O. M. Manyk, *cand phys – math sciences*[1]
T. O. Manyk, *cand phys – math sciences*[2]
V. R. Bilynskyi-Slotylo, *cand phys – math sciences*[1]

[1]Yuriy Fedkovych Chernivtsi National University,
2 Kotsiubynskyi str., Chernivtsi, 58012, Ukraine,
e-mail: o.manyk@chnu.edu.ua,
e-mail: slotulo@gmail.com
[2] Military University of Technology Jaroslaw Dombrowski,
str. gene Sylwester Kaliskiego, 2,
Warsaw 46, 00-908, Poland,
e-mail: tetjana.manyk@wat.edu.pl

THEORETICAL MODELS OF ORDERED ALLOYS OF TERNARY SYSTEMS OF THERMOELECTRIC MATERIALS.

4. CHEMICAL BOND AND STATE DIAGRAMS OF *Bi-Cd-Sb*

A comprehensive approach has been developed for the construction of theoretical models of ordered alloys of ternary systems based on Bi-Cd-Sb.
A diagram of distribution of phase regions and isothermal sections based on intermediate binary compounds Bi-Cd, Bi-Sb, Cd-Sb in the Bi-Cd-Sb system have been constructed.
Calculations of effective radii, redistribution of electron density and dissociation energy of non-equivalent chemical bonds depending on interatomic distances in the Bi-Cd-Sb ternary system are presented. Bibl. 7, Fig. 4, Tabl. 6.

Key words: theoretical models, chemical bond, effective radii, dissociation energy, state diagrams, non-equivalent hybrid orbitals (NHO).

Introduction

Cadmium antimonide is one of the promising thermoelectric materials [1]. Depending on the mode of heat treatment and the method of cooling, cadmium alloys with antimony can crystallize in accordance with the stable and metastable diagrams of alloys [2]. The nature of the chemical bond in such alloys varies from metallic to ionic, covalent and intermediate.

Considering also that the search for new thermoelectric materials increasingly comes down to the need to study multicomponent systems, the study of ternary systems based on *Bi-Cd-Sb* becomes especially relevant, both from the standpoint of chemical bonding and from the standpoint of state diagrams. This will make it possible not only to establish the limits of phase equilibrium in the liquid-crystal regions (melting diagrams), but also to predict cases of incongruent melting.

In this regard, the choice of bismuth as a constituent component of *Bi-Cd-Sb* was not accidental. Bismuth in compounds can have different degrees of oxidation (from -3 to +5) [3]. In addition, according to the state diagram (*Bi-Sb*), both components (*Bi* and *Sb*) are infinitely soluble in liquid and solid states and do not form chemical compounds. At the same time, the state diagrams of *Cd-Sb* and *Bi-Cd* are eutectic diagrams, where both compounds and solid solutions can be formed [4]. In accordance with the above, the task was set to calculate the parameters of chemical bonds depending on the interatomic distances and to construct phase distribution schemes in the *Bi*-*Cd*-*Sb* system.

Theoretical models of state diagrams

This work is devoted to the construction of theoretical models of ordered alloys of ternary systems based on *Cd*-*Bi*-*Sb*. What was new in the study of bismuth and cadmium antimonides was that to solve the problem, the equilibrium method was used based on the geometric properties of a triangle - the triangulation method [5].

When building theoretical models, this approach made it possible to generalize the results of experimental studies of *Cd*-*Bi*, *Bi*-*Sb* and *Cd*-*Sb* binary systems; physico-chemical properties and quantum regularities of the initial components. Next, by constructing conoid triangles, the quantitative ratios and equilibrium limits of phases in the liquid-crystal regions were determined. This made it possible to predict cases of congruent and incongruent melting.

The obtained results are shown in Fig. 1 - 4, where the following designations are entered:

α – solid phase based on *Cd*;
β – solid phase based on *Bi*;
γ – solid phase based on *Sb*;
ε – solid phase based on intermediate *Cd*-*Bi* binary compounds;
ρ – solid phase based on intermediate *Bi*-*Sb* binary compounds;
δ – solid phase based on intermediate *Cd*-*Sb* binary compounds;
σ – solid phase based on *Bi*-*Cd*-*Sb* ternary system.
L – liquid.

