Science of Sintering, **38** (2006) 3-6

DOI: 10.2298/SOS0601003P

UDK 538.9:622.785

Contribution of Frenkel's Theory to the Development of Materials Science

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Abstract:
The original and comprehensive research of Yakov Ilich Frenkel in physics and physical chemistry of condensed states, nuclear physics, electrodynamics, science of sintering has significantly contributed to the development of modern scientific knowledge and his scientific ideas are still an inspiration to many scientists. Having in mind the wealth of scientific ideas he had in the research of electroconductivity in metals, crystal structure imperfections and phase transitions and in founding the science of sintering, the contribution of individual theories of Frenkel of significance to materials science are presented in this paper.
Keywords: *Frenkel's theory, Materials Science, Science of sintering*

Introduction

It is well known that materials engineering represents the very foundation of technical development and that, together with electric engineering and automatization encompasses almost all-modern technology. The development of new materials is often associated with the long and arduous experimental process of synthesizing materials with required properties. The complexity of synthesis is not only in resolving the research and development issues characteristic to every type of material processing, but also in the essential understanding of the fundamental principles of the synthesis of the material whose characteristics have been determined beforehand [1]. According to them, some of the basic tasks of the synthesis of materials with defined properties is in establishing the relationships "synthesis-structure" and "structure-properties", where the structure has the role of a parameter through which the "synthesis-properties" relationship is determined [2]. Taking this into account, one of the main tasks of materials science is to understand and realize the controlled dependence between a material’s structure and its properties. That is why modern materials science is not only based on the technological disciplines of material synthesis, but also on the principles of condensed matter physics and chemistry. Considering the substantial contribution of Frenkel's theories to the understanding of the condensed state, in this paper the contribution of these theories to the development of material science has been presented.

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Frenkel's contribution to the study of electric conductivity of metals

Many concepts of modern materials science, such as the concept of electric conductivity and carrier mobility are based on the electron theory of metals. In his early papers Frenkel specifically deals with developing a quantum theory of metals. Namely, the classic theory of metals had some significant successes but many failings as well. One of the main successes was derivation of Ohm's Law into a form that connected the electric current with the electric field, and the establishment of a correlation between electric and heat conductance. However, this theory could not explain the paramagnetic susceptibility, or the thermal capacity of conductive electrons. Since, the electronic contribution to thermal capacity as determined experimentally was not greater than 0,01 of the value reached by the application of the classic statistical mechanics, the question of how can electrons participate in the process of electric conductance, yet without contributing to the thermal capacity occurred. Although this question was answered in full only after the discovery of the Paulie exclusion principle, Frenkel in 1924. made a model of electro conductivity, which was in accordance with all experimental data that confirmed the classic theory, while eliminating its fundamental contradiction, later called "a catastrophe of thermal capacity" by Paul Ehrenfest. In this model Frenkel showed that, contrary to the classic theory, the kinetic energy of electrons in a metal was independent of temperature and instead, depended on the quantum character of the electron's motion. According to this model, only electrons that go through collectivization of valence may influence the electric conductivity. Frenkel later outlined the quantum theory of electro conductivity in metals, in which he pointed out that the ideal lattice must be transparent for electrons to move through it without any resistivity. According to this theory, electrical resistance is created due to electrons being scattered by the lack of homogeneity of the lattice created primarily by temperature fluctuations. These ideas were later implemented and further developed by Felix Bloch.

Frenkel's contribution to studying imperfections of the crystalline structure

An understanding how the structure of a material and the dynamics of its constituents determine material's properties and behaviour is impossible without the understanding of the physics of different type of defects which may occur in material. It is certain that Frenkel's greatest contribution to the research of imperfections in crystalline structures is his study of point defects. Based on his theoretical work, Frenkel introduced a special type of structural defect that is formed when an atom or ion leaves its normal lattice position and takes up an interstitial one, forming a vacancy in its former position. This type of defect, which includes a vacant lattice site with an associated interstitial atom or ion, was later named after him. By introducing this type of defects, Frenkel calculated the electric conductance of ion crystals and showed that the conductivity ability of ions is enormously enhanced by the presence of vacancies. He also used this type of defects while developing the theory of vibrational-translation motion of molecules in liquids.

