Theoretical models for structural phase transitions in molecular clusters and crystals of inorganic compounds

A.G.Grebenyuk

Institute of Surface Chemistry, National Academy of Sciences of Ukraine, 17 Gen. Naumov St., 03164 Kyiv, Ukraine

The modern theoretical approaches to investigation of polymorphism and structure phase transitions in inorganic compounds are reviewed. The emphasis is made on new ideas of solid state thermodynamics, structure and energy simulation of polymorphs, and results of application thereof to simple substances and binary compounds.

Статья содержит обзор современных теоретических подходов к исследованию полиморфизма и структурных фазовых переходов неорганических соединений. Основное внимание уделено новым идеям в термодинамике твердого тела, методам моделирования структуры и энергетики полиморфных форм и результаты их применения к простым веществам и бинарным соединениям.

The polymorphism of chemical substances has been known for more than 200 years [1]. The phase transitions between various structures caused by external effects have been studied for a great number of compounds that made it possible to develop a consistent theory of such processes [2]. The transformations conditioned by the changes in atomic coordination surrounding are of a particular interest because they are due to a fundamental rearrangement of the substance spatial structure and are accompanied by considerable heat effects [3].

The concept of preference energy. The considerable gap between fast accumulation of the structural information on complex compounds and slow rate of the laborious thermochemical studies stipulated a development of new methods for estimation of thermodynamic properties of substances. The choice of coordination polyhedron as a structure fragment determining these properties allows us to apply a united approach to the consideration of amorphous, glass-like, nano-crystalline, and crystalline states [4]. The primary occupation of definite positions by cations is defined by crystallographic and thermodynamic factors; that

became a base for the concept of preference energy to a certain coordination surrounding. The Al^{3+} ion transition enthalpy from tetrahedral O^{2-} surrounding to octahedral one was first determined in [5] to be of -44.4 kJ/mol. Later, a problem was formulated [6] of the choice of key ΔH, ΔG and ΔS values for change in cationic coordination numbers related to the tetrahedron-to-octahedron transitions within the oxygen surrounding. In [7], the values of thermodynamic functions for changes in coordination of both transition and non-transition metal cations were systematized, and the structural detailing taking into account the type of oxide or sulfide coordination polyhedron was shown to be an optimum one for comparing thermochemical and structural characteristics of coordination compounds. Recently [8], a versatile equation was deduced relating the enthalpy of cationic preference to alternative positions in any anionic closest packing with typical interatomic distances and a self-consistent system of the cationic preference enthalpies was proposed for sulfides, selenides, and hydrides.

The concept of preference energy proved to be rather fruitful. So, the enthalpies of

changes in cationic coordination numbers are used to calculate respective values for the processes of simple-to-complex oxide formation, to analyze theoretically the stabilization of metastable oxide forms due to modifying additives, to simulate power-consuming high-temperature processes (crystallization of amorphous oxides and self-spreading high-temperature synthesis of multi-elemental oxides) [9].

The first attempts to apply quantum chemical methods for calculation of energy change values in cationic coordination surrounding gave only qualitatively correct results whereas the absolute values exceeded the experimental ones by several times [10]. Nevertheless, for example, modern non-empirical calculations taking into account electron energy correlation for the process

$$MgO + \alpha-Al_2O_3 <\!\!-\!\!> MgAl_2O_4$$
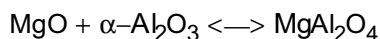
accompanied by transition of magnesium ions from the octahedral coordination surrounding to tetrahedral one [11], reproduce the experimental data to within 5 to 7 %.

Structural transformations in clusters. Clusters — systems of bound atoms and molecules — are rather convenient objects to study structural transformations [12]. The cluster structures may differ fundamentally from those of crystals what is dictated significantly by the form of interatomic potential [13] as well as by cluster size (multiatomic clusters may be very similar to crystals in structure) and temperature. A search procedure was described in [14] for transition states between isomeric forms of the clusters using potential energy surfaces described by simple analytical pair potentials. As examples, argon and potassium clusters were considered. It is the authors' opinion, this method opens a way for more detailed insight into relationships between energy, reactivity, and potential energy surfaces of such systems. Later, the study methods of the structural transformations in clusters were summarized in the review [15].

Several works are devoted to investigation in the energy of structural transformations of metal clusters. So, in [16], dependence of the energy of small clusters of the metals possessing fcc lattice in the bulk state (Al, Ca, Ni, Cu, Sr, Rh, Pd, Ag, Ce, Yb, Ir, Pt, Au, Pb, and Th) on atomic coordination was studied. The equilibrium structures, transition states and transformation mechanisms in the transition metal (nickel, silver, and gold) clusters consisting of 10 to

148 atoms were also examined [17], the Lennard-Jones, Morse, Satton-Chen, and Marrell-Mottram empirical interatomic potentials being used.

