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Quasi-2D crystals as an electrode material for high energy storage devices

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The high value of the specific surface area in quasi-2D crystals, with the possibility of a large variation of their properties due to external factors, allows us to consider them as electrode materials for supercapacitors. In order to describe the specific physical properties of such crystals due to the different types of chemical bonds in them, a model is proposed. The electronic spectrum obtained has the structure (discrete levels) + (two-dimensional bands) or (mini-bands) + (two-dimensional bands). A significant relationship between the geometrical, spectral and statistical properties of the quasi-2D crystals has been found by studying the energy density of the accumulation *W* within the microscopic model. Contrary to existing models, the proposed model shows that under certain conditions there are two or more optimal crystal sizes where the experimentally observed maximum energy density *W* is realised. The model and its qualitative conclusions should be considered as the result of a microscopic approach to the problem.

Keywords: high-energy storage, quasi-2D crystal, porous material, supercapacitor, energy density.

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Introduction

The creation of energy storage devices with both high energy capacity and high power is one of the most important modern scientific and technological problems. Capacitors and electrochemical batteries are the traditional energy storage devices. However, the former have high power and low capacity. The latter have low power but high capacity. The creation of supercapacitors (or ultracapacitors) is one way of bridging the gap between capacitors and batteries. Their efficiency depends strongly on the electrode characteristics [1-5]. In modern supercapacitors, most of the energy is stored in the double layer at the interface between the electrodes and the electrolyte. Therefore, the search for electrode materials with high specific surface area is of great importance.

Following the discovery of graphene in 2004, it became evident that this two-dimensional material possessed unique physical properties, including high strength, thermal conductivity, mobility, and the highest possible specific surface area. As a consequence of these attributes, graphene was considered an excellent candidate material for electrodes for supercapacitors. However, in addition to a large specific surface area, such electrodes also require high conductivity. Graphene, like its conventional inorganic counterparts, is typically a semiconductor or insulator with low electronic conductivity. Therefore, the use of graphene as an electrode material requires additional research [10]. In the search for an alternative to graphene, there has been renewed interest in quasi-2D (or layered) crystals. These crystals are actually three-dimensional. However, in some aspects they are very similar to two-dimensional crystals. Although there has been some research into the use of quasi-2D crystals as electrodes in supercapacitors and batteries [11-15], similar research remains relevant.

In nature there are many quasi-2D crystals with pronounced anisotropic properties. The most common are graphite, TMDs (transition metal dichalcogenides or MX_2 where M: Mo, Ta, Ti, W, Nb, Sn, Zr, Hf, V; X: S, Se, Te), compounds $A_3 B_6$ (A: Ga, In; B: S, Se, Te) and others. Representatives of such families are shown, for example, in Figure 1. Despite some differences between quasi-2D crystals, an important similarity can be identified, namely that quasi-2D crystals can be represented as a set of monoatomic planes (as in the case of graphite) or packages of monoatomic planes S-Mo-S (in the case of TMD) and Se-Ga-Ga-Se (in the case of A_3B_6) with strong, covalent or ionic-covalent interatomic bonds in them. However, the inter-planar or inter-packet bonds are realised by much weaker van der Waals forces. This similarity allows the study of quasi-2D crystals from a single point of view.

Different types of bonding cause pronounced anisotropy in the physical properties of quasi-2D crystals, especially in the mechanical properties [16,17]. Thus, the analysis of the elastic modulus along the normal C_{33} to the packets and the elastic modulus in the plane of the layers C_{11} and the degree of anisotropy C_{33}/C_{11} for graphite and some known layered crystals (GaS, GaSe, InSe) shows that C_{11} significantly larger (30 times larger for graphite and on average 3 times larger for other crystals) than C_{33}.

There are a number of ways to significantly alter the physicochemical properties of quasi-2D crystals. The most common of these is intercalation. This is the introduction of foreign atoms or organic and inorganic molecules into the van der Waals vacancies of TDM or A_3B_6 [18,19].

Some aspects of this phenomenon are important to note:

1. Normally, intercalates fall into each van der Waals gap of the layered crystals. However, the so-called n-stage ordering (n >1) is possible (especially in graphite). This occurs when the intercalate fills every *n*-th van der Waals gap (see [18]).
2. Depending on the nature of the intercalate, it can significantly modify the van der Waals gap by surrounding it [20]. Among these studies, it is worth mentioning the work of [21], which is very important for us). In it, studies on 50 TMDs of TaS_2 and $NbSe_2$ have shown that their intercalation by organic and inorganic molecules leads to an increase in their van der Waals gap. This increase depends on the nature of the intercalating molecule. For example, the van der Waals gap reached 56 Å (TaS_2 van der Waals gap is ~ 3 Å) when 2H- TaS_2 was intercalated with octadecylamine.

