Тарас Михайлович Брик
Іван Іванович Клевець

Домішкові іони на основній поверхні льоду: Дослідження методом першопринципної молекулярної динаміки

Роботу отримано 22 грудня 2008 р.

Затверджено до друку Вченою радою ІФКС НАН України

Рекомендовано до друку відділом комп'ютерного моделювання багаточастинкових систем

Виготовлено при ІФКС НАН України

Національна академія наук України

ІНСТИТУТ
ФІЗИКИ
КОНДЕНСОВАНИХ
СИСТЕМ

ICMP–08–21E

T.Bryk, I.Klevets

SOLUTE IONS AT THE ICE BASAL SURFACE: AB INITIO MOLECULAR DYNAMICS STUDY

ЛЬВІВ

УДК: 538.971; 539.21; 544.272

PACS: 61.43.Bn, 61.72.-y, 68.43.Bc

Домішкові іони на основній поверхні льоду: Дослідження методом першопринципної молекулярної динаміки

Т.Брик, І.Клевець

Анотація. Поведінка іонів Na^+ та Cl^- в об'ємному гексагональному льоді та на основній поверхні льоду досліджується методом першопринципної молекулярної динаміки. Аналізуються парні та тричастинкові функції розподілу з метою визначення рівноважних позицій домішкових іонів у об'ємі гексагонального льоду. Для поверхні льоду отримано, що іон Na^+ є домішкою заміщення у верхньому поверхневому шарі, тоді як для випадку іона Cl^- на поверхні льоду спостерігалась сильна поляризація поверхневих молекул води без проникнення іону в поверхневий шар.

Solute ions at the ice basal surface: Ab initio molecular dynamics study

T.Bryk, I.Klevets

Abstract. Behavior of Na^+ and Cl^- ions in the bulk of Ih ice and at the basal surface of ice is studied by ab initio molecular dynamics. The pair distribution functions as well as bond-angle distributions are analyzed in order to estimate the equilibrium positions of solute ions in the bulk hexagonal ice. At the ice basal surface we have found the equilibrium position for Na^+ ion to be a substitutional impurity in the top surface layer, while Cl^- ion polarized the surface water molecules, however did not penetrate the top surface layer.

Подається в Chem. Phys. Lett.
Submitted to Chem. Phys. Lett.

1. Introduction

It is well known, that in nature the impurities at low temperatures are expelled from the bulk of crystalline ice, while close to the melting temperature the solute ions facilitate the surface melting [1]. Recently the interest to the issue of solute ions in bulk crystalline ice and at the ice surface was revived in connection with the studies of ion transfer across the ice/water interface and the origin of the Workman-Reynolds effect [2]. Experimental and theoretical studies of the ice/water interface are of great interest because of their fundamental presence in nature and importance in chemical, biological, environmental and atmospheric processes. Especially fruitful are the simulation studies of the ice/water interfaces [3,4] based on realistic atomistic models of molecules and molecular interactions.

Many fundamental phenomena occurring on the ice surface and ice/water interface still have not been explained on a microscopic level. More than fifty years ago, Workman and Reynolds [2] claimed to observe a massive charge separation occurring during the freezing of dilute aqueous solutions, and imputed a relevance to thunderstorm electricity. Only recently these experiments have been duplicated successfully [5]. However, the observed emergence of the freezing potential during the freezing of weak electrolyte solutions still has not been clearly explained on a model level, although some attempts were made within kinetic models [6].

A number of classical molecular dynamics simulations were focused on estimation of the free energy of ion transfer across the ice/water interface [7–9] in order to explain a selectivity in positive/negative ion hydration at the ice/water interface. The problem of classical MD simulations of the ions in the ice/water system is in absence of correct interaction potentials between the solute ions and water molecules in bulk ice phase. For the case of SPC/E model of water molecules used in [7,8] the inconsistency in the "bare"charge of solute ions ±1 and effective charges on atoms in forming ice structure water molecules led to huge number of defects when the ions were put into the ice crystal. Similarly, a strong melting of ice surface was observed in classical MD simulations of solute ions placed at the ice surface of SPC/E molecules.

Only ab initio MD simulations can correctly reflect all the polarization effects, changes in molecular geometry and local hydration structure of ions in bulk hexagonal ice or in the interfacial regions. Recently there was an attempt to calculate from the first principles the energy of substitutional deffects in hexagonal ice for Na^+ and Cl^- ions [11]. The aim of this study is to apply the ab initio simulations for estimation of equilibrium positions and local hydration structure of solute ions in the bulk ice as well as on the ice basal surface.

