ELECTRICAL PROPERTIES OF VARIOUS AGGREGATE STATES OF MATTER

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DOI: 10.5937/vojtehg65-11900
FIELD: Electrodynamics
ARTICLE TYPE: Original Scientific Paper
ARTICLE LANGUAGE: English

Summary:

Electrical properties of solids are caused by elastic polarization of clusters in case of metals while those of dielectrics result from the orientation polarization of induced and built-in electric dipoles. Orientation polarization stems from the interaction of free built-in electric dipoles with an external electric field. A physical model of the dielectric permittivity formation of metals, electrolytes, plasma, ferrites, and ferroelectrics has been developed. Theoretical calculations of the dielectric permittivity of a number of ferrites and barium titanate have been performed in particular.

Key words: *permittivity, aggregate states, metals, plasma, electrolytes, ferroelectrics.*

Introduction

The dielectric permittivity of a medium is introduced to describe the behavior of various substances in electric fields. There are relative dielectric permittivity and absolute dielectric permittivity considered in the SI system. The resulting permittivity of a medium presents the product of the absolute permittivity of vacuum and the relative permittivity of the medium. The notion of the absolute dielectric permittivity of classical vacuum ($\varepsilon_0 = 1/4\pi 9\cdot 10^9$ *F/m*) was introduced by Arnold Sommerfeld (Sommerfeld, 1952). The relative permittivity of vacuum is equal to 1 while the relative permittivity of a medium is considered relative to vacuum. Under the effect of an external electric field, a displacement of internal electric charges occurs which is characterized by the electric displacement vector:

$$\vec{D} = \varepsilon_0 \vec{E}_э + \vec{P} = \varepsilon_r \varepsilon_0 \vec{E}_э . \tag{1}$$

Here, $E_э$ is the external field intensity and P is the electric polarization vector of the medium. Since the electric polarization vector of a medium depends linearly on the external applied field for the majority of substances ($P = \kappa E_э$, where κ is dielectric susceptibility), then the relative permittivity of a medium is as follows:

$$\varepsilon_r = 1 + \kappa / \varepsilon_0 . \tag{2}$$

Therefore, in order to determine the dielectric permittivity of a medium, it is essential to know dielectric susceptibility which determines the polarization properties of the medium. Elastic polarization and orientation polarization are distinguished. Elastic polarization is caused by: 1 – deformation of electron shells of atoms, molecules, so called electronic polarization; 2 – atom polarization stemming from the shifting of dissimilar atoms inside a molecule; 3 – ionic polarization stemming from the shifting of positive and negative ions relative to each other, and 4 – elastic dipolar polarization resulting from dipoles turning relative to their position of the equilibrium inside the substance. The orientation polarization of a medium is associated with built-in electric dipole moments positioning along the field direction inside the substance. For some substances, elastic polarization and orientation polarization appear together.

General definitions are clear and intelligible. However, when an external electric field is applied to a substance, appropriate processes causing polarization remain unclear. In actual practice, experimental data are used. This is because of the fact that no physical model which can adequately reflect all possible processes of medium polarization is available now. The reason is that there was no clear understanding of various aggregate states and, what is even more important, no physical model of built-in electric dipole moments in various atomic structures and molecular structures has been developed yet. When considering various aggregate states, no cluster formations, completely substantiated in some works (Gretchikhin, 2004), (Gretchikhin, 2008a), were taken into account. Charles Coulson (Coulson, 1961) who drew attention to the formation of built-in electric dipole moments in atomic structures of rather large values, showed that the intra-atomic electron interaction *p-s, d-s, f-s* results in a noticeable deformation of the *s*-state and, correspondingly, in a formation of a built-in electric dipole of considerable value. A more strict two-particle quantum theory of *p-s, d-s, and f-s*-interactions was developed in the work by Leonid Gretchikhin (Gretchikhin, 2008a) and was presented in great detail in the work of Leonid Gretchikhin, Juliya Shmermbekk (Gretchikhin, Shmermbekk, 2010). Such quite a general definition of the dielectric permittivity of a medium sets the following goal: to develop a physical model of the formation of the dielectric permittivity of a medium with taking into account the cluster structure of various aggregate states of the matter, the appearance of built-in electric dipole moments in the process of hybridization of wave functions resulting from the interactions of intra-atomic electrons and induced electric moments in molecular structures caused by the exchange of valence electrons. The goal can be reached through solving the following problems:

- to find out the way the elastic polarization of a medium takes place with taking into account the cluster structure of substances;
- to determine the way elastic polarization occurs in metals;
- to ascertain how the electric dipole behaves under the action of external electric fields;
- to provide an explanation of ferroelectricity formation.

Let us consider, one after the other, these problems.