Structural transformations in crystals of simple substances. Phase transitions in simple bodies may occur under normal or elevated pressure. A crystal chemical estimation of the polymorphous transformation pressures for covalent substances was proposed in [18] that made it possible to obtain qualitatively correct conclusions. The phase transition in silicon under hydrostatic compression (from the cubic diamond structure to that of β-tin) accompanied by the increase in atomic coordination number from four to six was simulated as dependent on the atomic volume in [19] with use of the Tersoff empirical interatomic potential as well as on the base of non-empirical calculations of the total energy. The existence possibility of unusual crystalline structures of elements under high pressure has been discussed in the review [20].

Structural transformations in binary compounds. For the most part, theoretical articles are devoted to simulation of phase transitions in AX(AB), $AX_2(AB_2)$, and A_2B_3 crystals. Non-empirical quantum chemical calculations of structural properties and phase transition pressure were carried out in [21] for sodium chloride, calculated values being in a good agreement with experimental ones. The authors of [22] have studied the phase transition thermodynamics, mechanism, and kinetic aspects in alkali halides and alkali earth oxides with use of both two-body potentials and ab initio periodic calculations. The results obtained testify that both the mechanisms proposed before (the Burger and Watanabe-Tokonami-Morimoto ones) can be realized, since the activation energy values for these two mechanisms are very close, the way of transformation being dependent essentially on the external pressure value. An investigation of structural phase transitions induced by ultra-high pressure in alkali halide crystals was carried out in [23, 24]. The transition pressure for crystal of infinite size was calculated, the self-consistent potentials of pair interaction of ions obtained within the frameworks of the inhomogeneous electron gas theory being used. The relative changes in volume of B1 and B2 modifications were calculated for a number of compounds within the approximation of seven coordination spheres. The authors of [25, 26] have calculated the transition pres-

sure for limited-size crystals, showed a dependence of this value on the initial crystal size, and analyzed the contribution from vacancies to the character of the size effect discovered.

Non-empirical calculations were made in [27] within the frameworks of density functional theory on the transition in cesium hydride from cubic structure to orthorhombic one that occurs under pressure of 17 GPa. The qauthors of [28] considered a series of B4 → B3 → B1 phase transitions in beryllium oxide taking place under pressure of up to 95 GPa, and in [29], a relative stability of the B4 and B1 phases was studied theoretically for magnesium oxide and gallium nitride. The effect of high pressure on the B3 → B1 structural transformations in silicon carbide was studied in [30] within the frame of the molecular dynamics method, and the existence of an intermediate orthorhombic phase was predicted besides of B1 and B3 ones [31]. The electronic structure and chemical stability of five titanium monocarbide polymorphous modifications with the B1–B4 and B8 structures were studied in [32]; it was established basing on calculations of total band energies that the stability of modifications decreases in a sequence of B1 > B8 > B3 ≈ B4 > B2.

Calculations were made in [33] of the rutile → fluorite transition pressure using the Hartree-Fock and molecular dynamics methods; the 30 GPa value obtained agrees well with experimental one. Nevertheless, it was shown later [34] that the fluorite structure should be always unstable and if the pressure increases, the compound undergoes a number of transformations in a sequence of stable phases: rutile → α-PbO_2 → PdF_2 → α-$PbCl_2$.

Silicon is tetra-coordinated in the majority of silica polymorphs except for stishovite where it is six-coordinated. Periodic calculations of the probable reaction path between crystalite and stishovite were carried out in [35]. The transition pressure calculated (6 GPa) is consistent with the experimental conditions of the stishovite systhesis; the activation energy at 0 K under this pressure was found to be 125 kJ/mol. Further stishovite transformation into a phase of a $CaCl_2$-type structure under pressure of above 100 GPa was considered by the same authors in [36] where the transition mechanism was shown to include a rotation of the SiO_6 octahedra around their C2 axes. Later, it was shown [37] that the transition of stishovite into a