Ultrasonic treatment and compression are other active factors in changing the van der Waals gap [22 - 24]. Although the mechanism of ultrasonic treatment is not fully understood, the increase in thickness of the layered crystal along the normal to the layers due to the increase in van der Waals gaps caused by ultrasonic treatment (as well as by intercalation) is undoubtedly an important factor in changing the physical properties of the layered crystal.

Quasi-2D crystals can be identified in porous materials. In such crystals, strictly spatially ordered van der Waals gaps of equal width play the role of pores [25]. According to the characteristic sizes of van der Waals gaps in the classification of porous crystals, layered crystals belong to mesoporous materials [26]. Thus, the problems of layered crystals are closely related to those of porous crystals.

Thus, the modification of the physical properties of layered crystals or porous structures by intercalation, compression or ultrasonic treatment makes it possible to solve a pressing scientific and technological problem such as the creation of high-capacity electricity storage devices, particularly based on sodium and potassium, as opposed to lithium-ion energy storage [18].

To this end, we propose a model that takes into account the defining characteristics of the 2D crystal. It allows qualitative conclusions to be drawn for each of them.

I. Quantum capacitance

The energy density in the electrode at an applied voltage U is an important technical characteristic of any electrode:

$$W(U) = \int_0^U VC(V)dV \qquad (1)$$

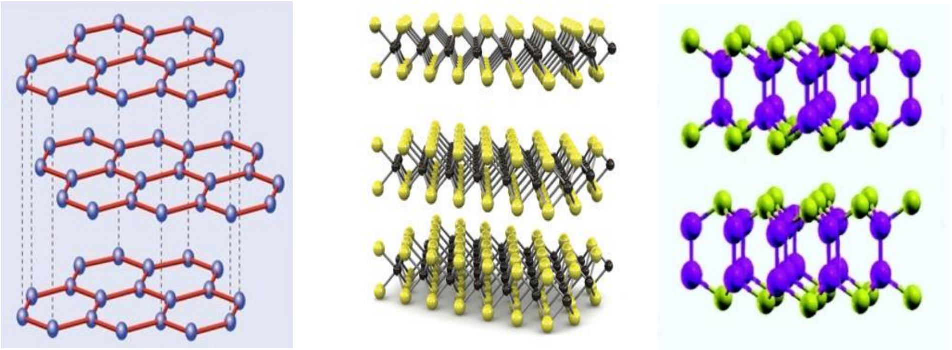
Here C is the differential capacitance, which is defined as the derivative of the charge with respect to the chemical potential [27], viz:

$$C = \frac{dQ}{d\mu} \Rightarrow e\frac{d}{d\mu}\sum_a f(E_a) \qquad (2)$$

where $f(E_a) = \frac{1}{exp\left(\frac{E_a - e\mu + eV}{kT}\right)+1}$ is the Fermi-Dirac distribution.

All the quantum states of the system are summed up in (2).

This is easy to see: (1) can alternatively be written as



a) b) c)

Fig. 1. Characteristic representatives of the quasi-2D crystal families: a) graphite, b) MoS_2, c) GaSe.

$$C = \frac{dQ}{dV} \Rightarrow -e\frac{dQ}{d\mu}$$

In addition to the electrostatic (or classical) capacitance C_{el} associated with the electrical double layer, the quantum capacitance C_q of the electrode is another important contributor to charge accumulation. Normally $C_q \gg C_{el}$, in series and therefore $C \approx C_{el}$. However, with the appearance of nano-objects, the opposite situation occurs [28, 29].

As C_q is a key factor in determining the total capacitance and the storage mechanism in 2D materials, its research has been particularly intense recently [15, 30].

II. Quasi-2D crystal model

Consider a quasi-2D crystal with orthogonal symmetry described by a one-electron potential

$$V(\vec{r}) = V(x,y) + V(z) \qquad (3)$$

Here $V(x,y)$ is the potential of the electron in the plane XOY of the packets and its dispersion law can be described by a parabolic dependence:

$$E(k_x,k_y) = \frac{\hbar^2(k_x^2+k_y^2)}{2m},$$

where $\vec{k}_{II} = (k_x,k_y)$ are the quasimomentum in the plane of the packets, and $m = m_x^*, m_y^*$, are the effective masses along the corresponding axes.