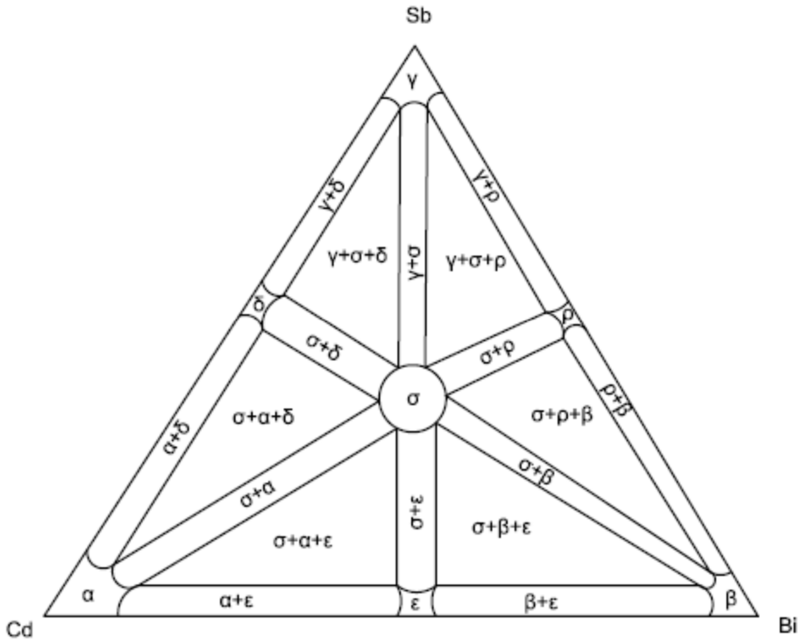

Fig. 1. A diagram of the distribution of Cd-Bi-Sb equilibrium phase regions in the solid state

Fig. 1 shows a diagram of the distribution of *Cd*-*Sb*-*Bi* phase regions in the solid state. This made it possible to divide *Cd*-*Bi*-*Sb* ternary system into six ordered ternary subsystems and consider interatomic interaction both from the standpoint of state diagrams and chemical bond.

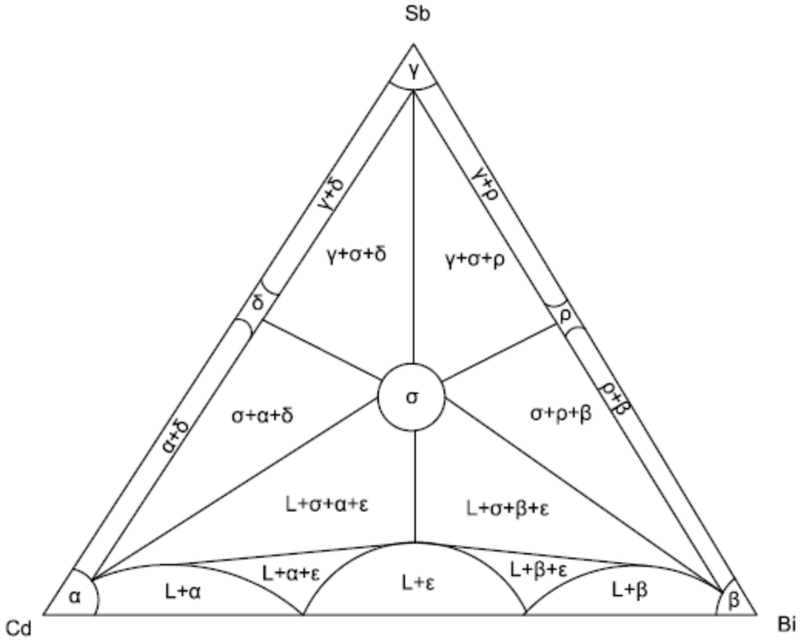

Fig. 2. Cd-Bi-Sb isothermal section at t = 200 °C

Fig. 2 shows an isothermal section at a temperature of $t = 200$°C. This temperature is lower than the melting temperature of the original components *Bi*, *Cd* and *Sb* and at the same time higher than the temperature of the first eutectic of the *Bi*-*Cd* system ($E_1 = 144$°C). Part of the *Cd-Bi* section is occupied by liquid *L*, and the two-phase equilibrium (*L*+α), (*L*+ε), (*L*+β) is carried out by primary crystals α and β, as well as ε-crystals (based on Cd_nBi_m compounds).