Polarization of Electron Shells

On the basis of the cluster structure of various aggregate states of matter, let us consider in what way the external electric field weakens inside a substance. Polarization of electron shells of individual atoms, molecules, and clusters takes place under the action of the external electric field. The strength of the interaction between the external electric field and a valence electron of every particle must be compensated by the change in internal forces of the valence electron bond with the particle effective charge. Then (Gretchikhin, 2008b):

$$eE_{\text{э}} = \frac{Z^{*}e^{2}}{4\pi\,\varepsilon_{0}r^{2}} - \frac{Z^{*}e^{2}}{4\pi\,\varepsilon_{0}(r+\Delta r W_{\text{з}})^{2}}, \qquad (3)$$

Here Z^* is the effective charge of the particle under consideration; *e* is the electron charge; *r* is the particle effective radius, and W_3 is the probability that the valence electron, after shifting for the value of Δr, will fill this energy state which was previously vacant.

Simple transformations with neglected small values of the second order from equation (3) yield the induced electric dipole moment as follows:

$$p_{э} = \frac{er}{W_{з}} \frac{E_{э}}{E_{вн}} . \tag{4}$$

where $E_{вн.}$ Is the electric field intensity produced by the positive charge of the particle under consideration.

The product of equation (4) and the particles density ($n = 1/(2r)^3$) gives a vector of electric polarization

$$P = \frac{e}{8r^2 W_{з}} \frac{E_{э}}{E_{вн}} . \tag{5}$$

The probability that the energy level at the distance Δr will be occupied by the displaced charge depends on the structure of the particle under investigation and the nature of medium polarization. The nature of medium polarization is determined by the mechanism of external electric field compensation owing to the separation of bound charges.

In the nature, there are substances with atoms and molecules polarized, under the action of the external electric field as a result of the displacement of valence electrons relative to the nucleus (elastic polarization) as well as substances with atoms and molecules possessing built-in electric dipole moments which are positioned, under the action of the external electric field, along the field direction (orientation polarization). Some substances feature both appreciable polarizations: the elastic one and the orientation one. The appropriate specific type of polarization must be considered for every substance. Elastic polarization is typical for gases and metals while orientation polarization is inherent mostly in dielectrics.

Polarization of Atoms and Molecules in the Gaseous State

A general approach to polarization of atoms and molecules in the gaseous state was considered in some works (Skanavi, 1949), (Feynman, et al, 1970), (Tamm, 1979). However, these works did not take into consideration the fact that individual atoms of various degrees of ionization possess their own built-in electric dipole moments neither additional induced electric dipole moments which arise when molecular structures are formed. Let us use an example of a quite common molecule of water to consider the formation of built-in and induced electric dipole moments.

The water molecule is formed step-by-step in the following sequence. First, a radical OH is formed, then the OH radical interacts with a hydrogen atom thus forming a water molecule. When the radical OH is formed, the oxygen atom, possessing affinity to electron, resides primarily in the state of a negative ion while the hydrogen atom resides as a positive ion. Under this assumption, the negative ion of hydrogen atom possesses a built-in electric dipole moment of $5.325 \cdot 10^{-30}$ C·m (Gretchikhin, Shmermbekk, 2010). Since the covalent bond between two interacting atoms is the most essential one, built-in electric dipole moments are directed against each other in the process of exchanging valence electrons. In the case of the OH radical, only the oxygen atom possesses a built-in electric dipole moment while the excess negative charge formed between interacting atoms produces additional induced built-in electric dipole moments for the atoms of oxygen and hydrogen thus increasing the bonding energy of interacting atoms in a molecule.

A reference book (Babichev, et al, 1991) specifies the nucleus-nucleus distance in the OH radical to be equal to 9706 Å. At this nucleus-nucleus distance, the covalent bond is positive which indicates that such a nucleus-nucleus distance is not equilibrium one for the OH molecule. That is why the nucleus-nucleus distance between the atoms of oxygen and hydrogen was considered as a variational parameter and was determined in accordance with the value of dissociation energy. The resulting nucleus-nucleus distance for water molecule is 1.126 Å, with its value exceeding the tabulated one by 16%. At this nucleus-nucleus distance, the dissociation energy is produced owing to summing the energies caused by the following bonds: 1) covalent bond 2.000 eV; 2) ionic bond 1.261 eV, and 3) previously unknown bond of a negative electron cloud formed when the exchanging valence electrons of atoms interact with the positive molecule frame 1.143 eV. The resulting value is 4.404 while the experimental value of dissociation energy is equal to 4.4 eV (Radzig, Smirnov, 1985).

