

плавах реалізується більш високий ступінь впорядкованості атомів міді у порівнянні з чистою міддю, що приводить і до більш впорядкованого розподілу атомів алюмінію з найближчого оточення атомів міді.

**РЕЗЮМЕ.** Проведено рентгенодифракційне дослідження структури расплавов системи Al—Cu з содержанием 0, 14, 25, 30, 40 и 100 % ат. Cu при температурах вблизи линии ликвидуса. Методом обратного Монте-Карло, с использованием экспериментальных кривых структурного фактора (СФ), реконструированы структурные модели, согласно которым рассчитаны парциальные характеристики локального упорядочения атомов в расплавах. Установлено, что существование предпика на кривых СФ есть следствие корреляции в положении атомов меди на расстояниях 4.7 Å, которые преимущественно реализуются в политетраэдрических кластерах икосаэдрического типа, существенно обогащенных, в сравнении с составом расплава, атомами меди. Характер упорядочения атомов в кластерах определяет структуру и свойства расплавов Al—Cu. Заметное сокращение межатомных расстояний коррелирует с характером концентрационной зависимости термодинамических свойств расплавов, которые указывают на существенные отрицательные отклонения от идеальности.

**SUMMARY.** Structure of Al—Cu liquid alloys with 0,14,25,30,40 % at. Cu has been studied by X-ray diffraction at temperatures near liquidus. The structural models of liquid alloys have been reconstructed by means of Reverse Monte-Carlo method with use of experimental curves of the structural factor (SF). The partial characteristics of local ordering of atoms in alloys were calculated from these models. It have been established, that the prepeak on the experimental SF curves is caused by a correlation in arrangement of copper at a distances of about 4.7 Å atoms in polytetrahedral clusters of icosahedral type. These clusters more enriched atoms of copper in comparison with melt composition. Character of atomic ordering in clusters defines structure and properties of liquid Al—Cu alloys. The significant decreasing of interatomic distances corre-

lates with concentration dependence of thermodynamic properties of melts that points on deviations from ideality.

1. Shechtman D., Blech I., Gratias D., Cahn J.W. // Phys. Rev. Lett. -1984. -**53**, № 20. -P. 1951—1954.
2. Grushko B., Wittmann R., Urban K. // Phil. Mag. Letters. -1993. -**67**, № 1. -P. 5—33.
3. Баталин Г.И., Белобородова Е.А., Казимиров В.П. Термодинамика и строение жидких сплавов на основе алюминия. -М.: Металлургия, 1983.
4. Найдич Ю.В., Еременко В.Н., Кириченко Л.Ф. // Журн. неорганич. химии. -1962. -**7**, вып. 2. -С. 333—336.
5. Bretonnet J.-L., Auchet J., Gasser J.-G. // J. Non-Cryst. Solids. -1990. -**117—118**, № 1. -P. 395—398.
6. Диаграммы состояния двойных металлических систем. Справ.: в 3-х т. / Под ред. Н.П. Лякишева. -М.: Машиностроение, 1996. -Т. 1.
7. Brillo J., Bytchkov A., Egry I. et al. // J. Non-Crystalline Solids. -2006. -**352**, № 38—39. -P. 4008—4012.
8. Роук А.С., Самсонников А.В., Казимиров В.П., Сокольский В.Э. // Металлы. -2006. -№ 3. -С. 24—31.
9. Ильинский А.Г., Слюсаренко С.И., Слуховский О.И., Кабан И.Г. // Металлофиз. новейших техн. -2001. -**23**, № 8. -С. 1127—1136.
10. Vahvaselka K.S. // Phys. stat. sol. (a). -1984. -**83**, № 1. -P. 103—111.
11. McGreevy R.L., Pusztai L. // Mol. Simulation. -1988. -№ 1. -P. 359—367.
12. McGreevy R.L. // J. Phys.: Condens. Matter. -2001.-**13**, № 46. -P. R877—R913.
13. Роук А.С., Казимиров В.П., Сокольский В.Э. // Журн. структур. химии. -2004. -**45**, № 4. -С. 682—691.
14. Медведев Н.Н. Метод Вороного—Делоне в исследовании структуры некристаллических систем. -Новосибирск: НИЦ ОИГГМ СО РАН, Изд-во СО РАН, 2000.
15. Наберухин А.И. // Журн. структур. химии. -1981. -**22**, № 6. -С. 62—80.
16. Киттель Ч. Статистическая термодинамика. -М.: Наука, 1977.
17. Крипякевич П.И. Структурные типы интерметаллических соединений. -М.: Наука, 1977.