In contrast to the previous case, the section contains conoid triangles with equilibrium phases (*L*+α+ε) and (*L*+ε+β), which are formed by primary crystals α, β, ε (based on Cd_nSb_m and Bi_kSb_l compounds) and liquid L. This division of ternary systems into separate sectors of dual state diagrams makes it possible to study the fine structure of cooling and heating of individual elements depending on their environment and the processes of forming the short-range order of chemical bonding.

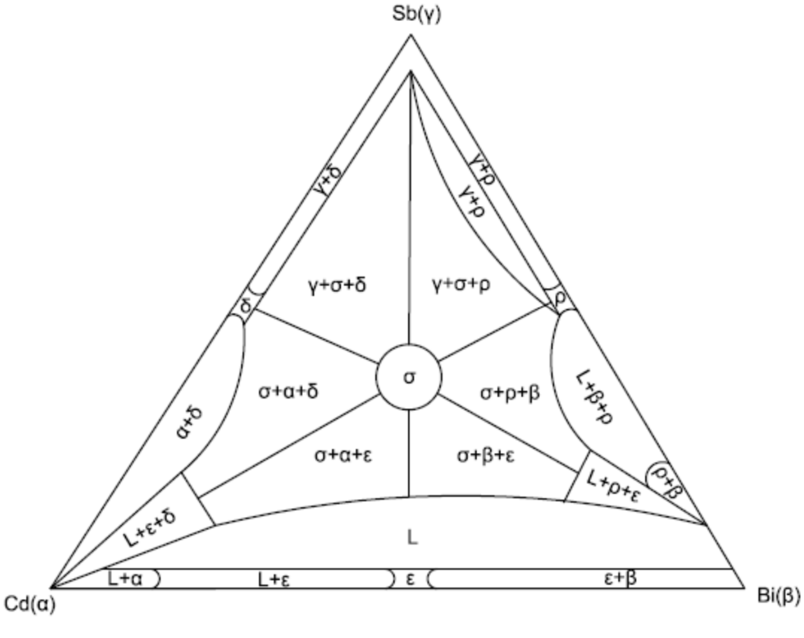

Fig. 3. Cd-Bi-Sb isothermal section at t = 300 °C

Fig. 3 shows an isothermal section at a temperature of *t* = 300 °C, which is higher than the melting point of bismuth and lower than the melting point of cadmium and antimony. In this case, most of the *Cd-Bi* cross-section is occupied by liquid *L*, and the equilibrium phases with conoid triangles (*L*+ε+α) and (*L*+β+ε) are replaced by phases with conoid triangles (*L*+ε+δ) and (*L*+ε+ρ), and this already makes it possible to study the fine structure of cooling and heating using state diagrams of binary alloys.