To ensure the agreement between the value of the electric dipole moment of the water molecule and the experimental value, it is necessary to assume that the negative charge cloud caused by valence electrons exchange is shifted towards the center of the hydrogen atom. Under the action of the built-in electric dipole moment of the oxygen atom and the gravity of the positive nucleus of the hydrogen atom, this cloud coincides with the center of the hydrogen atom with an effective charge of 0.0245·e (e is the electron charge). The formed negative charge cloud does not compensate entirely the charge of the hydrogen atom nucleus.

When performing measurements of the dielectric permittivity of water, an external electric field is applied to it. Under the action of the external electric field, the built-in electric dipole moments of interacting atoms are positioned strictly along the field direction thereby weakening the fields (orientation polarization). In order to find the resulting dielectric permittivity of water equal to $\varepsilon_r = 80$, it is necessary to assume that a displacement of the negative electron cloud, caused by exchanging interaction of valence electrons within the oxygen atom radius, takes place and that an additional displacement of the valence electron of the negative oxygen ion arises. Thus, with respect to water, formulas (3) and (5) are used to calculate electric dipole moments for the negative oxygen ion only with the internal field determined by the affinity energy of the oxygen atom to the electron. A similar situation appears for other atoms and molecules when it is necessary to consider three mechanisms of polarization: elastic polarization of the built-in electric dipole, polarization with covalent bond formation, and elastic polarization of electron shells of interacting atoms. It turns out that the polarization of atomic gases and even more so the polarization of molecular gases presents a rather complicated process. Let us consider the way metals and dielectrics are polarized.

Metals

In metals, the electrons within the valence band obey Fermi-Dirac quantum statistics. When an external electric field is applied, the valence electrons are displaced only at the upper edge of the valence band i.e. at the Fermi level. The probability of the free state formation vicinity of the Fermi level is equal to:

$$W_{своб.} = 1 - \frac{1}{e^{\frac{E-\varepsilon_F}{k_Б T}} + 1}. \tag{6}$$

Here $E = \varepsilon_F + \Delta E$ while ΔE is the energy of the binary inter cluster interaction ($\Delta E = \theta_{i,кл.}/2$ and $\theta_{i,кл.}$ is the cluster ionization energy) and ε_F is the Fermi level.

For most metals under normal conditions, $\Delta E \gg k_Б T$. Hence,

$$W_{своб.} = 1 - e^{-\frac{\Delta E}{k_Б T}}, \tag{7}$$

And the probability that the valence electron of the cluster will fill in the state is:

$$W_з = 1 - W_{своб.} = \exp\left(-\frac{\Delta E}{k_Б T}\right). \tag{8}$$

So, for most metals, the vector of electric polarizations is:

$$P_{Э} = \frac{e^2}{16 r_{кл.} \Delta E} e^{\frac{\Delta E}{k_Б T}} E_э , \tag{9}$$

while it follows from the general definition of the vector of electric displacement that relative permittivity is equal to:

$$\varepsilon_r = 1 + \frac{e^2}{16 r_{кл.} \varepsilon_0 \Delta E} e^{\frac{\Delta E}{k_Б T}} . \tag{10}$$

Table 1 shows specific calculations of relative permittivity for a number of metals.

Table 1 – Ionization energy of cluster formations in eV and relative permittivity for various metals

Таблица 1 – Энергия ионизации кластерных образований в эВ и относительная диэлектрическая проницаемость для разных металлов

Табела 1 – Јонизациона енергија формирања кластера у eV и релативна диелектрична пермитивност за различите метале

Parameter	Substance					
	Na	*Al*	*α-Fe*	*Cu*	*W*	*Ti*
$\Theta_{кл.}$, eV	0.714	1.56	1.46	1.63	4.64	1.53
$\varepsilon_r \cdot 10^{14}$	$2.24 \cdot 10^{-7}$	1.05·	0/185·	4.64	$1 \cdot 10^{-14}$	0.397
$\rho \cdot 10^{-8}$. $\Omega \cdot m$	4.28	2.50	8.6	1.55	4.89	42
$\varepsilon_r \cdot 10^{14}$	1.746	5.117	0.432	13.3	1.337	0.0181

If we consider electric current as the propagation of electromagnetic waves, by Nikola Tesla’s definition, and take into account the experimental data of resistivity (Table 1), we obtain the relative dielectric constant (Table 1) which is significantly different from the values obtained from the electron theory of metals. Additionally, in accordance with the electron theory, dielectric permittivity increases with temperature, and decreases proportionally to the propagation of electromagnetic waves. In the first case, the obtained permittivity values do not correspond to the experimental results while in the second case, they are verified by the experimental results.

It turns out that permittivity presents a huge value for metals with the exception of tungsten.