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## **KDP CRYSTALS MODIFIED WITH ORGANIC MOLECULES: LUMINOPHORE EMBEDDING CRITERATION**

Experimental study results on the conditions of KDP single crystal growing doped by organic luminophors have been presented. A possible coherent conjugation scheme for crystal-chemical parameters of KDP lattice with some

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organic luminophores has been shown. Basing on quantum-chemical calculations of luminophore average molecular radii, consideration of their dissociated ion charges as well as on experimental results of the molecules entering into crystals, the coherent criterion of the built-in molecule conjugation (CCC) with the lattice points has been proposed. That approach can be proposed for modifying various water-soluble crystals with organic luminophores.

It is known that crystals of inorganic compounds grown from aqueous solutions can be doped in the course of growing with molecules of organic substances being dissolved in the mother solution [1]. Those crystals modified with organic compounds gain new physical and chemical properties and can be applied in various fields of science and engineering. Doping of KDP crystals with organic luminophores allow to develop the scintillation detectors of ionizing radiation or solid elements for dye lasers. In this work, the experimental results are presented on KDP crystals doped with luminophores on the base of naphthalic and perylene tetracarboxylic acid derivatives, phthalocyanines, and some naphthalene derivatives as well as generalized literature data on building-in of various organic substances into KDP crystal lattice [2–4].

The KDP single crystals were grown by decreasing temperature from 50 to 40 °C. The solution supersaturation during the growing was provided to be at least 5 %. Organic luminophores were introduced as aqueous solutions of luminophores with KDP into mother liquid at the crystal growing temperature. The concentration of doping luminophore was varied from  $10^{-1}$  to  $10^{-4}$  wt %. No influence of luminophore admixtures on the solution acidity (pH) or saturation temperature was observed. Stoichiometric solutions with pH 4.0–4.1 were used. The luminophores fluorescing in KDP solution under UV radiation were chosen for the study. Emission spectra of solutions and crystals were measured using Cary Eclips and Hitachi F4010 spectrofluorimeters. The building-in of luminophores into the KDP lattice was judged from the crystal fluorescence. The structures of organic luminophores used in our experiments as well as of compounds used by other authors to dope KDP crystals are shown in table 1. In all cases, the building-in of dye molecules into KDP crystal lattice was proven by the absorption or fluorescence electron spectroscopy [2–4]. The quantum-chemical optimization of molecular geometry was provided using the AMI method (MOPAC 2000 software [8, 9]). The average molecule radius was determined as the geometrical mean of ellipse axes using the formula  $R=1/2\sqrt{abc}$ , where  $a$  is the segment  $[a]$  length between the most distant of the molecule atoms (molecular "length");  $b$ , the segment  $[b]$  length between the most distant atoms in any direction perpendicular to segment  $[a]$  (molecular "width");  $c$ , the segment  $[c]$  length between the most distant atoms in the direction

perpendicular to the plane defined by segments  $[a]$  and  $[b]$  (molecular "height"). When calculating the segment lengths, the Van der Waals atomic radii were taken into account.

As is shown in [3, 5], the organic dye admixtures enter selectively in various segments of a growing KDP crystal. Such micro-impurity distribution can be explained by charge state of the growing crystal faces. In [6], basing on experimental data on X-ray diffraction from KDP growing faces at small angles of incidence, it is shown that  $K^+$  ions emerge on the face  $[101]$ , and alternate rows of  $K^+$  and  $H_2PO_4^-$  ions — on the face  $[100]$ . As a result, the  $[101]$  face has a total positive charge while  $[100]$  is neutral. In aqueous solution, the organic luminophore molecules dissociate forming both negative and positive ions, which tend to be adsorbed on opposite charged crystal faces. The spatial structures of luminophore molecules differ too much from KDP unit cell; however, when the difference between interatomic distances on the crystal face surface and in the organic molecules is negligible, the local stoichiometric conformity is possible, and the molecule can be captured by the growing face [7].

