hydration to additional expansion and compression of the volume of the unit cell. These phenomena are explained below.

Calculation of Deformations of the Crystal Lattice of Montmorillonite. The theory on which the calculation is based is presented in [2]. The formula for estimating the ratios of the changes in the volume of the crystal lattice for any intermediate stage of sorption to the change in the volume in the initial period of sorption, obtained based on the approach developed in [3], is written as follows:

$$\frac{\Delta V}{\Delta V_0} = \frac{\sum_{i=1}^h \frac{1}{r^3} \left( \frac{x^4 + y^4 + z^4}{r^4} - 0.6 \right) \left( \frac{R_j}{R_0} \right)^3}{\sum_{i=1}^n \frac{1}{r^3} \left( \frac{x^4 + y^4 + z^4}{r^4} - 0.6 \right) \left( \frac{R_j}{R_0} \right)^3}, \quad (1)$$

where  $i$  is the number of defects (adsorbate atoms), entering into a bond with different centers on the surface at different stages of sorption,  $R_0$  is the radius of one of the sorbing atoms;  $R_j$  are the radii of other sorbing atoms.

For subsequent calculations, we selected the sizes of the crystal based on determinations of the specific surface area and estimates of the dimensions of microaggregates from

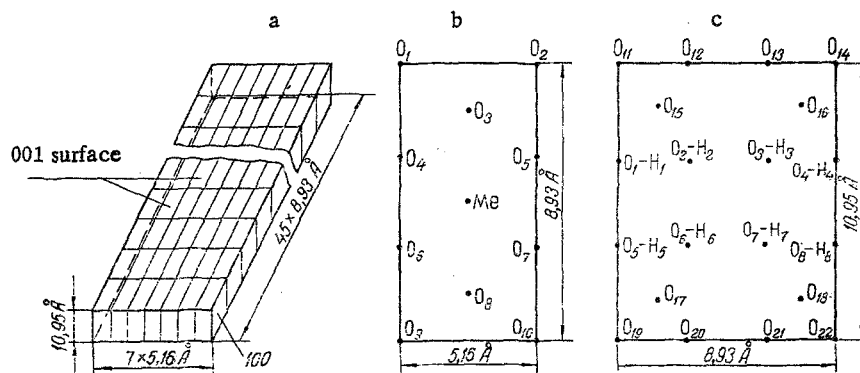


Fig. 2. Diagram of a crystal of montmorillonite: overall view of packet (a), distribution of surface centers on the 001 (b) and 100 (c) planes.

electronic microphotographs. The specific surface area in the first approximation was estimated to be 870 m<sup>2</sup>/g. According to [4], the following parameters of the unit spatial cell were used:  $a_0=5.16\text{\AA}$ ;  $b_0=8.93\text{\AA}$ ;  $c_0=10.95\text{\AA}$  (where  $c_0$  is the thickness of the packet).

The general parameters of the working crystal, consisting of 315 unit spatial cells, are presented in Fig. 2, and the coordinates of the center of gravity of this crystal are  $X_0=17.5\text{\AA}$ ;  $Y=202.5\text{\AA}$ ;  $Z_0=252\text{\AA}$ . The coordinates of atoms (surface centers, shown in Fig. 2) of all flat unit cells were determined and the coefficients

$$K = \left( \frac{x^4 + y^4 + z^4}{r^4} - 0.6 \right) \frac{1}{r^3}$$

were correspondingly determined for these atoms.

It should be noted that in the space between the packets of montmorillonite, the exchange cations are not situated on each flat unit cell (as shown in Fig. 2) and the surface area of the crystal, per exchange position, can be calculated as follows:

$$S_0 = \frac{S_{bs}}{\sum_{m=1}^t \frac{a}{n_0} A}, \quad (2)$$

where  $S_{bs}$  is the specific surface area of the basal surfaces of montmorillonite,  $\text{\AA}^2/\text{g}$ ;  $a$  is the number of sorbed cations with a single valence,  $\text{mg}\cdot\text{equivalents}/\text{g}$ ;  $n_0$  is the valence of the cation;  $A$  is Avogadro's number; and,  $t$  is the number of the types of ions with different valence. In our case,  $S_0=185\text{\AA}^2$ , i.e., there are four flat unit cells per exchange cation. Knowing the distribution of the active centers on the surface of the crystal, we can estimate the change  $\Delta V/\Delta V_0$  in the course of sorption of water and of organic compounds ( $\Delta V_0$  is the change in the volume of the unit cell accompanying hydration from 0 to 1%). We shall examine in detail the effect of water and nitrobenzene on deformation.