Plasma

Under the effect of the external electric field applied to plasma, a displacement of free electrons within the field of positive ions takes place, i.e. causes plasma polarization. Spontaneous polarization of plasma occurs within the Debye length. A value of the Debye length is determined from the energy conservation law when the work of charges separation is compensated by the energy of thermal motion. Hence (Gretchikhin, 2008a)

$$h_D = \left(\frac{\varepsilon_0 k_{\text{Б}} T}{e^2 n_e} \right)^{1/2}, \tag{11}$$

where n_e – is the concentration of ions in plasma. The Debye length presents the radius of plasma shielding.

When the external electric field is superimposed on the system of the bonded electron and the positive ion, the force of $F_e = eE$ will act on the electron while the force of $F_i = eE$ will act on the ion. The action of these forces will cause plasma polarization. An induced electric moment proportional to the external electric field intensity will occur for each electron-ion pair, i.e.,

$$p_{\text{э}} = \alpha E = e(d - h_D), \tag{12}$$

where α is the factor of plasma polarizability, d is the resulting displacement of charges inside plasma.

Then, the electric polarization vector will be as follows: $P_{\text{Э}} = n_e p_{\text{э}} = e n_e (d - h_D) = \kappa E$.

Based on (2), the following formula for dielectric permittivity can be derived:

$$\varepsilon_r = 1 + \frac{\kappa}{\varepsilon_0} = 1 + \frac{e n_e (d - h_D)}{\varepsilon_0 E_{\text{э}}}. \tag{13}$$

In the case of equilibrium plasma, the concentration of electrons is determined by the Saha equation. Ehen applied to weak single ionization, the Saha equation becomes:

$$\frac{n_e^2}{n_0} = \frac{\left(2\pi m_e k_{\text{Б}} T\right)^{3/2}}{h^3} \exp\left(-\frac{e\Theta_i}{k_{\text{Б}} T} \right). \tag{14}$$

Here h is Planck's constant; Θ_i is the effective potential of ionization of plasma particles.

The plasma of the positive column of the arc discharge can be considered as an equilibrium one at a temperature of 5000 *K*. Then, for the arc discharge in argon under atmospheric pressure in the positive column, $n_e = 4.04 \cdot 10^{17}$ m^{-3}. For the distance between the electrodes equal to 1 *cm* and the voltage drop across the positive column equal to 1, V: $\varepsilon_r = 7.3 \cdot 10^7$. For glow discharge in argon, $n_e = 1 \cdot 10^{18}$ m^{-3} and for the distance between the electrodes equal to 10 *cm* and a pressure of 0.133, *Pa:* $\varepsilon_r = 1.6 \cdot 10^9$.

Permittivity turns out to be a rather substantial value. Therefore, such a medium is electroconductive. At that, the higher plasma density is, the lower voltage drop is across the positive column and, therefore, permittivity rises. Plasma polarization covers the entire discharge gap and so it seems that electrical current is accompanied by the movement of electric charges. As a matter of fact, the energy within discharge is carried not by charges but by the electromagnetic field produced by an external source of electromagnetic force. The charges form the medium which serves as a waveguide for electromagnetic waves.

Electrolytes

In electrolytes, in the same manner as in plasma, spontaneous polarization occurs within the Debye length. The difference is that the formation of free electric charges is caused not by ionization but due to dissociation of complex molecules into cations and anions. The dissociation energy of complex molecules does not exceed 10 *eV*. If any electrolyte is diluted with water, then dissociation energy decreases by the value of dielectric permittivity approximately equal to 80 for water. The dissociation energy of water is equal to 5.12 *eV*.

To prepare electrolytes, appropriate alkalis or salts with dissociation energy lower than that of water are chosen, i.e. 2…3 *eV*. In that case, a spontaneous dissociation of complex molecules in water takes place at ambient temperature. As a result of the process, free cations and anions occur in the electrolyte. The concentration of introduced alkalis or salts does not exceed 1 wt%. Hence, the concentration of cations and anions will amount to ~ $3.3\cdot10^{24}$ *м*$^{-3}$. After having connected the external source of electromotive force to a pair of electrodes with a 1 cm gap, we will obtain dielectric permittivity equal to $6\cdot10^{14}$ with the value corresponding to the dielectric permittivity of pure metals. Electromagnetic waves propagate through such a medium like through a waveguide.

Orientation Polarization of Dielectrics

Orientation polarization is mainly characteristic for magnetic dielectrics (ferrites) and dielectrics of all kinds. Polarization properties of dielectrics within an external electric field are determined, in the long run, by the electric properties of individual atoms or molecules the dielectrics consist of. However, the polarization properties of some crystalline dielectrics are determined mainly by built-in electric dipole moments in individual atoms (molecules) and their positions within the crystal. There are two kinds of possible electric moments: both naturally built-in electric moments and artificially induced ones caused by external effects through increased pressure or applied electric fields. Crystals of the first type are called ferroelectrics while crystals of the second type are called piezoelectrics and piroelectrics.