The water solutions of KDP and luminophores 1, 2, 6, 10, 11 investigated by us fluoresce in 350 to 600 nm range. On the contrary, the KDP single crystals grown with luminophores 1, 2, 6 admixtures, show no fluorescence as well as the crystals grown without fluorescent substances additives (with a micro-impurity content at most  $1 \cdot 10^{-4}$  wt %). Thus, we have concluded, that 1, 2, 6 do not enter the KDP lattice. The crystals grown with luminophores 10 and 11 fluoresce in 580 and 400 nm range, respectively.

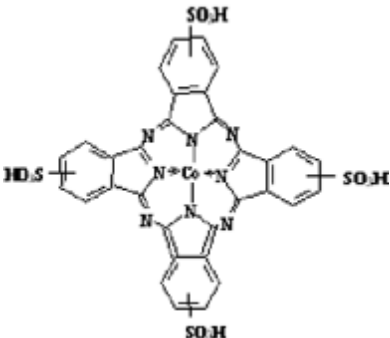
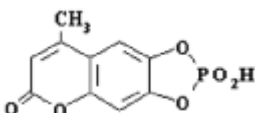
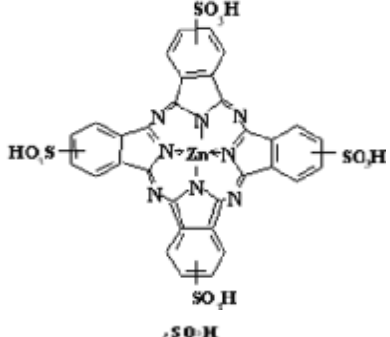
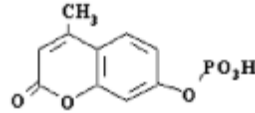
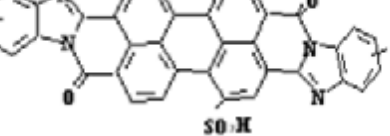
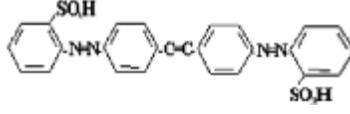
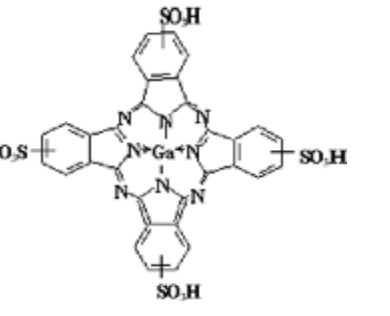
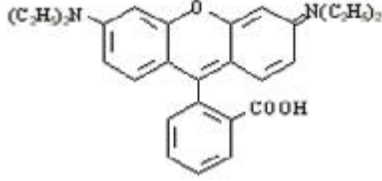
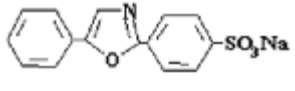
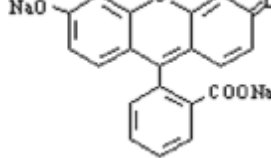
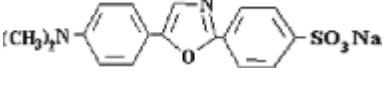
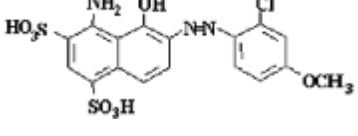
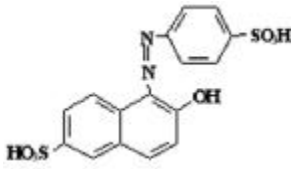
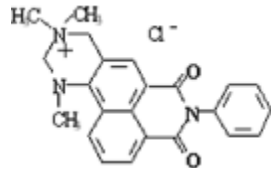
The interatomic distance comparison between  $K^+$  ions in pyramid face  $[101]$  with geometrical molecular parameters of 10 and 11 has shown that the distance between negatively charged dissociated sulfonic acid groups of luminophores differ from that between  $K^+$  ions in the direction  $[011]$  by less than 5 %. The luminophores 1 and 2 molecules, which are not built-in, are similar in size to those of 10 and 11, but differ therefrom because contain only one sulfonic acid group. Thus, it follows from the experimental results that the negative ions of the dissociated luminophore molecules enter the KDP lattice in positively charged pyramid growth segment only when the organic molecule contains at least two  $SO_3^{2-}$  functional groups in its structure. The  $SO_3^{2-}$  groups must be located in the