The scheme of the calculation is presented in [2] and reduces to successive summation of the contributions (coefficients  $K (R_J/R_0)^3$ ) of adsorbed atoms. The complete calculation (usually presented in tabular form) is quite cumbersome, so that in this paper only the finite results are shown in Fig. 1. We assumed in the calculation that prior to the onset of sorption of water the nitrobenzene molecules are distributed on all surfaces of the crystal lattice.

Following [5], Fig. 3a shows the  $\pi$  electronic distribution in the ground state of  $\text{C}_6\text{H}_5\text{NO}_2$  (in units of  $e/1000$ ). The nitro-group in this molecule is a typical acceptor of electrons.

Therefore, adsorption of nitrobenzene is due to both transfer of charge on the surface of the crystal lattice (in this case, the oxygen atoms or the carbon atom situated next to the  $\text{NO}_2$  group are donors of electrons in the molecule, and the OH groups and the exchange cations are acceptors in the crystal lattice), and the pulling away of electrons from the solid phase (in this case, the nitrogen atom and the remaining carbon atoms in the molecule will be electron acceptors, and the oxygen atoms will be the donor in the crystal lattice).

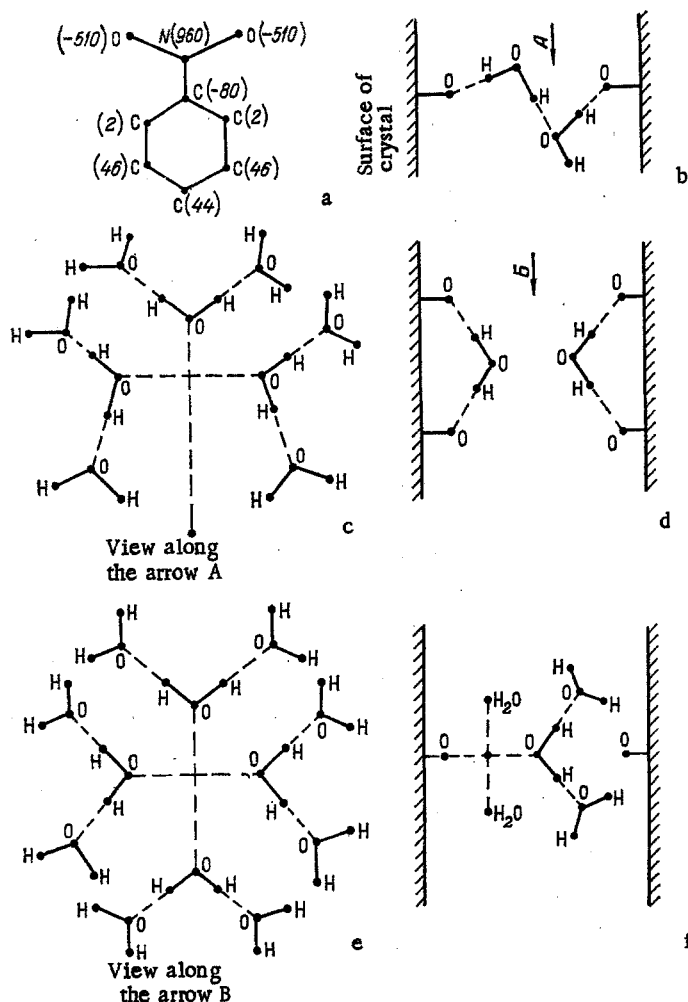


Fig. 3. Diagram of adsorption of water molecules on montmorillonite.

At the stage of sorption of nitrobenzene on the dehydrated surface on 100 planes, we take the centers of adsorption to be the hydroxyl groups  $O_7-H_7$  ( $O_7'-H_7'$ ) and the oxygen groups  $O_{18}(O_{18}')$ , placing on them diametrically opposite carbon atoms of the benzene ring and placing the exchange cations and oxygen groups  $O_7(O_7')$  on the 001 planes.

The sum of the coefficients  $K (R_1/R_0)^3$  and, therefore, the initial deformation  $\Delta V_1$  of the dehydrated spatial cell are usually comparatively small. This result is confirmed by experimental measurements (see Fig. 1).

It is natural to assume that the initial period of sorption or termination of the process of desorption of water molecules are related to their presence on sections of the cleavage plane of the mineral, represented primarily by the 100 planes.

The water molecules are rigidly attached to the surface, forming unsymmetrical complexes. In addition, the OH groups, exchange cations, and uncompensated charges  $Si^{+2}$  or  $Al^{+3}$  can be active centers.