Magnetic dielectrics present artificial heterogeneous ferroimagnetics consisting of ferromagnetic particles bound together into a single conglomerate thus forming a continuous dielectric phase. Such a class of oxides is formed by ferrites. Ferrites represent ionic crystals with the chemical composition $MeFe_2O_4$, where *Me* means one of metal ions. The best known composition of this group is magnetite Fe_3O_4. Atoms with a large built-in electric dipole moment are used as a metal. When sintering a mixture of metal and magnetite, the following reaction occurs: $Me + Fe_2O_4 \leftrightarrow MeO\cdot\cdot Fe_2\,O_3$; molecules of the metal oxide are formed with a further transformation of metal oxide molecules into haematite molecules which feature the strongest bond. This way, ferrites of various kinds are produced.

Orientation polarization of dielectrics for bound electric dipoles is determined by the interaction of the electric dipole with the external electric field. Fig. 1 shows this situation in a simplified way.

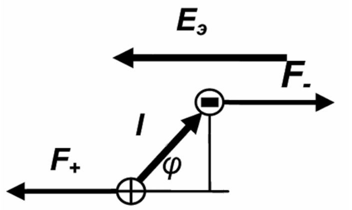

Figure 1 – Interaction of external field $E_э$ with electric dipole
Рис. 1 – Взаимодействие внешнего поля $E_э$ с электрическим диполем
Слика 1 – Интеракција спољашњег поља $E_э$ с електричним диполом

The interaction energy of the electric dipole with the external field is equal to product:

$$U = -p_э E_э \cos\theta \tag{15}$$

For relative dielectric permittivity, we obtain:

$$\varepsilon_r = 1 + \frac{n_0 p_э^2}{3\varepsilon_0 k_Б T}. \tag{16}$$

As an example, let us consider the cluster lattice structure of haematite reinforced with various metal oxides. Table 2 shows the dipole electric moments of free metal oxide molecules introduced into the cluster lattice structure of haematite while their concentration in the unit of volume is $2/(24\, r^3_{кл.})$. ($r_{кл.}$ is the radius of the haematite molecule (Fe_2O_3)).

Table 2 – Electric dipole moments of biatomic molecules of metal oxides and their dielectric permittivities in ferrites
Таблица 2 – Дипольный электрический момент двухатомных молекул оксидов металла и их диэлектрическая проницаемость в ферритах
Табела 2 – Моменти електричног дипола двоатомских молекула металних оксида и њихове диелектричне пермитивности у феритима

Parameters	Molecules			
	MgO	MnO	BaO	FeO
r_e, Å	1.75	1.77	1.94	1.63
$p_э$,$\cdot 10^{30}$ C·m	25.25	32.24	26.12/26.66	24.22
ε_r	21.13	33.83	1	34.52

Table 2 shows the values of ε_r of ferrite spinels reinforced with MgO, MnO, and FeO. The experimental data were obtained for $MnOFe_2O_3$ $\varepsilon_r = 9.66$ at a frequency of 4.55 GHz. A noticeable decrease in dielectric permittivity for the external field of the electromagnetic wave is caused by an oscillation lag of electric dipole moments of free oxide molecules inside haematite inter cluster cavities.

For ferrite garnet $BaOFe_2O_3$, permittivity tends to the unit since free molecules with built-in electric dipole moments are not available; such ferrite is typical dielectric.

Permittivity of ferroelectrics depends on temperature. Relative permittivity tends to the unit as temperature increases. The electric properties of Rochelle salt $NaKCuH_4O_6 \cdot 4H_2O$ were investigated for the first time in 1930-1934. One more important ferroelectric is barium titanate $BaTiO_3$.

Let us consider the properties of ferroelectrics using barium titanate as an example. This is a simpler system consisting of molecules BaO and TiO_2.

In the case of the bound electric dipole, the situation differs. Particle binding energy, with taking into account the interaction between the electric dipole and the external electric field (shown in Fig. 1 in a simplified manner), is represented in a general form as follows:

$$E_{св.} = E_{св.,0} - 3k_Б T + p_э E_э \cos\varphi . \tag{17}$$

Based on (17), the share of free particles which overcome thermal energy and energy of interaction with the external electric field for each binary bond will amount to:

$$\eta_{\text{св.}} = 1 - \int_{0}^{E_{\text{св.}}} f(E,T)dE \,, \tag{18}$$

where $f(E,T) = \frac{2}{\sqrt{\pi}}\left(k_{Б}T\right)^{-3/2} E^{1/2} \exp\left(-\frac{E_{\text{св.}}}{k_{Б}T}\right)$ i αs the Maxwell-Boltzmann energy distribution. Then, the total amount of all free particles of all particles possessing built-in electric dipole moments is determined as follows:

$$n_{\text{св.}} = \eta_{\text{св.}} n_{ч} \,. \tag{19}$$

At the temperature when all particles possessing built-in electric dipole moments become free, $E_{\text{св.},0} = 3k_{Б}T$. Hence

$$T_{K} = (E_{\text{св.},0} + p_{Э} \cdot E_{Э} \cos\varphi) / 3k_{Б} \,. \tag{20}$$