Table 1

## Geometry and charge density of dye molecules

Compound	Dye Formula	Geometrical parameters for anionic/cationic forms, Å	Compound	Dye Formula	Geometrical parameters for anionic/cationic forms, Å
1		$a=8.7$ $b=7.0$ $c=2.4$ $r=2.6$ $Z/r=-0.38$	10		$a=14.6$ $b=9.8$ $c=4.3$ $r=4.3$ $Z/r=-0.46$
2		$a=10.6$ $b=8.1$ $c=4.0$ $r=3.5$ $Z/r=-0.29$	11		$a=12.4$ $b=10.5$ $c=3.2$ $r=3.7$ $Z/r=-0.54$
3		$a=14.4$ $b=8.5$ $c=4.3$ $r=4.1$ $Z/r=-0.25$	12		$a=9.9$ $b=6.1$ $c=3.8$ $r=3.1$ $Z/r=-0.65$
4		$a=19.5$ $b=8.4$ $c=6.4$ $r=5.1$ $Z/r=-0.20$	13		$a=16.2$ $b=10.5$ $c=6.8$ $r=5.2$ $Z/r=-0.38$
5		$a=11.0$ $b=7.4$ $c=1.8$ $r=2.6$ $Z/r=+0.38$	14		$a=14.6$ $b=9.0$ $c=4.4$ $r=4.2$ $Z/r=-0.71$
6		$a=10.6$ $b=8.1$ $c=4.0$ $r=3.5$ $Z/r=-0.29$	15		$a=14.5$ $b=9.4$ $c=5.1$ $r=4.4$ $Z/r=-0.45$
7		$a=14.7$ $b=7.2$ $c=4.4$ $r=3.9$ $Z/r=+0.51$	16		$a=28.7$ $b=5.7$ $c=6.0$ $r=5.0$ $Z/r=-0.81$
8		$a=10.9$ $b=7.4$ $c=4.0$ $r=3.4$ $Z/r=-0.14$	17		$a=21.4$ $b=9.1$ $c=2.9$ $r=4.1$ $Z/r=-0.49$
9		$a=19.5$ $b=8.4$ $c=6.4$ $r=5.1$ $Z/r=-0.2$			

Continue table 1

Compound	Dye Formula	Geometrical parameters for anionic/cationic forms, Å	Compound	Dye Formula	Geometrical parameters for anionic/cationic forms, Å
18		$a=18.5$ $b=18.5$ $c=2.9$ $r=5.0$ $Z/r=-0.79$	24		$a=9.0, b=5.5$ $c=3.1$ $r=2.7$ $Z/r=-0.37$
19		$a=18.5$ $b=18.5$ $c=2.9$ $r=5.0$ $Z/r=-0.79$	25		$a=11.1, b=7.9$ $c=3.7$ $r=3.4$ $Z/r=-0.58$
20		$a=21.2$ $b=9.3$ $c=4.0$ $r=4.8$ $Z/r=-0.83$	26		$a=24.3, b=7.6$ $c=4.0$ $r=4.5$ $Z/r=-0.44$
21		similar to 19 $Z/r=-0.59$	27		$a=13.7$ $b=12.1$ $c=5.7$ $r=4.9$ $Z/r=-0.20$
22		$a=13.6, b=6.2$ $c=1.6, r=2.5$ $Z/r=-0.39$	28		$a=9.7$ $b=9.7$ $c=5.6$ $r=4.0$ $Z/r=-0.50$
23		$a=5.8, b=6.5$ $c=3.0, r=3.4$ $Z/r=-0.30$	29		$a=17.0, b=7.9$ $c=3.8$ $r=4.0$ $Z/r=-0.50$
			30	$\text{CH}_3\text{SO}_3^-$	$a=3.48, b=3.34$ $c=3.25, r=1.68$ $Z/r=-0.60$
			31	$\text{C}_2\text{H}_5\text{SO}_3^-$	$a=4.69, b=3.23$ $c=3.18, r=1.82$ $Z/r=-0.55$
			32		$a=14.6$ $b=7.4$ $c=4.6$ $r=4.0$ $Z/r=-0.50$
			33		$a=14.3$ $b=8.3$ $c=3.8$ $r=3.8$ $Z/r=+0.26$

structure in such manner that the charge distribution thereon conforms to periodic distribution of  $K^+$  charges in growing plane [101].

It is necessary to note that the planar molecule of a luminophore may be located within limits of several crystal unit cells. In this case, the coherent conjugation of crystal lattice parameters with luminophore molecular anion is provided. The luminophore may be adsorbed by the growing plane and disposed within the interplanar space during crystal face [101] layer-by-layer growing.