The amount of water, coordinating near the exchange cations, situated on 100 planes, does not exceed 0.13-0.15%, and the amount of water bound tightly on Si and Al atoms does not exceed 0.05-0.07%.

Thus, the main contribution to deformation in the final period of desorption for moisture contents ranging from 0 to 5% comes from water molecules adsorbed on OH groups and oxygen atoms. The configuration of these centers is presented in Fig. 2. And, as is evident from Fig. 1, this deformation gives rise to an expansion of the crystal. The same conclusion is arrived at in [6], where it is indicated that the largest deformation of the  $SiO_mH_n$  tetrahedra in  $SiO_2$  oxides is observed on sections of the surface with the highest concentration of OH groups.

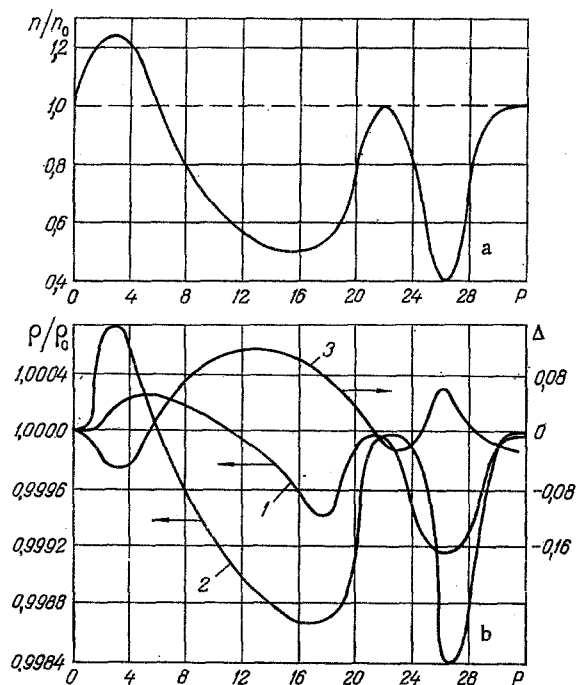


Fig. 4. Change in the structural characteristics of the dispersed medium. The dependences on  $P$ : a) relative number of adsorbed molecules of nitrobenzene on the crystal lattice of the natural form of montmorillonite; b) density of the dispersed medium (nitrobenzene) in the montmorillonite-adsorbed water-liquid system according to the following data: 1) experiment; 2) estimates of the deformations of the crystal lattice of montmorillonite; 3) relative deviations of the computed values from the experimental values.  $\Delta$ , %.

As already noted, with complete dehydration of montmorillonite, nitrobenzene molecules are oriented so that the plane of their benzene rings is oriented parallel to the 100 faces, but an analogous position is maintained also with adsorption of the first groups of water molecules in amounts up to 1%, i.e., with this degree of hydration, neither the orientation nor the amount of nitrobenzene molecules on the 100 faces changes.

The existence of such adsorbed groups of  $H_2O$  (we denote their mass by  $P_0$ ) is of fundamental significance for calculating the density of bound water.

In the course of further hydration (for  $P > P_0$ ) on 100 faces, the mechanism of adsorption of nitrobenzene molecules remains unchanged, i.e., both electron donors and electron acceptors of  $C_6H_5NO_2$  participate simultaneously in the intermolecular interaction, but deposition of the benzene ring in some molecules relative to the 100 faces remains vertical. For this reason, as the accessibility of active centers increases, the number of adsorbed molecules at first increases, and then gradually is displaced (Fig. 4) and by the time of complete hydration of 100 faces the nitrobenzene molecules are distributed on the adsorbed water molecules.

Subsequent sorption is related to the formation of complexes consisting of water and nitrobenzene molecules in the interpacket space of montmorillonite. Compression of the crystal lattice in the interval 5-9 and 17-23%, as well as expansion in the interval 9-17 and 23-32% of the moisture content of the mineral (see Fig. 1), is observed. This nature of the deformation determines the existence of two stages of filling of active centers.

Compression of the lattice arises with the transfer of charge on the adsorbed molecule with the formation of hydrogen, donor-acceptor bonds between oxygen atoms on the crystal surface and water and nitrobenzene molecules. The expansion of the lattice occurs with the transfer of charge on the crystal due to interaction of water and nitrobenzene molecules with the exchange cations.