This temperature presents the Curie temperature; at this temperature, all particles which possess built-in electric dipole moments are free. Therefore, at temperatures exceeding the Curie temperature, some particles located along the applied external electric field will rotate by a spatial angle *dφ* in a spheroidal cone after having overcome the energy of thermal motion; the number of the particles is as follows:

$$dN = C\left[1 - \exp\left(-\frac{p_{э}E_{э}\cos\varphi}{k_{Б}T}\right)\right]\sin(\varphi)d\varphi \,. \tag{21}$$

Provided that $p_{э}E_{э}\cos\varphi / k_{Б}T \ll 1$, the integral of equation (21) with its limits in the spheroidal cone from zero to 2π is equal to 2*C*. Hence, the constant of integration *C* = *N/*2, i.e. we obtain the total number of the particles within the hemisphere. As a result of that, the vector of electric polarization with taking into account the exponential term in (21) expanded into series can be obtained through the integration of the following expression:

$$P_{Э} = \frac{n_{\text{св.}}}{2}\int p_{э}\cos\varphi \, \frac{p_{э}E_{э}\cos\varphi}{k_{Б}T} E_{э} d(\cos\varphi) \cdot \tag{22}$$

Here $n_{\text{св.}}$ is the number of electric dipole moments within a unit of volume. As a result of that and with taking into account (22), the following expressions for relative permittivity are obtained:

$$\varepsilon_{r} = 1 + \frac{\eta_{\text{св.}} n_{ч} p_{э}^{2}}{3\varepsilon_{0} k_{Б} T} \,. \tag{23}$$

The obtained expression takes into account both thermal energy and energy of interaction of electric dipole moments inside a solid.

In accordance with the minimum of interaction energy, barium titanate is formed by the clusters of titanium oxide thus creating a crystal lattice reinforced by barium oxide molecules as shown in Fig. 2. Barium oxide molecules reinforce the inter'cluster crystal lattice of titanium oxide; in doing so, they neutralize the electric dipole moment of each titanium oxide reducing it virtually down to zero. The built-in electric dipole moment of barium ion is equal to $19.16 \cdot 10^{-30}$ C·m while the built-in electric dipole moment of ttanium ion is equal to $20.0 \cdot 10^{-30}$ C·m. Built-in electric dipole moments of oxygen ion amount to $2.55 \cdot 10^{-30}$ C·m, therefore decreasing the built-in electric dipole moment of barium inside barium oxide molecules and, in contrast to this, they increase the electric dipole moment of the titanium ion inside titanium dioxide molecules. The concentrations of barium oxide molecules and titanium oxide clusters in the unit of volume are equal; therefore, the concentration of titanium oxide is equal to $n_{BaO} = 1/8\, r^{3}_{кл.}$ ($r_{кл}$ is the radius of the titanium oxide cluster).

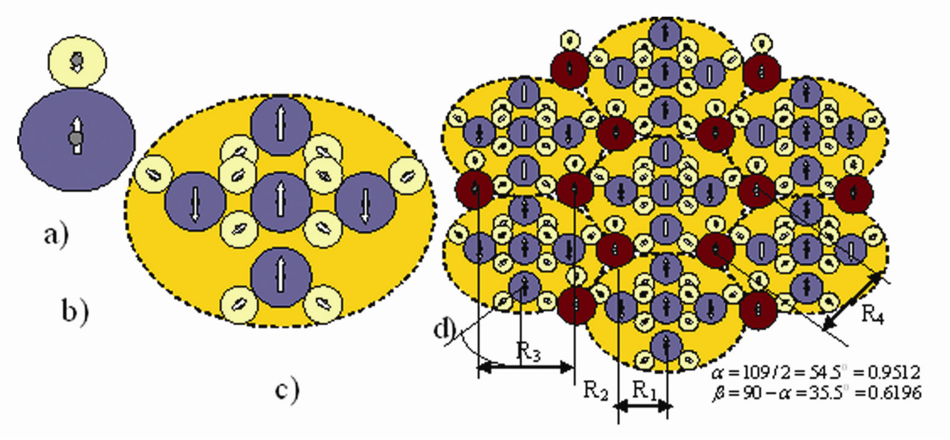

Fig. 2 – Formation of barium titanate ferroelectric : a) barium oxide molecule; b) titanium oxide molecule; c) main cluster of titanium oxide, and d) inter cluster structure of titanium oxide reinforced by barium oxide molecules