We choose $V(z)$ as the Kronig-Penney potential shown in fig. 2, which describes the behaviour of the electron along the normal to the layers. This potential allows a good qualitative modelling of the degree of anisotropy along OZ by choosing the value of V_0. Thus, when the potential is infinite, the dispersion law has the form

$$E_n = \frac{\hbar^2\pi^2}{2m_z a^2}n^2 \qquad (n=1, 2, 3\ldots)$$

where m_z is an electron mass along OZ.

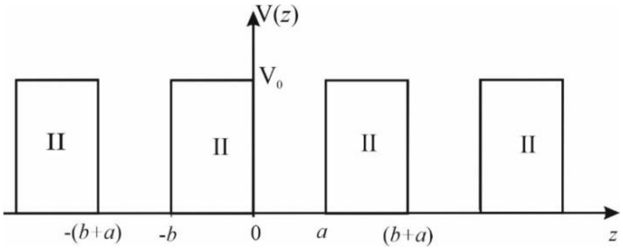


Fig. 2. *V(z)* as the Kronig-Penney potential (a is the distance between the barriers, b is the thickness of the barrier and V_0 is its height).

The total dispersion law is therefore

$$E(n\vec{k}_{II}) = \frac{\hbar^2 k_{II}^2}{2ma_{II}^2} + \frac{\hbar^2\pi^2}{2m_z a^2}n^2 \qquad (4)$$

In the case of transition to barriers surrounding holes of finite height and width b, the electron is collectivised by tunneling between the pores. This leads to the formation of mini-zones instead of discrete states, with a value that is greater the greater the tunneling. The lowest mini-zones will have the least blurring. In any case, the mini-zones will also be discrete. As further analysis of the problem at higher temperatures has shown, this does not alter the qualitative conclusions presented below. This fact has allowed us to limit the analysis of the energy density to the infinite barrier potential.

Taking into account (2), (4),

$$C_q = a\frac{d}{d\mu}\sum_{n\vec{k}_{II}}\frac{1}{exp\left(\frac{E(n\vec{k}_{II})-e\mu+eV}{kT}\right)+1} \Rightarrow \frac{e^2}{4kT}\sum_{n\vec{k}_{II}} ch^{-2}\left(\frac{E(n\vec{k}_{II})-e\mu+eV}{2kT}\right) \qquad (5)$$

The calculated quantum capacitance $C_q(\mu)$ shows a sharp peak at small with further damping of the oscillations as the zone is filled (the increase in the chemical potential is clearly related to the increase in the width of the van der Waals gap a). An analogous situation occurs when mini-zones are present [31].

The expression for the energy density, taking into account (1) and (5), after integration over V [32], has the form:

$$W(U) = \pi kT\sum_m \int_0^{\frac{2\pi^2}{a_{II}^2}} dk_{II}^2\left((A_2 - A_1)thA_2 + ln\frac{chA_1}{chA_2}\right) \qquad (6)$$

where $A_1 = \left(\frac{\hbar^2\pi^2 n^2}{2ma^2} - e\mu + eU\right)/2kT$,

$A_2 = A_1 + \frac{\hbar^2}{2m}\left(\frac{\sqrt{2\pi}}{a_{II}}\right)^2/2kT$, (6) is obtained by assuming that the dispersion in the plane of the layers is parabolic throughout the Brillouin zone and replacing the summation over (k_x,k_y) by integration over (k_{II},φ) in the polar coordinate system with $k_{II} = \sqrt{k_x^2 + k_y^2}$.

III. Results and discussion

Using (6), the calculated dependence of the energy density on the applied voltage U and the van der Waals