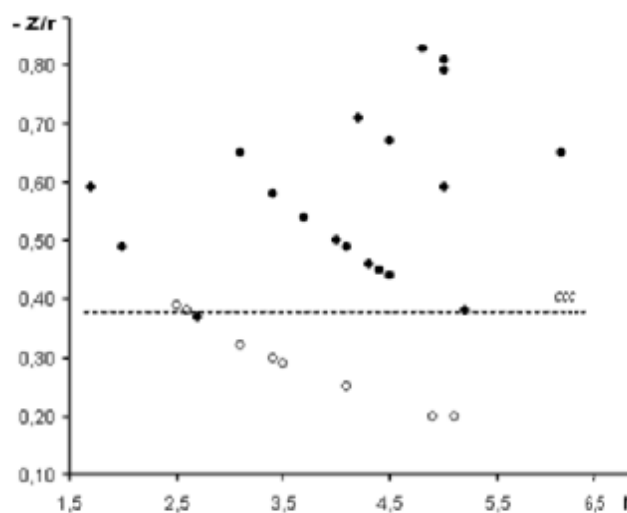
Consideration of the results obtained as well as literature data shows that molecules of cationic and neutral dyes do not build-in into KDP crystal lattices. As to anionic dyes, their building-in is observed mainly for two-, three-, and four-charged anions. Singly charged anionic dyes may behave in different manners, depending on the particle size. So, large-size single-charged anions do not build-in in KDP crystal grate. At the same time, anions of small average radius  $r$ , for example, cumarin derivatives 24 and 25 or alkylsulfates 30 and 31, may be absorbed in crystals.

Unfortunately, at present, there is no unified criterion, which would define the capability of an organic molecule entry into crystal lattice and provide a provisional selection of luminophores without obligatory experimental examination of their absorption in crystals. Obviously, this criterion should take into account not only the anion charge and size, but also opportunity of coherent conjugation between the crystal lattice parameters and the arrangement of the charged groups in the luminophore molecule.

The probability of organic anion building-in into a lattice depends on potential of an electric field created by it, as well as on potential of the field in the lattice layer, where building-in of an ion takes place. Therefore, it is logical to assume that a criterion for estimation of building-in capability should have the same nature. Taking into account all the above, we have proposed the coherent conjugation criterion (CCC) equal to the dye ion charge/average radius. This criterion has dimension of potential of electric field created by this ion:

$$CCC = -Z/r. \quad (1)$$

Figure shows the dependence of CCC on the parameter  $r$  calculated by us using quantum-chemical methods (table 1). Black circles mark organic ions, which were included in lattice KDP, the cases when introduction of anions in a lattice was not observed are marked by open circles. As follows from these



Dependence of luminophore introduction into crystals from  $-Z/r$  parameter and its average radius.

data, the building-in of organic ions into KDP crystals is observed if the CCC value exceeds  $0.38 \text{ e}/\text{\AA}$ . The deviation from that value does not exceed 2.6% for all studied dyes. In our opinion, the cause of deviations (compounds 1, 13, 22 with  $CCC=0.38$  to  $0.39$  do not build-in, while compound 24 with  $CCC=0.37$  builds-in), consists in that the parameter  $r$  is estimated roughly and electron density in organic anions is distributed inhomogeneously.

It is obvious that CCC parameter is also defined by the crystal lattice type, ion charge and size of ions forming it. That is why the value 0.38 is typical only for KDP crystals and will be different at doping crystals of other salts by organic anions.

The coherent conjugation criterion also can be used for more detailed analysis of dye molecules building-in capabilities into salt crystal lattices. Thus, for example, proceeding from CCC value, we can define the limiting ion average radius ( $R_{lim}$ ), above which the adsorption becomes impossible.  $R_{lim}$  value comes to  $\sim 2.6 \text{ \AA}$  for single charged ions, and  $5.3, 7.9 \text{ \AA}$  for two- and three-charged ions, respectively.