2. Simulation Method

We simulated ions in bulk ice by Car-Parrinello molecular dynamics [12] in NVT ensemble using 3D periodic boundary conditions. The simulation box contained 96 H_2O molecules in hexagonal proton-disordered ice phase plus a single solute ion. Initial configuration for crystalline ice was taken from previous classical MD simulations and subsequent equilibration over 2 ps was performed. Since the electronic density in bulk ice is far from uniform we used the generalized gradient approximation for energy functional in PBE form [13]. The ultrasoft Vanderbilt pseudopotentials and the cut-off energy of 25 Ry were used.

The basal ice surface with Na^+ and Cl^- ions was simulated in the NVT ensemble at the temperature of 160 K. The system consisted of 120 H_2O molecules in the ice phase and almost half of the box (Δz 15Å) contained the vacuum region. The solute ions were initially placed in the vacuum region at the distance approximately 5Åfrom the opposite surfaces, respectively. The surface simulations were performed with the VASP package, and we made use of ultrasoft Kresse-Hafner pseudopotentials [14] with cut-off energy of 20.79 Ry and the same energy functional as in the bulk case.

3. Results and Discussion

3.1. Hydration of ions in bulk ice

Ab initio molecular dynamics permits to obtain a stable structure of water molecules around solute ions in the crystalline ice. It is obvious, that the correct reproduction of polarization effects leads to essentially smaller number of defects of crystal structure, than it was observed in the classical molecular dynamics simulations with the rigid SPC/E model of water molecules in ice. We did not observe the local melting of crystal structure around the Cl^- ion in contrast to classical simulations.

Partial pair distribution functions ion-water molecules are shown in Fig.1. Main peaks of partial pair distribution functions permit to estimate average distances for nearest neighbors in hexagonal ice for ions Na^+ 2.3Å, and for Cl^- ion ~2.05Å. It is seen, that the effects of molecular polarization (reorientation of water molecules) is much stronger in the case of Cl^- ion, when the protons are reoriented towards the impu-