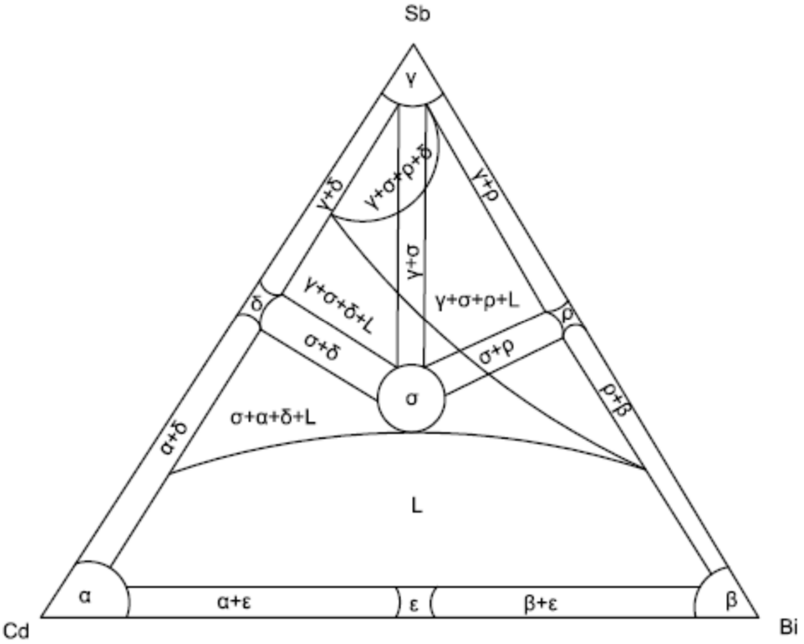

Fig. 4. Cd-Bi-Sb isothermal section at t = 400 °C

Fig. 4 shows an isothermal section at *t* = 400 °C, which is higher than the melting temperature of the original components of cadmium and bismuth and makes it possible to study the cooling and heating processes of ternary compounds of solid solutions depending on the composition, chemical bond, and technological parameters. Thus, the given isothermal sections make it possible to:

1. Divide the *Cd-Bi-Sb* ternary system into six ordered subsystems and consider the issue of interatomic interaction from the standpoint of state diagrams and chemical bonding.
2. Establish the relationship between phase equilibrium in the liquid-crystal regions and transformations in the solid state.
3. Distinguish between eutectic and peritectic state diagrams.

In this regard, it should be noted that the isothermal sections alone do not yet indicate the numerical values of the temperatures of phase transitions in multicomponent systems. In such cases, the methods of calculating the interatomic interaction from the standpoint of chemical bond are additionally used.

Theoretical models of chemical bonding of ordered *Cd-Bi-Sb* alloys

The combination of experimental and theoretical approaches in the quantitative method for calculating the parameters of the electronic structure of matter is associated with a revision of the system of views on interatomic interaction, with the emergence of qualitatively new, non-standard ideas that are not the result of the development of various directions of existing theories, but also deny some of them. The way to solving the problem lies only through an objective analysis of empirical material [6].

The foundations of such an analysis were laid by Mendeleev when he discovered the periodic law. However, at the current stage, it is impossible to obtain qualitatively new conclusions based on the generalization of experimental data only on the system of neutral unexcited atoms. Further development of the theory of the periodic system is needed, taking into account the quantum nature of atoms, the relationship between the physical and chemical properties of the elements of Mendeleev's table with the structure of their electronic shells, with the properties and electronic structure of the compounds formed by them, depending on the number of electrons n in the orbitals of the interacting atoms.

The analysis of diverse empirical information about the properties of atoms and their ions showed that they can be linked together and generalized by introducing the concept of effective ionic radii R_U. The systems of equations relating the value of R_U to the electron density on atomic orbitals make it possible to calculate the redistribution of electron density depending on interatomic distances and to overcome the difficulties of modern theories of interatomic interaction [7].

The most useful when searching for the form of a graphical solution to the problem of the connection between R_U and n turned out to be the relationship between $tg\alpha = \frac{\Delta log R_U}{\Delta n}$ and electronegativity, fixing the position of the lines in $log R_U = f(n)$ coordinates.

A good agreement of the set of experimental data with the values of R_U and tgα gives the postulated dependence:

$$log R_{UA}^{x} = log R_{UA}^{0} - x tg\alpha, \tag{1}$$

where R_U^0 is radius of atoms in the unexcited state, x is valence.

The usefulness of such equations is determined by the extent to which their use allows obtaining a fairly accurate and physically justified result of interatomic interaction. The existence of a minimum interatomic distance d_{min} during the formation of a chemical bond and two possible values of Z_{eff} for interatomic distances $d_i > d_{min}$ з from the standpoint of the crystal chemical approach is justified by the increase of the internuclear distance when ionicity and covalency change.

The main drawback of this approach is that in many cases the internuclear distances between atoms A and B are smaller than the d_{min} value, and it is impossible to calculate the charge of the ions from the diagrams of the dependence of the effective charges Z_{eff} on the interatomic distances. Difficulties can be overcome by translating the crystal chemical system into the language of quantum chemistry. It should be taken into account that in the zone of binding localized orbitals, the spherical symmetry of the electron density is broken and for $d_i > d_{min}$ the formation of bonds (A-B) is accompanied by the transition of electrons to other directions of interatomic interaction and this bond becomes a donor.

Thus, when $d_i \neq d_{min}$ the effective values of the charges must change. Removal of $(+\Delta e)$ electrons or their localization $(-\Delta e)$ change the values of the charges that a given pair has at $d_i = d_{min}$, i.e. $Z_{eff} A(B) = Z_{min} A(B) + \left(\frac{\Delta e}{Z}\right)$.

