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Changes in the Physical Properties of the Layered Crystals Caused by Ultrasonic Treatment

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Recently, there has been an interest in porous materials and nanoscale compounds and compounds with the presence of nanoscale objects. It is due to the possible use of them as materials to create high-capacity electrical energy storage. Such materials include the family of layered crystals. Layered crystals can be considered as a set of monatomic layers or packages with covalent or ion-covalent interactions within them and much weaker, van der Waals between them. Typical distance between packages, van der Waals gap is about several angstroms, but it can be varied significantly by external factors — intercalation, ultrasonic treatment. Therefore, van der Waals gaps may be considered as nanoscale objects or pores. The specifics of such pores, they are spatially strictly ordered and have the same width. By changing magnitudes of the pore, we can achieve characteristics suitable for practical use. Below we analyze the changes in the quantum capacitance caused by the ultrasonic treatment of the layered crystal. Consider the layered crystal in the framework of the one-dimensional Kronig-Penny model. This potential along the normal to the layers is shown in Fig. 1 (I is a van der Waals gap, II is a package, and a and b are their width, respectively, $d = a + b$ is a lattice parameter).

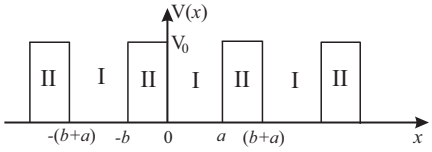

Fig.1.

It is known, that in the general case the electronic capacitance of a crystal is the sum of two serial connected capacities — the classical C_{el} and the quantum ones C_q. Classical capacitance has electrostatic nature, whereas quantum capacitance is associated with the filling of electronic states, namely

$$C_q = -\frac{dQ}{d\mu} \Rightarrow -\frac{e\sum\limits_n f\left(E_n\right)}{d\mu} \Rightarrow -e\frac{d}{d\mu}\sum_n \left(\exp\left(\frac{E_n-\mu}{kT}\right)+1\right)^{-1} \qquad (1)$$

where the summation is over all quantum states of the system. As a rule, $C_q \gg C_{el}$, therefore $C \approx C_{el}$, i.e. C_q is ineffective. However, the situation in nano-objects can

be opposite. It has been experimentally found that ultrasonic treatment changes the widths of the van der Waals gaps, practically without changing of the packet widths. In the case of the Kronig-Penny model, the dispersion law of an electron is a solution of the transcendental equation

$$\cos k(a+b) = -\frac{\alpha^2+\beta^2}{2\alpha\beta}\sin\alpha a \cdot \sin\beta b + \cos\alpha a \cdot \cos\beta b, \tag{2}$$

where k is the quasi-momentum, $\alpha = \sqrt{\frac{2mE}{\hbar^2}}$, $\beta = \sqrt{\frac{2m(E-V_0)}{\hbar^2}}$. Using the results of numerical solutions of the (2) in equation (1) dependencies on chemical potential μ of $C_q(\mu)$ at fixed values of the width of the package $b = 0.8$ nm, the height of the barriers $V_0 = 1.2$ eV and a temperature $T = 200$ K at different values well widths $a = 0.2$, 0.4, 0.6, 0.8 nm were obtained (Fig. 2). In Fig. 2 shaded areas show the electron bands.

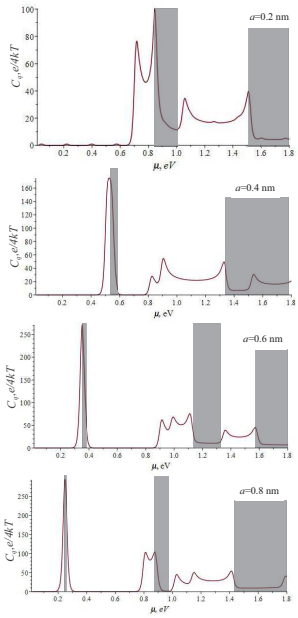

Fig.2.

Conclusions

— The structure $C_q(\mu)$ is dictated by dimensional quantization;

— There is a correlation between of the peaks $C_q(\mu)$ and the location of the allowed zones: their maximums coincide with the bottom of the zones.

— The magnitude of the $C_q(\mu)$ peaks decreases with increasing μ. Since C_q is closely related to the density of states, a qualitative explanation of its fall can be obtained from the fact that the density of states in one-dimensional crystals with a parabolic dispersion law has a similar dependence ($\sim -1/\sqrt{E}$). It explains why the maximum peak values are greater for electrons for narrower wells.

The structure of $C_q(\mu)$ differs sharply from the analogous one in a similar one-dimensional problem with an infinitely deep potential well, that is, in the Kronig-Penny model in the absence of tunneling [1]. In the latter case, the electron spectrum is discrete levels and, as a consequence, $C_q(\mu)$ has the structure of strongly pronounced peaks. In our case, the complex structure of its peaks is a consequence of the splitting of levels by the tunneling effect.

[1] *Matulka D. V., Lukiyanets B. A.* Quantum Capacitance in Nanostructures with Different Electrical Properties / Phys. Chem. Solid St. 2011, **4**, No.12, p.1–6 (in Ukrainian).