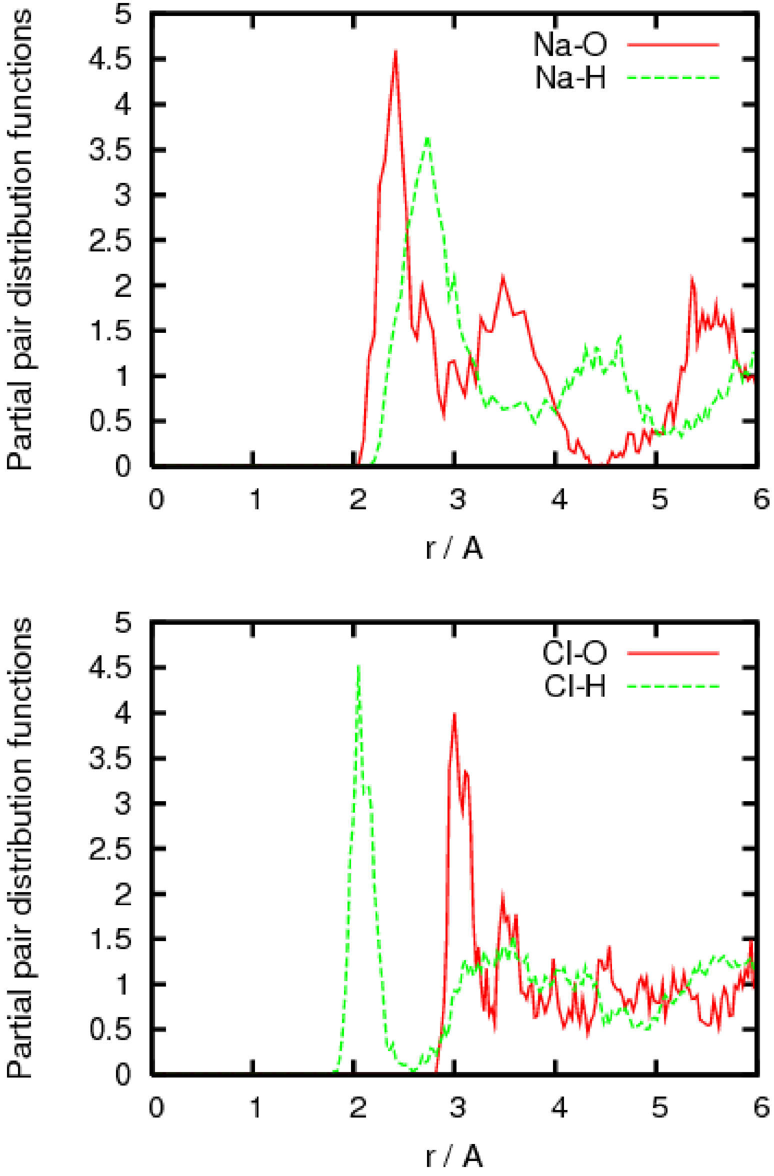

Рис. 1. Pair distribution functions for Na^+ and Cl^- in bulk hexagonal ice.

rity ion. From the partial pair distribution functions we estimated the running coordination numbers for solute ions in hexagonal ice (Fig.2). The analysis of running coordination numbers reveals, that there are five nearest neighbor water molecules for Na^+ in hexagonal ice, while for the case of Cl^- ion there are only four nearest water molecules, which are reoriented by their protons towards the negative ion. This is different from what was observed in classical molecular dynamics with SPC/E rigid model of water molecules. The correct treatment of electron density and polarization effects leads to correct hydration structure of Cl^- ion obtained by means of ab initio simulations.

The analysis of local hydration structure of ions in hexagonal ice is not complete without three-particle angle-dependent distribution functions. These bond-angle distribution functions are shown in Fig.3 for two cases, when the impurity ions are located between two Oxygens (red curves in Fig.3), and when the molecular OH vector oriented with respect to the impurities (green dashed curves). It is seen from the Fig.3, that for the Cl^- ions the water molecules reorient towards the ion, while for the case of Na^+ ion the molecules are partially ordered with the almost direct angle H-O-Na.

3.2. Behavior of solute ions on the ice basal surface

The ions were initially placed approximately at the distance of 5Å from the surface, then we allowed the ions to approach to the interface, and only after that started the production runs. We have observed completely different behavior of Na^+ and Cl^- ions at the ice basal plane in the ab initio simulations. The main stages of their behavior are shown as the snapshots of relevant configuraions in Figs. 4 and 5. By approaching the ice surface the Na^+ ion penetrates the top surface layer and pushes out one of the water molecules beyond the surface layer. In fact, this mechanism supports the idea of substitutional hydration of Na^+ ion in ice proposed in [11]. For the case of Cl^- ion we observed a completely different behavior. The Cl^- ion was not allowed to penetrate the top surface layer - it polarized the top surface water molecules and found some local energy minimum, which is almost above the center of hexagonal hole (see Fig.5). One of the surfacewater molecules left its position at the surface, that implies, that after a long period of time the Cl^- ion can also take a position in the surface layer making a substitutional defect as in the case of Na^+ ion.