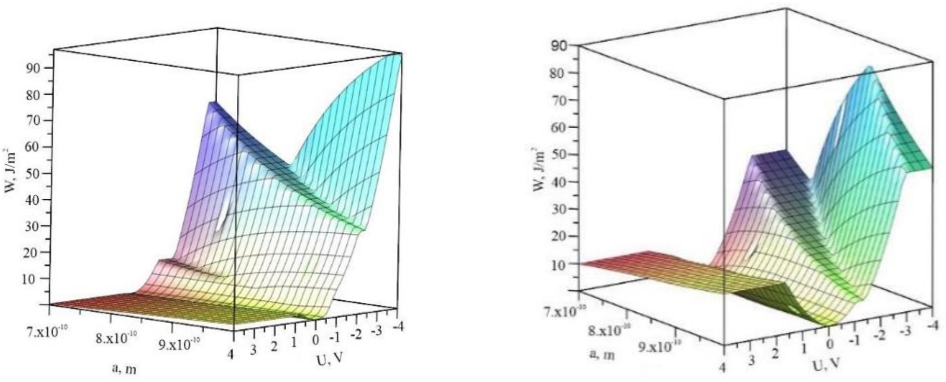


Fig. 3. Dependence of the energy density W on the applied voltage U and the van der Waals gap width a at different chemical potentials μ: μ = 1 V (left) and μ= 2 V (right).

size a at different values of the chemical potential μ (μ=1 V and μ=2 V). (The other parameters used are:a_{II} =0.7 nm, T= 50 K, $m = m_e$). The areas $W(U, a)$ in Fig. 3 show their significant dependence on the zone filling.

Figure 4 shows two sections of $W(U, a)$with planes a=0.7 nm and a=0.8nm at different values of chemical potential. On some of them, the curves intersect at one, two or three points $\widetilde{U}_i$, which can be obtained by solving the system of equations

$$\begin{cases} \sum_m \int_0^{\frac{2\pi^2}{a_{II}^2}} dk_{II}^2 \left((A_2 - A_{11}) \tanh A_2 + ln \frac{cosh\, A_{11}}{cosh\, A_2} \right) = \sum_m \int_0^{\frac{2\pi^2}{a_{II}^2}} dk_{II}^2 \left((A_2 - A_{12}) \tanh A_2 + ln \frac{cosh\, A_{12}}{cosh\, A_2} \right) \\ \sum_n \int_0^{\frac{2\pi^2}{a_{II}^2}} dk_{II}^2 \left((A_2 - A_{11}) \tanh A_2 + ln \frac{cosh\, A_{11}}{cosh\, A_2} \right) = \sum_n \int_0^{\frac{2\pi^2}{a_{II}^2}} dk_{II}^2 \left((A_2 - A_{1extr}) \tanh A_2 + ln \frac{cosh\, A_{1extr}}{cosh\, A_2} \right) \end{cases}$$

where $A_{11} = \left(\frac{\hbar^2 k_{II}^2}{2m} + \frac{\hbar^2 \pi^2 n^2}{2ma^2} - e\mu + e\widetilde{U} \right) / 2kT,$

$$A_{12} = A_{11} + \frac{\hbar^2}{2m} \left(\frac{\sqrt{2}\pi}{a_{II}} \right)^2 / 2kT,$$

$$A_{1aextr} = \frac{\hbar^2 k_{II}^2}{2m} + \frac{\hbar^2 \pi^2}{2m_z a_{extr}^2} n^2 - e\mu + \ e\widetilde{U}$$

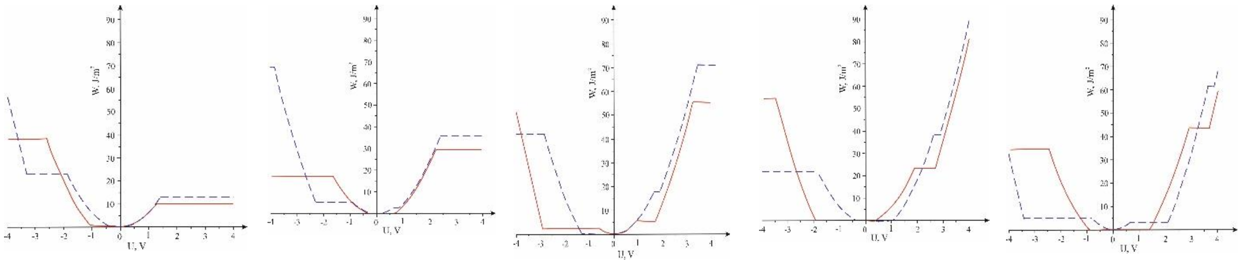
The maximum of the $W(U, a)$ is realised at such points. Thus, the larger the region of change of the $W(U_i, a)$ the more such maxima there may be.

Let us compare our conclusions with those obtained in the studies of other authors. Recently, much attention has been paid to the anomalous behaviour of capacitance as a function of pore size in porous crystals. However, a clear understanding of this behaviour is still lacking [33,34].