In case of organic anions capable of step-by-step dissociation, the CCC use allows to estimate the minimal charge necessary for the ion building-in into KDP crystal lattice and then to calculate pH of solution at which absorption of the anion will take place. Thus, for adenosine di-, three-, and tetraphosphate ions, the minimal charge must be at least  $-2e$  (table 2). Besides  $R_{lim}$  value, limiting the built-in ion size, the presence of another limiting parameter  $R_{max}$  can be supposed that is associated with the interlayer distance in the KDP crystal lattice. If, in the multi-charged ions case,  $R_{lim} > R_{max}$ , the dye ions will not

Table 2

Molecules sizes and CCC values for adenasynepolyphosphates anions

Ion	Ion charge	<i>a</i>	<i>b</i>	<i>c</i>	<i>r</i>	<i>Z/r</i>
ADP	1	12.35	6.96	6.13	4.04	0.25
	2	13.23	6.89	4.98	3.84	0.52
ATP	1	11.21	10.56	6.16	4.50	0.22
	2	13.55	4.55	6.48	3.68	0.54
	3	14.78	7.13	6.24	4.35	0.69
AQP	1	16.27	7.71	5.3	4.36	0.23
	2	16.05	7.73	4.89	4.23	0.47
	3	16.20	4.48	6.52	3.90	0.77
	4	13.89	8.49	7.95	4.89	0.82

build-in into the lattice, despite of  $CCC > 0.38$ . However, at present, the analysis of disposable anionic dyes does not allow to determine the  $R_{max}$  value.

Finally, it should be noted that the suggested parameter CCC is close in dimension to the Semenchenko parameter of the generalized moment. However, this parameter is used to describe ionic and metal liquids as well as for thermodynamic calculations of the surface phenomena involving ions at the liquid/gas interface [10].

Thus, the adsorption of organic luminophore anions by KDP crystal growing faces is limited both by the molecular spatial parameters and charge distribution in the molecular dissociation products. The coherent conjugation criterion (CCC) has been proposed equal to organic anion charge/average radius ratio. It has dimension of electric potential created by this ion. The CCC parameter is also defined by crystal lattice type, charges and sizes of ions forming it. Thus, CCC will be different for crystals of different salts. For KDP crystals, this value is 0.38.

РЕЗЮМЕ. Представлено результати експериментальних досліджень умов вирощування монокристалів КДП, легованих органічними люмінофорами. Подано

схему можливого когерентного спряження кристалохімічних параметрів ґратки КДП з деякими органічними люмінофорами. На підставі квантово-хімічних розрахунків середнього радіусу молекул люмінофорів, аналізу величин зарядів їх дисоційованих йонів, а також експериментальних результатів щодо входження молекул у кристали запропоновано критерій когерентного спряження (ККС) молекули, яка входить у вузли ґратки. Даний підхід може бути запропонований для модифікування органічними люмінофорами різних водорозчинних кристалів.

РЕЗЮМЕ. Представлены результаты экспериментальных исследований условий выращивания монокристаллов КДП, легированных органическими люминофорами. Показана схема возможного когерентного сопряжения кристаллохимических параметров решетки КДП с некоторыми органическими люминофорами. На основе квантово-химических расчетов усредненного радиуса молекул люминофоров, анализа величин зарядов их диссоциированных ионов, а также экспериментальных результатов по вхождению молекул в кристаллы предложен критерий когерентного сопряжения встраиваемой молекулы с узлами решетки. Данный подход может быть предложен для модифицирования органическими люминофорами различных водорастворимых кристаллов.

1. Buckley G. Crystal Growth. -Moscow: IL, 1954 (in Russian).
2. Kahr B., Gurney W. // Chem. Rev. -2001. -**101** -P. 893.
3. Hirota S., Miki H., Fukui K. et al. // J. Cryst. Growth. -2002. -**235**. -P. 541.
4. Subramong J., Jung S., Kahr B. // Ferroelectrics. -1997. -**191**. -P. 292.
5. Eryomina T.A., Kusnetzov V.A., Okhrimenko T.M. et al. // Kristallografia. -1996. -**41**. -P. 717.
6. De Vries S.A., Goedtkindt P., Bennett S.L. et al. // Phys. Rev. Lett. -1998. -**80**. -P. 2229.
7. Whetstone J. // Chem. Soc. -1956. -№ 12. -P. 4841.
8. Dewar M.J.S., Zoebisch E.G., Healy E.S., Stewart J.P.P. // J. Amer. Chem. Soc. -1985. -**107**. -P. 3902.
9. Stewart J.P.P. МОРАС 2002. -Tokyo: Fujitsu Ltd., 2002.
10. Semenchenko V.K. Surface Phenomena in Metals and Alloys. -Kyiv: Nauk. Dumka, 1957 (in Russian).

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