$CaCl_2$-like orthorhombic phase can occur already under pressure 47 GPa, then at 98 GPa a structure of *Pnc2* should be formed that at 226 GPa transforms into a pyrite-like phase. A non-hydrostatic compression of silica can result in the formation of a structure where silicon atoms are five-coordinated. Theoretical calculations have shown [38] that α-quartz under these conditions transforms into a phase possesing the $P3_221$ spatial symmetry group, the transition being reversible. A generalized theory of reconstructive phase transitions between silica polymorphs was proposed in [39] considering the phases of stishovite, coesite, β-quartz, tridimite, β-crystobalite as well as $CaCl_2$-like and α-PbO_2 structures from the viewpoint of a disordered bcc structure where different fractional occupancy of oxygen atomic positions generates all the polymorphs under consideration. An investigation of pressure-induced phase transitions in crystobalite by non-empirical molecular dynamics method has shown [40] the crystobalite stishovite transition to be a two-stage process (first, a rotation of SiO_4 tetrahedra occurs followed by a lattice distortion to yield the six-coordinated silicon atoms), and further compression yields the $CaCl_2$-like structure followed by another six-coordinated structure with $P2_1/n$ symmetry, which then transforms into a nine-coordinated $P2_1/m$ structure.

The structural properties and relative stability of six alumina polymorphs (corundum, phases like Rh_2O_3 (II), perovskites, and rare earth sesquioxides) were considered in [41, 42] using non-empirical method. The calculations testify that corundum transforms into a structure of Rh_2O_3 (II) type at 78 GPa and then into a *Pbnm* perovskite at 223 GPa. These results were supported in [43] within the frame of non-empirical perturbed ion method, and the transition between corundum and Rh_2O_3 (II) type structure at room temperature was shown to be probable already under pressure of about 4 GPa. A number of works is devoted to examination of the structure and stability of defect forms of alumina. So, it was found in [44] that the energy of θ-phase is higher than that of corundum by 42 kJ/mol. The role of admixture hydrogen atoms in the formation of "transition" alumina forms (γ-, η-, and δ-phases) was also studied [45]. The role of surface reconstruction in the formation of surface aprotic acid sites of the γ- and η-modifications was dis-

cussed in [46]. The effect of the specific surface value and of water adsorption on the relative stability of γ- and α-modifications of alumina was considered in [47]. It was shown, in particular, that if the specific surface was 175 m^2/g, the values of formation enthalpy for these modifications became the same.

In conclusion, the modern studies on polymorphism of chemical componds and on structural phase transitions under external effects along with use of direct experimental methods (mostly crystallography and calorimetry) utilize widely the simulation methods based on the employment of up-to-date progress in solid state theory, quantum mechanics, and molecular dynamics. Such a combined approach, providing the progress in the development of computers is used, makes it possible to obtain the results characterized by high accuracy and validity.

References

1. N.B.Leonidov, *Ross. Khim. Zh.*, **41**, 10 (1997).

2. Yu.M.Gufan, Structural Phase Transitions, Nauka, Moscow (1982) [in Russian].

3. L.A.Reznitsky, Solid State Calorimetry (Structural, Magnetic, Electron Transformations), MGU Publ., Moscow (1981) [in Russian].

4. L.A.Reznitsky, Chemical Bond and Oxide Transformations, MGU Publ., Moscow (1991) [in Russian].

5. A.Navrotsky, O.J.Kleppa, *J. Inorg. Nucl. Chem.*, **29**, 2701 (1967).

6. L.A.Reznitsky, *Izv. AN SSSR. Neorg. Mater.*, **12**, 1909 (1976).

7. L.A.Reznitsky, *Zh. Fiz. Khim.*, **67**, 2379 (1993).

8. Ya.A.Kesler, D.S.Filimonov, *Neorg. Mater.*, **37**, 1047 (2001).

9. L.A.Reznitsky, S.E.Filippova, *Zh. Neorgan. Khim.*, **47**, 711 (2002).

10. M.S.Shubin, G.P.Popov, A.O.Litinsky, A.N.Men', *Zhurn. Strukt. Khim.*, **17**, 160 (1976).

11. M.Catti, G.Valerio, R.Dovesi, M.Causa, *Phys. Rev. B*, **49**, 14179 (1994).

12. V.D.Lakhno, Clusters in Physics, Chemistry, and Biology, SRC "Regular and Chaotic Dynamics", Izhevsk (2001) [in Russian].