It should be noted that starting from the experimentally observed change in the volume of the spatial unit cell in the course of sorption or desorption, it is possible to establish the order of filling of the surface centers of the basal surfaces. It turns out that at the first stage of sorption of the crystal lattice (in the interval 5-9%) only part of the oxygen atoms enters into an adsorption interaction with water molecules, and then the stage of adsorption around exchange cations appears, i.e., the oxygen atoms within a unit cell of the 001 plane are energetically nonequivalent. In calculations, to estimate the deformations in the course of expansion of the crystalline lattice, we used the results of IR spectroscopic investigations, which establish the existence of symmetrical complexes consisting of adsorbed water molecules, when an octahedral environment consisting of associates, including groups of three water molecules, is formed near exchange cations [7].

Let us follow the change in the sorption of the nitrobenzene molecules on 001 surfaces. For this, we shall make use of the results of experimental measurements of the density of montmorillonite as a function of the moisture content presented in Fig. 1. The technique and procedure of the measurement are described in [8, 9]. As is evident from Fig. 1, there is a distinct separation of the density for arbitrary concentration of adsorbed molecules of water depending on the mass of the adsorbent or the ratio  $m/V$  ( $m$  is the mass of the dehydrated adsorbent,  $V$  is the volume of the dispersed system). At the same time it turned out that the ratio  $m/V = 0.013 \text{ g/cm}^3$  (the mass of the powder is 1 g, curve 2 in Fig. 1b) is "critical" for such a separation, i.e., for small values of  $m/V$  there are no changes in the density of the hydrated sample for any concentration of water molecules.

The relative change in the density of the dispersed medium (nitrobenzene) was calculated from the formula

$$\frac{\rho}{\rho_0} = \frac{\left(d - \frac{m}{V}\right) d'_0}{\left(d'_0 - \frac{m}{V}\right) d}, \quad (3)$$

where  $\rho/\rho_0$  is the relative change in the density of the dispersed medium;  $d'_0$  is the density of the hydrated specimen, while  $\rho_0$  is the density of the liquid, corresponding to the mass of the solid phase equal to the critical value;  $d$  is the density of the hydrated specimen, while  $\rho$  is the density of the liquid, corresponding to the mass of the solid phase greater than the critical value.

The results of the calculation are presented in Fig. 4. Three regions can be identified on the curves of the changes in the density of the dispersed system. The first region, for 1-11% moisture content, corresponds to a high concentration of nitrobenzene molecules, i.e., their sorption on the 100 planes; the second region occurs in the interval 11-21%; and, the third region occurs in the interval 21-32% - low concentration of molecules of the dispersed medium, i.e., their sorption on 001 planes.

The nature of the dependences of the changes in the density of the dispersed medium and the deformation of the crystal lattice made it possible to understand the mechanism responsible for this sorption.

With complete dehydration of the surface the nitrobenzene molecules fill all possible vacancies on the 001 planes. Adsorption occurs on the exchange cations and oxygen atoms. As the hydration of the interpacket space increases, i.e., as water molecules are sorbed on oxygen atoms in the scheme illustrated in Fig. 3b and near exchange cations in the scheme illustrated in Fig. 3c (view along the arrow A in Fig. 3), nitrobenzene molecules are displaced until (approximately up to 18-19% moisture content) a sharp jump appears in the increase of the interpacket distance. This jump corresponds to the second stage of adsorption of water molecules on oxygen atoms (Fig. 3d).

As the interplanar distance increases, in the range of 18-22% moisture content, the nitrobenzene molecules penetrate into the interpacket space, entering into an interaction with the exchange cations and oxygen atoms of the adsorbed water molecules.

The next stage in the displacement of nitrobenzene out of the interpacket space in the range of 22-26% moisture content is determined by the second stage of adsorption of water molecules on exchange cations according to the scheme in Fig. 3e (view along the arrow B). The process of deformation of the crystal lattice terminates at this stage of its expansion,

and in the region of 26-32% moisture content the water molecules form complexes in a direction perpendicular to the 001 planes, detaching the exchange cation from one of the planes of the interpacket space, and the next jump in the increase of the interplanar distance is created (Fig. 3f). Nitrobenzene molecules again penetrate into the interpacket space, entering into an interaction with exchange cations and oxygen atoms in the crystal lattice. And, in this manner, the exchange cations appear in the octahedral environment only consisting of water and nitrobenzene molecules.