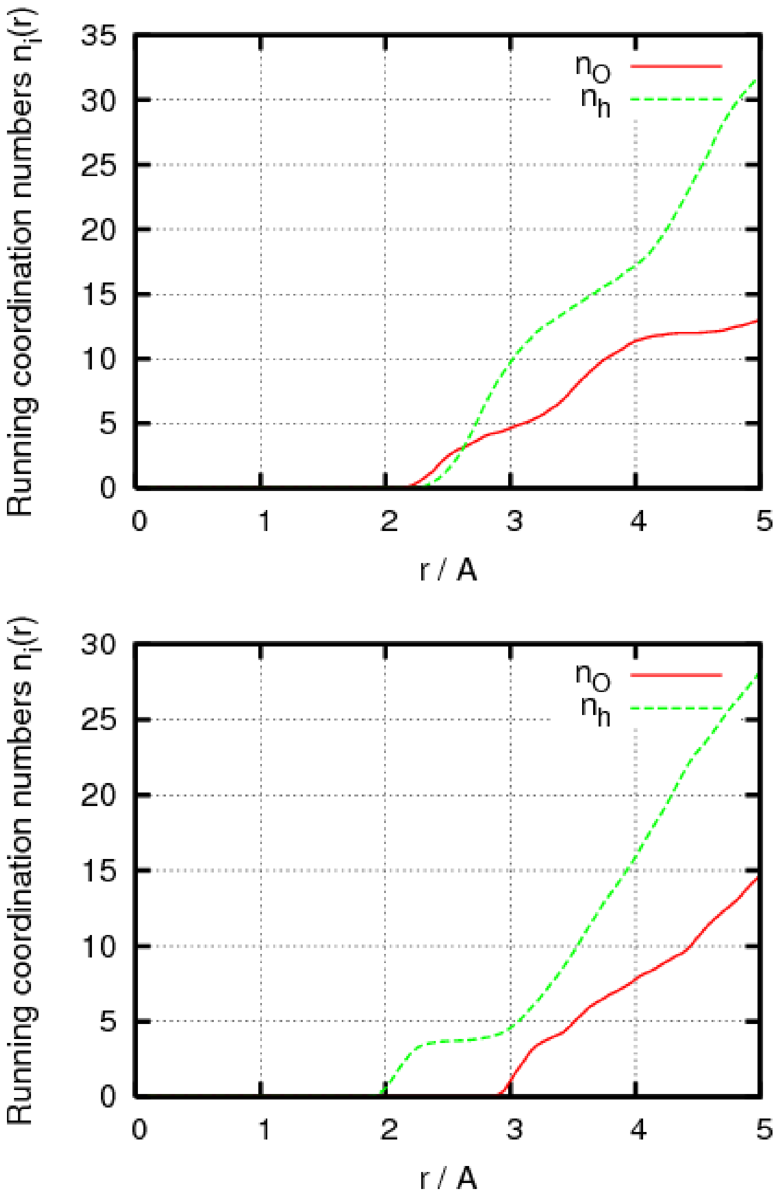

Рис. 2. Running coordination numbers for Na^+ and Cl^- in bulk hexagonal ice.

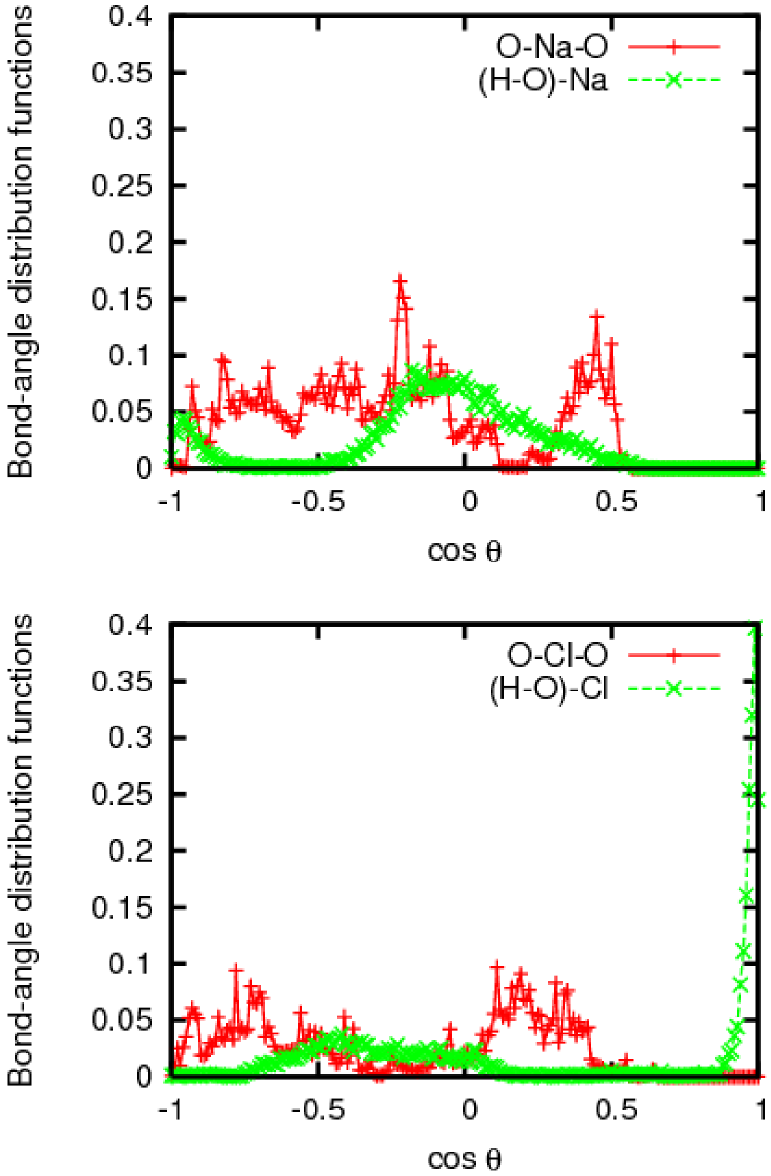

Рис. 3. Bond-angle distribution functions for Na^+ and Cl^- in bulk hexagonal ice.