Рис. 2 – Последовательность образования сегнетоэлектрика титаната бария: а) молекула оксида бария; б) молекула оксида титана; ц) основной кластер оксида титана и д) межкластерная структура оксида титана, армированная молекулами оксида бария

Слика 2 – Формирање фероелектрика баријум титаната: а) молекул баријум оксида; б) молекул титанијум оксида; ц) главни кластер титанијум оксида и д) међукластерна структура титанијум оксида појачана молекулима баријум оксида

Taking into account the superposition principle of electric fields, the structure of the crystal lattice of barium titanate (Fig. 2d) as well as the fact that the bond energy of BaO molecules inside the titanate oxide inter-cluster lattice is determined mainly by the dipole-dipole interaction, we obtain the following value of the bond energy for barium oxide molecules in the lattice structure of titanium oxide clusters:

$E^{-}_{св.} = -0.301 - 0.071 - 0.033 = -0.405$ eV,

Therefore, *negative bond energy* is formed by three components while the *positive binary bond* is formed mainly by a single component $E^{+}_{св.} = 0.352$ eV. Each binary bond inside the TiO_2 crystal lattice is repeated twice. Therefore, the resulting bond energy of barium oxide molecules in the titanium oxide crystal lattice amounts to $E_{св.,0} \cong 0.106$ eV.

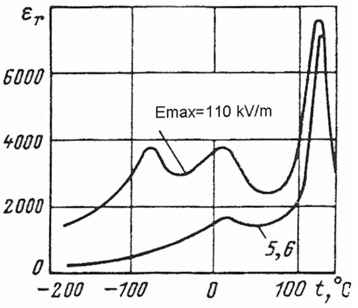

Fig. 3 – Dependence of barium titanate relative permittivity on temperature under applied electric field of 5.6 kV/m and 110 kV/m

Рис. 3 – Зависимость относительной диэлектрической проницаемости титаната бария от температуры при внешней напряженности электрического поля 5,6 и 110 кВ/м

Слика 3 – Зависност релативне пермитивности баријум титаната од температуре примењеног електричног поља од 5,6 kV/m и 110 kV/m

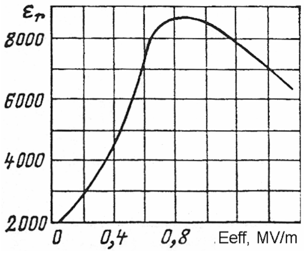

Fig. 4 – Dependence of barium titanate relative permittivity on external electric field at normal temperature

Рис. 4 – Зависимость относительной диэлектрической проницаемости титаната бария от внешней напряженности электрического поля при нормальной температуре

Слика 4 – Зависност релативне пермитивности баријум титаната од спољашњег електричног поља на нормалној температури

Based on (17), the Curie temperature when bound electric dipole moments of BaO molecules become completely free amounts to 137 °C while the experimental value is equal to 125 °C shown in Fig. 3 (Babichev, et al, 1991). The difference between the calculated value and the experimental one amounts to ~ 3% which proves that the model of barium titanate crystal is correct.

Fig. 3 shows the experimental dependence of barium titanate relative permittivity on the temperature under various values of the applied electric field; Fig. 4 shows the experimental dependence of barium titanate relative permittivity on the applied electric field at room temperature (Babichev, et al, 1991).

As the bond energy of titanium oxide molecules is determined by three components, there will be two intermediate Curie temperature values in addition to the main Curie temperature. The bond energy equal to 0.033 eV corresponds to 145 °C while the experimental value corresponds to ~ 120 °K and occurs under a relatively high external electric field intensity. Under a low external electric field intensity, this component of the titanium oxide bond energy is annulled completely. The second component of the bond energy of barium oxide in the inter-luster gaps of titanium oxide 0.071 eV determines the temperature of ~ 1.5 °C which is close enough to the second maximum (see Fig. 3) which occurs both under high and low external electric field intensity. The values of relative permittivity at the third maximum at a temperature of ~ 125 °C differ from each other slightly which proves that the process of electric polarization of barium oxide comes into play.

Fig. 4 shows the dependence of barium titanate relative permittivity on the external electric field at a constant temperature. At first, ε_r increases nearly exponentially under the applied electric field with an intensity of ~ 0.8 MV/m, then reaches its maximum and then decreases linearly. What does it suggest? It may be assumed that the electric dipole moment of BaO under the effect of the applied electric field of high intensity is determined, mainly, by its elastic polarization with its maximum value of $p_{Э,\max.} \approx e \cdot r_{кл.}$ Then, (23) is transformed as follows:

$$\varepsilon_r = 1 + \frac{e^2}{24\varepsilon_0 k_Б T}\frac{1}{r_l}, \qquad (24)$$

where r_l is the distance determined by crystal deformation along the field; the distance increases linearly under the effect of the applied external electric field.