With this approach, a system of equations of type (1) makes it possible to match the theoretical part with the experimental part and was solved for all possible values of d_i in the compounds under consideration. Thus, as a result of taking into account the quantum interpretation of empirical material, the expression for the dissociation energy of chemical bonds d_i takes on the form:

$$D_{A-B}^{(i)} = \left(\frac{C_1\left(R_{UA}^0 + R_{UB}^0\right)}{(\operatorname{tg}\alpha_A + \operatorname{tg}\alpha_B)}\right)\left(\frac{C_2 d_i}{d_i^2 - R_{UA} R_{UB}} - \frac{1}{d_i}\right), \tag{2}$$

where $R^0_{UA(B)}$, R^0_{UB} as before, are the radii of atoms in the unexcited state;

R_{UA}, R_{UB} are effective radii of ions of atoms A, B;

d_i is interatomic distance of i-bond;

i is the number of non-equivalent interatomic distances in the compounds under study;

C_1 is coefficient reflecting the relationship between dimensional and energy characteristics of interatomic interaction (measured in electron volts);

C_2 depends on the type of crystal structure (dimensionless).

With regard to the above remarks, calculations of effective charges, effective radii, dissociation energies for chemical bonds φ_i at different interatomic distances d_i, and various structural modifications of *Bi-Cd-Sb* were carried out in this work. In the tables, the values of the coefficients C_1 and C_2 in the first approximation are chosen to be equal to unity.

Table 1

Effective charges, effective radii, dissociation energies depending on interatomic distances of Bi-Bi NHO

Bi-Bi NHO / Parameters	*Bi-Bi*					
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
d_i(Å)	2.8	2.9	3.0	3.1	3.2	3.3
R_U^{Bi}(Å)	1.40	1.45	1.50	1.55	1.60	1.65
$\Delta q_i(\varphi_i)$	+0.85	+0.7	+0.5	+0.3	+0.1	-0.1
$D(\varphi_i)$ ev	2.854	2.755	2.663	2.577	2.497	2.421

Table 2

Effective charges, effective radii, dissociation energies depending on interatomic distances of Cd-Cd NHO

Cd-Cd NHO / Parameters	*Cd-Cd*					
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
d_i(Å)	2.8	2.9	3.0	3.1	3.2	3.3
R_U^{Cd}(Å)	1.4	1.45	1.5	1.55	1.6	1.65
$\Delta q_i(\varphi_i)$	+0.33	+0.18	+0.025	-0.05	-0.27	-0.4
$D(\varphi_i)$ ev	1.853	1.789	1.730	1.674	1.622	1.572

Table 3

Effective charges, effective radii, dissociation energies depending on interatomic distances of Sb-Sb NHO

Sb-Sb NHO / Parameters	*Sb-Sb*					
	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
d_i(Å)	2.8	2.9	3.0	3.1	3.2	3.3
R_U^{Sb}(Å)	1.4	1.45	1.5	1.55	1.6	1.65
$\Delta q_i(\varphi_i)$	0.2	0	-0.2	-0.39	-0.6	-0.75
$D(\varphi_i)$ ev	2.232	2.252	2.177	2.107	2.041	1.980

Table 4

Effective charges, effective radii, dissociation energies depending on interatomic distances of Cd-Bi NHO

Cd-Bi NHO	*Cd-Bi*					
Parameters	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
d_i(Å)	2.8	2.9	3.0	3.1	3.2	3.3
R_U^{Cd}(Å)	1.32	1.37	1.43	1.49	1.54	1.60
R_U^{Bi}(Å)	1.48	1.53	1.57	1.61	1.66	1.70
$\Delta q_i(\varphi_i)$	0.62	0.42	0.25	0.07	-0.1	-0.2
$D(\varphi_i)$ ev	2.256	2.179	2.108	2.042	1.979	1.920

Table 5

Effective charges, effective radii, dissociation energies depending on interatomic distances of Bi-Sb NHO