Figure 1 shows several experimental values of the volumes of the unit cell of montmorillonite, obtained with adsorption of water and toluene. These measurements were performed in order to show how the volume of the cell changes with adsorption of different molecules. As is evident from the figure, the experimental points near 6, 15, 18, and 27% moisture content are found on the curve and, as follows from an analysis of the deformation of the cell (with adsorption of water and nitrobenzene), for these values of the moisture content the toluene molecules are either situated on the adsorbed water molecules in the 100 planes with 6% moisture content, or are displaced by water molecules out of the interpacket space with 15, 18, and 27% moisture content. The experimental points near 8 and 20% fall below the curve, but in these cases the toluene molecules remain in the interpacket space, they are adsorbed only on oxygen atoms and, therefore, make an additional contribution to the compression of the lattice.

Figure 1a also shows the values of  $\Delta V/\Delta V_0$ , taken from the experimental curve 1 and obtained based on a calculation. The close coincidence between the experimental and theoretical quantities gives some reassurance that the idea and scheme of the calculation were chosen correctly. Here we should point out that an ideal crystal surface was examined in the calculations, i.e., only the active centers, represented by the hydroxyl groups, oxygen atoms, and exchange cations, were taken into account and sections of the cleavage surface, when uncompensated Si and Al atoms protrude outside were not taken into account. More detailed investigations of the topography of the surface of the crystal lattice, performed by other methods, would permit performing the calculations with greater reliability and more accurately. But one more result follows from the experimental data obtained and the analysis performed.

Figure 4 shows the change in the relative number of nitrobenzene molecules adsorbed on montmorillonite as a function of the moisture content. This change is analogous in appearance (but not according to absolute magnitudes) to the change in the density of the dispersed medium. But it is completely obvious (and this was already noted) that the reason for the change in the density of the dispersed medium as a function of moisture content is the existence of a different concentration of molecules of this medium in surface layers. Knowing the change in the concentrations of molecules, it is possible to calculate the change in the density of the dispersed medium, referred to the entire volume of the dispersed system.

Figure 4 also shows the experimental and computed change in the relative density of nitrobenzene as a function of moisture content, as well as the relative deviation of the computed values from the experimental values.

The existence of this deviation can be explained by the circumstance that as the molecules are reoriented in the surface layers, the orientation (neutral position) of molecules far away from the surface of the adsorbate also changes, and the interplanar distance likewise changes when these molecules are introduced into or displaced from the interplanar interpacket space.

Thus the possibility (a new method) of studying the structure of dispersed media based on the determination of their densities and deformations of the crystal lattice under the action of adsorbed molecules arises.

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HEAT TRANSFER BY COMBINED RADIATION AND CONDUCTION IN CRYOGENIC  
VACUUM-MULTILAYER THERMAL INSULATION

S. B. Mil'man and M. G. Kaganer

UDC 536.3

We have obtained an approximate analytical solution of the problem of heat transfer by combined radiation and conduction in vacuum-multilayer thermal insulation. Results of the calculations are compared with calorimetric measurements.

Vacuum-multilayer thermal insulation (VMI) is one of the most effective materials for protecting cryogenic equipment against the influx of heat from the surroundings. It consists of a large number of shields which reflect infrared radiation and have a low emittance, placed in an evacuated insulating cavity of the article, and separated from one another by thermal-insulation spacers.

The difficulty in analyzing heat transfer in VMI results largely from the strong interaction of radiation and conduction. This interaction, whose existence was confirmed experimentally in [1], is due to the absorption of radiation by the spacing material.

Most papers devoted to this problem treated combined heat transfer in media such as gases, liquids, glass, etc., which absorb but do not scatter radiation [2, 3]. Combined heat transfer in media which both absorb and scatter radiation has received relatively little attention. Mainly numerical solutions of special problems were obtained by computer, and were not compared with experiments [4-6].

In the present paper we have obtained an approximate analytical solution of the problem of heat transfer by combined radiation and conduction in a slab of material which absorbs, emits, and scatters radiation isotropically, and is bounded by two opaque surfaces at temperatures T<sub>1</sub> and T<sub>2</sub>. It is assumed that the properties of the medium do not depend on the wavelength of the radiation.

In this case heat transfer by combined radiation and conduction is described by a system of two linear integrodifferential equations:

$$\mu \frac{dI(\mu, \tau)}{d\tau} = -I(\mu, \tau) + \frac{\omega}{2} \int_{-1}^{+1} I(\mu', \tau) d\mu' + (1 - \omega) \frac{\sigma_0 T^4}{\pi}, \quad (1)$$

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Scientific-Industrial Union "Geliimash," Moscow. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 46, No. 5, pp. 754-760, May, 1984. Original article submitted March 4, 1983.