It turns out that after having passed the maximum, the value of barium titanate relative permittivity decreases linearly as the applied electric field intensity increases – as it has been found experimentally – even to the point of dielectric breakdown.

For each titanium oxide molecule, there is a barium oxide molecule. The resulting electric dipole moment is $p_{э,рез}$ = (16,46 + 23,5)·10^{-30} C·m. In titanium oxide clusters, electric dipole moments are positioned along one of the directions only for three molecules while for other molecules they are mutually compensated. Each titanium oxide cluster is surrounded with barium oxide molecules in the same amount as in the cluster itself. However, only two barium oxide molecules possess the electric dipole moment directed along not compensated electric dipole moments of the titanium oxide cluster. On average, merely five molecules of titanium oxide and barium oxide with their electric dipole moments are positioned along one of the directions. Then, in accordance with (24), relative permittivity amounts to ~ 1987. The experimental value is equal to ~ 2000 (see Fig. 4).

The proposed model of the barium titanate crystal structure is in agreement with the model obtained by means of the X-ray structure analysis and described in many reference books and textbooks. The difference is that it is not barium titanate molecules $BaTiO_3$ which form the crystal lattice but titanium oxide molecules TiO_2. Ba0rium oxide molecules are not chemically linked with TiO_2 molecules but introduced into the crystal lattice of titanium oxide clusters to fill inter-cluster gaps. Previously, researchers just had no idea what a crystal is in terms of the nano scale. In order to explain somehow experimental results in a qualitative sense, researchers believed further ions Ba^{2+}, O^{2-} and Ti^{4+} were available in the barium titanate crystal. However, enormous energy is necessary to produce positive secondary ions and even more so high order ions; it is not known what sources could supply energy for that. A secondary negative oxygen ion in principle is not possible. That is why the obtained results were difficult to explain in detail.

Conclusion

Thus, the electric properties of solids result from the elastic polarization of clusters in metals as well as from orientation polarization in dielectrics and ceramics. Orientation polarization is caused by the rotation of built-in practically free electric dipoles along the external field. For the first time, a correct theoretical approach was successfully used to obtain the dielectric permittivity of ferrites and ferroelectrics, conductors, plasma, and electrolytes. The following fundamental results have been obtained:

Most of atoms and molecules possess built-in electric dipole moments and these moments determine the value of dielectric permittivity in gases.

In liquids, dielectric permittivity is determined by the availability of electric dipole moments in free clusters as well as in weakly bound molecules and atoms which form a liquid.

In solids, dielectric permittivity is determined by the availability of electric dipole moments of free atoms and molecules situated within inter-cluster gaps.

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ЭЛЕКТРИЧЕСКИЕ СВОЙСТВА РАЗНЫХ АГРЕГАТНЫХ СОСТОЯНИЙ ВЕЩЕСТВА

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Краткое содержание:

Электрические свойства твердых тел обусловлены упругой поляризацией кластеров в металлах, а в диэлектриках - ориентационной поляризацией наведенных и встроенных электрических диполей. Ориентационная поляризация обусловлена взаимодействием свободных встроенных электрических диполей с внешним электрическим полем. Разработана физическая модель формирования диэлектрической проницаемости металлов, электролитов, плазмы, ферритов и сегнетоэлектриков. Конкретно выполнен теоретический расчет диэлектрической проницаемости ряда ферритов и титаната бария.

Ключевые слова: *диэлектрическая проницаемость, агрегатные состояния, металлы, плазма, электролиты, сегнетоэлектрики.*

ЕЛЕКТРИЧНА СВОЈСТВА РАЗЛИЧИТИХ АГРЕГАТНИХ СТАЊА МАТЕРИЈЕ

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Сажетак:

Електрична својства чврстих тела проузрокована су еластичном поларизацијом кластера у случају метала, док су диелектрична својства резултат оријентацијске поларизације индукованих и уграђених електричних дипола. Оријентацијска поларизација произлази из интеракције слободних уграђених електричних дипола са спољашњим електричним пољем. Пројектован је физички модел формирања диелектричне пермитивности метала, електролита, плазме, ферита и *фероелектрика. Теоријски је израчуната диелектрична пермитивност једног броја ферита и баријум титаната.*

Кључне речи: *диелектрична пермитивност, агрегатна стања, метали, плазма, електролити, фероелектрици.*

Paper received on / Дата получения работы / Датум пријема чланка: 26. 08. 2016.
Manuscript corrections submitted on / Дата получения исправленной версии работы / Датум достављања исправки рукописа: 29. 09. 2016.
Paper accepted for publishing on / Дата окончательного согласования работы / Датум коначног прихватања чланка за објављивање: 01. 10. 2016.