Bi-Sb NHO	*Bi-Sb*					
Parameters	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
d_i(Å)	2.8	2.9	3.0	3.1	3.2	3.3
R_U^{Bi}(Å)	1.49	1.54	1.58	1.64	1.69	1.74
R_U^{Sb}(Å)	1.31	1.36	1.42	1.46	1.51	1.56
$\Delta q_i(\varphi_i)$	0.57	0.35	0.2	-0.05	-0.25	-0.45
$D(\varphi_i)$ ev	2.568	2.480	2.396	2.322	2.250	2.182

Table 6

Effective charges, effective radii, dissociation energies depending on interatomic distances of Cd-Sb NHO

Cd-Sb NHO	*Cd-Sb*					
Parameters	φ_1	φ_2	φ_3	φ_4	φ_5	φ_6
d_i(Å)	2.8	2.9	3.0	3.1	3.2	3.3
R_U^{Cd}(Å)	1.42	1.48	1.53	1.6	1.65	1.71
R_U^{Sb}(Å)	1.38	1.42	1.47	1.5	1.55	1.59
$\Delta q_i(\varphi_i)$	0.27	0.1	-0.06	-0.22	-0.4	-0.55
$D(\varphi_i)$ ev	2.061	1.989	1.922	1.859	1.800	1.746

Discussion of the results

As follows from the results presented in Tables 1-2, with the growth of interatomic distances, the dissociation energy of the corresponding chemical bonds decreases, and the redistribution of electron density in the interval of interatomic distances $3 \le d_i \le 3$in the structural varieties of Bi-Sb changes sign The structural varieties of *Bi-Cd* behave similarly, but already in other intervals $3.1 \le d_i \le 3.2$.

This means that chemical bonds can be both donor and acceptor under certain conditions. This confirms the experimentally established fact [3] that in compounds bismuth has different degrees of oxidation from -3 to +5.

The use of the obtained research results makes it possible to predict the shape of the liquidus, and therefore the type of melting and rearrangement of atoms in melts [8] of the resulting material.

Conclusions

1. The diagram of the distribution of *Bi-Cd-Sb* phase regions is constructed.
2. Isothermal sections of *Bi-Cd-Sb* at different temperatures were studied, which made it possible to divide the *Cd-Bi-Sb* ternary system into six ordered subsystems and consider the interatomic interaction from the standpoint of state diagrams and chemical bond.
3. The parameters of the chemical bond in the *Bi-Cd-Sb* ternary systems were calculated depending on the interatomic distances for various structural modifications.
4. The results obtained can be used in the development of technological modes of new materials based on *Bi-Cd-Sb*.

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Маник О. М., *канд. фіз.-мат. наук*[1]
Маник Т. О., *канд. фіз.-мат. наук*[2]
Білинський-Слотило В. Р., *канд. фіз.-мат. наук*[1]

[1] Чернівецький національний університет імені Юрія Федьковича,
вул. Коцюбинського 2, Чернівці, 58012, Україна;
e-mail: o.manyk@chnu.edu.ua, slotulo@gmail.com
[2] Військово-технічний університет ім. Ярослава Домбровського,
вул. ген. Сільвестра Каліського, 2, Варшава 46, 00-908, Польща
e-mail: tetjana.manyk@wat.edu.pl

ТЕОРЕТИЧНІ МОДЕЛІ ВПОРЯДКОВУВАНИХ СПЛАВІВ ПОТРІЙНИХ СИСТЕМ ТЕРМОЕЛЕКТРИЧНИХ МАТЕРІАЛІВ.

4. ХІМІЧНИЙ ЗВ'ЯЗОК ТА ДІАГРАМИ СТАНУ *Bi-Cd-Sb*

Розроблено комплексний підхід для побудови теоретичних моделей упорядковуваних сплавів потрійних систем на основі Bi-Cd-Sb.
Побудовано схему розподілу фазових областей та ізотермічні перерізи на основі проміжних бінарних сполук Bi-Cd, Bi-Sb, Cd-Sb в системі Bi-Cd-Sb.
Представлено розрахунки ефективних радіусів, перерозподілу електронної густини та енергії дисоціації нееквівалентних хімічних зв'язків в залежності від міжатомних віддалей в потрійній системі Bi-Cd-Sb. Бібл. 8, рис.4, табл. 6.

Ключові слова: теоретичні моделі, хімічний зв'язок, ефективні радіуси, енергія дисоціації, діаграми стану, нееквівалентні гібридні орбіталі (НГО).

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