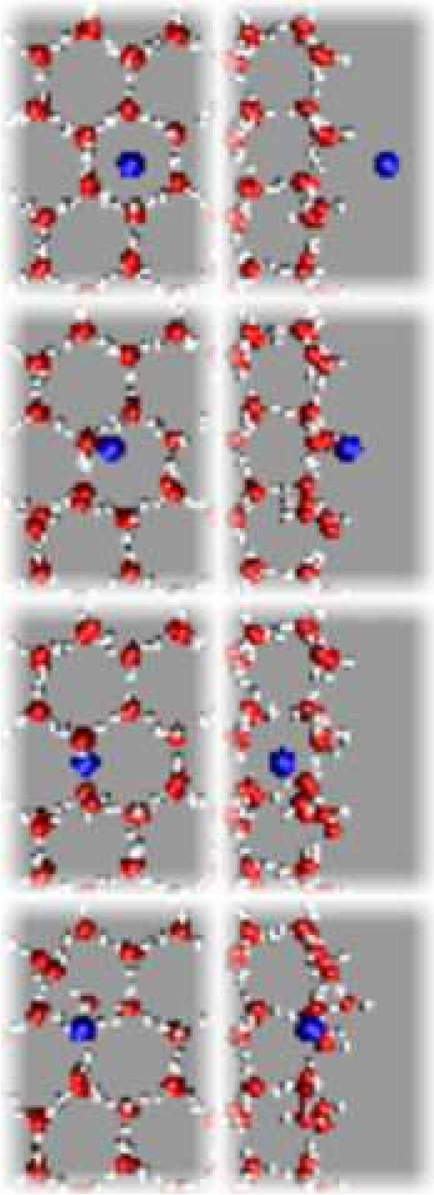

Рис. 4. Snapshots of configurations simulated in ab initio molecular dynamics for key positions of Na^+ ion at the ice basal surface.

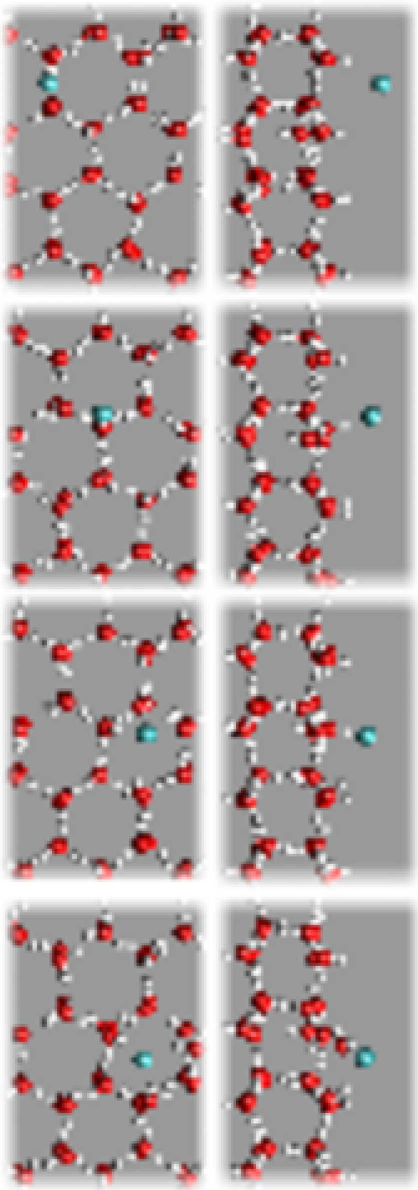

Рис. 5. Snapshots of configurations simulated in ab initio molecular dynamics for key positions of Cl^- ion at the ice basal surface.

4. Conclusions

In this study we investigated by ab initio MD computer simulations the behavior of Na^+ and Cl^- ions in bulk ice and at the ice basal surface. The first principle simulations permit to take correctly into account structural and electronic polarization effects in crystalline ice and at the ice surface. We have shown, that the equilibrium locations of solute ions correspond configurations with the four nearest water molecules oriented by their protons toward the Cl^- ion, while for the case of Na^+ ion there are five nearest water molecules. The water molecules around Na^+ ion are reoriented in such a way, that OH bonds form approximately direct angles with the directions Oxygens-Na^+. These results give more precise understanding of hydration structure of solute ions in crystalline ice, than it would be possible to obtain by classical molecular dynamics.