In [35], molecular dynamics modelling was used to study the dependence of the capacitance C on the pore size d of supercapacitors consisting of slit micropores with size d C= 0.67 ... 1.8 nm in an ionic liquid at room temperature. The existence of two peaks was observed, and as the pore size decreases, the micropore capacitance increases abnormally, which is in good agreement with the experimental data. The appearance of the second peak in the range of 1.0 to 1.8 nm is a new, not fully understood feature of the curve *C(d)*. The authors associate it with the interference of adjacent double electrical layers. Such interference not only explains the anomalous nature of the curve *C(d)* but, according to the authors, allows prediction of the non-monotonic decay behaviour of the above 1.8 nm. A similar anomalous growth of the *C(d)* has been obtained in atomistic simulations by [34]. The authors linked the explanation of such real but physically inexplicable behaviour to the critical role of "ion solvation" in controlling pore capacitance and the importance of the choice of anion/cation pairs.

Investigations into the properties of a nanoporous crystal as an electrode material as a function of the pore cross section have been carried out by [36]. In the framework of the double electrical layer, the authors perform a Monte Carlo simulation of the dependence of the infinite solitary pore. They use a suitable expression for the dependence of the charge Q on the applied voltage U. The presence of 4 parameters in this expression made it possible to simplify the technical side of the calculations. The theory is therefore phenomenological. The theoretical study revealed a single anomalous peak of specific differential capacitance in the region of the narrow pores, and the existence of an "optimal" pore size giving the maximum energy density was established from the analysis of the *Q(U)*. In other words, the reasons for the variation in energy density are deeper than those associated with geometric variations of the crystal, its active surface.

The microscopic model proposed by us confirms not only the existence of such an optimal pore, but also, under certain conditions, the existence of a number of such pores. This conclusion is confirmed by [36] for this type of pores. The conclusions obtained in our work are the result of the discreteness of the dispersion law, which is valid for any quasi-2D crystal. They can be considered as



μ=2 V μ=3 V μ=4 V μ=5 V μ=6 V

Fig. 4. Cross-sections of $W(U,a)$ in planes of a = 0.7 nm (solid curve) and a = 0.8 nm (longdash curve) at different values of the chemical potential μ.

an alternative or concomitant explanation for the anomalous behaviour of the differential capacitance with a change in pore size and the existence of more than one pore of the "optimal" size proposed above.

Conclusions

The work is a theoretical study of quasi-two-dimensional crystals from the point of view of their application as electrode materials for high-capacity energy storage devices - supercapacitors. The focus of the proposed theoretical model is on the existence in 2D crystals of sharply different interactions in different crystallographic directions, which is the cause of their sharply anisotropic character, in particular of the mechanical properties. An important prerequisite for such an application is the possibility of modifying their properties within wide limits by external factors - intercalation, pressure, ultrasound action.

Microscopic theory has revealed a deep connection between the geometry, spectral and statistical characteristics of quasi-2D crystals. In particular, at a certain ratio between them, the theory

- allows for the presence of an experimentally established sharp maximum energy density at a small van der Waals gap. In the works of other authors, only assumptions are made about the reasons for this maximum.
- indicates the existence of more than two ‘optimal’ sizes of van der Waals gap - the sizes at which the maximum energy density is achieved. The search for such maxima remains the subject of theoretical research by other authors using different assumptions.

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Б. А. Лукіянець, Д. В. Матулка

Квазі-2D кристали як електродний матеріал для високоефективних накопичувачів енергії

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Високе значення питомої поверхні в квазі-2D кристалах, з можливістю широкого варіювання їх властивостей під впливом зовнішніх факторів, дозволяє розглядати їх як електродні матеріали для суперконденсаторів. Запропоновано модель для опису характерних фізичних властивостей таких кристалів, зумовлених різними типами хімічних зв'язків у них. Отриманий електронний спектр має структуру (дискретні рівні) + (двовимірні зони) або (міні-зони) + (двовимірні зони). За допомогою вивчення густини енергії накопичення W в межах мікроскопічної моделі було виявлено значний зв'язок між геометричними, спектральними та статистичними властивостями квазі-2D кристалів. На відміну від існуючих моделей, запропонована модель показує, що за певних умов існують два або більше оптимальних розміри кристалів, де реалізується експериментально спостережуваний максимум густини енергії *W*. Модель та її якісні висновки слід розглядати як результат мікроскопічного підходу до вирішення цієї задачі.

Ключові слова: високоефективний накопичувач енергії, квазі-2D кристал, пористий матеріал, суперконденсатор, густина енергії.