13. J.P.K.Doye, D.J.Wales, *J. Chem. Phys.*, **103**, 4234 (1995).

14. D.J.Wales, *J. Chem. Phys.*, **91**, 7002 (1989).

15. R.S.Berry, *Chem. Rev.*, **93**, 2379 (1993).

16. L.Yang, A.E.DePristo, *J. Catal.*, **149**, 223 (1994).

17. D.J.Wales, L.J.Munro, J.P.K.Doye, *J. Chem. Soc., Dalton Trans.*, 611 (1996).

18. S.S.Batsanov, *Zh. Strukt. Khim.*, **34**, 112 (1993).

19. K.Mizushima, S.Yip, E.Kaxiras, *Phys. Rev.*, **B 50**, 14952 (1994).

20. T.N.Kolobyanina, *Usp. Fiz. Nauk*, **172**, 1361 (2002).

21. E.Apra, M.Causa, M.Prencipe et al., *J. Phys.: Condens. Matter*, **5**, 2969 (1993).

22. C.E.Sims, G.D.Barrera, N.L.Allan, W.C.Mackrodt, *Phys. Rev.*, **B 57**, 11164 (1998).

23. S.V.Karpenko, A.K.Kyarov, A.I.Temrokov, *Izv. VUZov. Fizika*, **44**, 66 (2001).

24. S.V.Karpenko, D.L.Vinokursky, A.I.Temrokov, *Materialovedenie*, No.5, 8 (2000).

25. S.V.Karpenko, A.K.Kyarov, A.I.Temrokov, D.L.Vinokurov, *Kristallografia*, **47**, 326 (2002).

26. S.V.Karpenko, A.K.Kyarov, A.I.Temrokov, *Materialovedenie*, No.3, 6 (2002).

27. A.M.Saitta, D.Alfe, S.De Gironcoli, S.Baroni, *Phys. Rev. Lett.*, **78**, 4958 (1997).

28. J.Boettger, J.M.Wills, *Phys. Rev.*, **B 54**, 8965 (1996).

29. S.Limpijumnong, W.R.L.Lambrecht, *Phys. Rev.*, **B 63**, 104103-1 (2001).

30. F.Simojo, I.Sebjo, R.K.Kalia et al., *Phys. Rev. Lett.*, **84**, 3338 (2000).

31. M.Catti, *Phys. Rev. Lett.*, **87**, 035504-1 (2001).

32. A.L.Ivanovsky, A.A.Safonov, *Izv. AN. Ser. Khim.*, 1821 (2000).

33. G.D.Barrera, M.B.Taylor, N.L.Allan, T.H.K.Barron, *J. Chem. Phys.*, **107**, 4337 (1997).

34. J.Haines, J.M.Leger, F.Gorelli et al., *Phys. Rev.*, **B 64**, 134110-1 (2001).

35. B.Silvi, L.-H.Jolly, Ph.D'Arco, *J. Molec. Struct. (Theochem)*, **260**, 1 (1992).

36. L.-H.Jolly, B.Silvi, Ph.D'Arco, *J. Chim. Phys.*, **90**, 1887 (1993).

37. B.B.Karki, M.C.Waren, L.Stixrude et al., *Phys. Rev.*, **B 55**, 3465 (1997).

38. J.Badro, D.M.Teter, R.T.Downs et al., *Phys. Rev.*, **B 56**, 5797 (1997).

39. V.P.Dmitriev, P.Toledano, V.I.Torgashev, E.K.H.Salje, *Phys. Rev.*, **B 58**, 11911 (1998).

40. D.D.Klug, R.Rousseau, K.Uehara et al., *Phys. Rev.*, **B 63**, 104106-1 (2001).

41. K.T.Thomsonn, R.M.Wentzcovitch, M.S.T.Bukowinski, *Science*, **274**, 1880 (1996).

42. W.Duan, R.M.Wentzcovitch, K.T.Thomson, *Phys. Rev.*, **B 57**, 10363 (1998).

43. R.Franco, J.M.Recio, L.Pueyo, *J. Molec. Struct. (Theochem)*, **426**, 233 (1998).

44. A.P.Borosy, B.Silvi, M.Allavena, P.Nortier, *J. Phys. Chem.*, **98**, 13189 (1994).

45. K.Sohlberg, S.J.Pennycook, S.T.Pantelides, *J. Amer. Chem. Soc.*, **121**, 7493 (1999).

46. K.Sohlberg, S.T.Pantelides, S.J.Pennycook, *J. Amer. Chem. Soc.*, **123**, 26 (2001).

47. J.M.McHale, A.Navrotsky, A.J.Perrotta, *J. Phys. Chem. B*, **101**, 603 (1997).

Теоретичні моделі структурних фазових переходів у молекулярних кластерах та кристалах неорганічних сполук

А.Г.Гребенюк

Стаття містить огляд сучасних теоретичних підходів до дослідження поліморфізму та структурних фазових переходів неорганічних сполук. Основну увагу приділено новим ідеям у термодинаміці твердого тіла, методам моделювання структури і енергетики поліморфних форм та результатам їхнього застосування до простих речовин і бінарних сполук.