For the case of solute ions at the ice basal surface we have found, that the Na^+ ion has preferable location inside the top surface layer, and it pushes out one of the water molecules from its lattice site by replacing it. For the case of Cl^- ion we did not observe the penetration of the ion inside the surface layers. The Cl^- ion strongly polarized the surface water molecules by reorienting their protons toward the ion, making perhaps a local minimum of potential energy for the Cl^- ion. Having the equilibrium positions of the ions Na^+ and Cl^- at the ice basal surface we will focus next our studies on estimation of hydrataion energy from the first principle simulations.

Acknowledgements

This research was supported by the RFFR-NASU Joint Research Program under Grant No. 05/2008. The calculations were performed at the Supercomputer Center of Kiev National Technical University using the ab-initio total-energy and molecular dynamics program VASP (Vienna *ab-initio* simulation program) developed at the Institute für Materialphysik of the Universität Wien [15–17].

Література

1. V.F. Petrenko, R.W. Whitworth. Physics of Ice. Oxford, University Press, 1999.
2. E.J. Workman, and S.E. Reynolds, Phys. Rev., 78, 254 (1950).
3. T. Bryk, and A.D.J. Haymet, J. Chem. Phys., 117, 10258 (2002)
4. T. Bryk, and A.D.J. Haymet, Mol.Simul., 30, 131 (2004)
5. P.W. Wilson, A.D.J. Haymet. J. Phys. Chem. B, 112, p.11750 (2008).
6. V.L. Bronshteyn, A.A. Chernov. J. Cryst. Growth, 112, p.129 (1991).

7. E.J. Smith, T. Bryk, and A.D.J. Haymet, J. Chem. Phys., 123, 034706 (2005)
8. A.D.J. Haymet, T. Bryk, and E.J. Smith, in *Ionic Soft Matter: Modern Trends in Theory and Applications*, Eds. D.Henderson, M.Holovko and A.Trokhymchuk (Springer, Dordrecht, 2005)
9. E.J. Smith, T. Bryk, and A.D.J. Haymet, J. Chem. Phys., 126, 237102 (2007)
10. T. Bryk, and A.D.J. Haymet, J.Mol.Liq., 112, 47 (2004)
11. P.Feibelman, Phys.Rev.B, 75, 214113 (2007)
12. CPMD, Copyright IBM Corp 1990-2006, Copyright MPI f№r Festkörperforschung Stuttgart 1997-2001.
13. J.P. Perdew, K.Burke, M.Ernzerhof, Phys.Rev.Lett. 77, 3865 (1996)
14. G.Kresse and J.Hafner, J.Phys.:Cond.Matt., **6**, 8245 (1994).
15. G.Kresse and J.Hafner, Phys. Rev.B 47, 558 (1993); ibid. 49, 14251 (1994).
16. G.Kresse and J.Furthmüller, Comput. Mat. Sci. 6, 15 (1996).
17. G.Kresse and J.Furthmüller, Phys. Rev.B 54, 11169 (1996).

CONDENSED MATTER PHYSICS

The journal **Condensed Matter Physics** is founded in 1993 and published by Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine.

AIMS AND SCOPE: The journal **Condensed Matter Physics** contains research and review articles in the field of statistical mechanics and condensed matter theory. The main attention is paid to physics of solid, liquid and amorphous systems, phase equilibria and phase transitions, thermal, structural, electric, magnetic and optical properties of condensed matter. Condensed Matter Physics is published quarterly.

ABSTRACTED/INDEXED IN:

- Chemical Abstract Service, Current Contents/Physical, Chemical&Earth Sciences
- ISI Science Citation Index-Expanded, ISI Alrting Services
- INSPEC
- Elsevier Bibliographic Databases (EMBASE, EMNursing, Compendex, GEOBASE, Scopus)
- “Referativnyi Zhurnal”
- “Dzherelo”

CONTACT INFORMATION:
Institute for Condensed Matter Physics
of the National Academy of Sciences of Ukraine
1 Svientsitskii Str., 79011 Lviv, Ukraine
Tel: +38(032)2760908; Fax: +38(032)2761978
E-mail: cmp@icmp.lviv.ua http://www.icmp.lviv.ua