While conducting research of the crystalline defect structure Frenkel also carried out a simple method for estimating the critical shear stress of perfect crystals. In this method the critical shear stress when the crystal undergoes slip can be expressed with:

$$\sigma_c = \frac{G \cdot a}{2 \cdot \pi \cdot d}$$

where G is the elastic constant, a is the distance between atoms in the direction of shearing, and d is the distance between lattice planes. Using the above formula enabled a rough estimation of the critical shear stress. But unfortunately this estimation showed a large discrepancy with the experimental results and was later explained by the motion of dislocations in real crystals.

Of particular significance to the development of materials science is Frenkel's theoretical work on collective excitations. Namely, in a number of semiconductors, a quantum absorbed light excites a valence electron, but in such a manner that it cannot jump into the conduction band. As a result the electron and the hole form an electron-hole system, which can travel within the crystal as a single whole. Frenkel termed this exited state an exciton and showed that excitation energy may be transmitted from atom to atom without charge transportation. Due to Coulomb interactions between electrons and holes, the formation of excitons can be observed in two approximations: when the electron-hole pair is tightly bound, with a small separation of the electron and hole (a Frenkel exciton), and when the electron-hole is weakly bound with a large separation (a Mott-Wannier exciton). Frenkel excitons are usually localized in one atom, or in its vicinity, and their presence has been observed in molecular crystals as well.

Frenkel's contribution to the study of soft condensed matter

An important segment of Frenkel's theoretical work belongs to investigations of soft condensed matter. The results of over twenty years of studing the theory of liquid state were generalized in the classic monograph "Kinetic theory of liquids". In the mid 30's Frenkel formed the "orientation melting" theory, in which a crystal loses its order in the long-range, while retaining the short-range order. This theory represents the basis for understanding the liquid-crystalline state and isotropic-nematic phase transitions. This type of transition was later described by Landau's theory of phase transitions that is based on the assumption that a system's state can be described by its state parameter and that free energy in the vicinity of the phase transition temperature is an analytic function. However it must be pointed out that Landau's theory only partially described this type of phase transitions due to discrepancies between the experimental and theoretical values of specific volume and specific thermal capacity in the vicinity of the phase transition temperature. This discrepancy can be explained by the fact that in the vicinity of the phase transition, some regions exist in the isotropic phase where the molecules are in a nematic state, and therefore the state parameter must depend on spatial coordinates, as opposed to Landau's theory.

During the 30's Frankel also published his theory of heterophase fluctuations in the vicinity of phase transitions, and a study of heat transfer and the thermodynamics of long molecular chains. These studies greatly influenced the further development of the physics and chemistry of polymers.

Frenkel's contribution to development of the science of sintering

By developing fundamental ideas of sintering kinetics, Frenkel not only contributed to the theory and practice of sintering, but also to the development of many technological processes for the production of various ceramic and metal-ceramic composites (cermets). In his theory of sintering the cause of this process and its transferring force are defined as sufficient of Gibb's surface energy. According to this concept, the process of viscous flowing takes place in crystalline structures whose vacancies have a clearly defined character and it can be characterized by the following equation:

$$\frac{1}{\eta} = \frac{D\delta}{kt}$$

where η is the coefficient of viscosity, δ is the crystal lattice constant, D is the diffusion coefficient and k is Boltzmann's constant.

According to Frenkel, sintering takes place in two stages. In the first stage of sintering particles of the powder adhere to each other. During this process the contact surface between particles grows, thus leading to the formation of pores. In the second stage sealing of pores transpires.

Frenkel's theory of sintering was based on his innovative understanding of mass transport within a solid body viewed as self-diffusion. It must be pointed out that his theory of self-diffusion greatly influenced further investigations of sintering and represents the foundation of modern understanding of mass transport occuring during sintering.

Conclusion

Frenkel greatly contributed to the development of concepts of quasi-free states and quasi-particles in condensed matter physics, the study of electroconductivity in metals, defects in crystalline structures and transport mechanisms in condensed systems. The ingenuity of Frenkel's ideas set the foundation of many scientific disciplines, from physics and physical chemistry of condensed states, to the science of sintering and materials science. The originality of his scientific ideas represents an unexhausted heritage still used by generations of scientists in numerous disciplines.

References

1. M.M.Ristic, Fundamental principles of the synthesis of materials with defined properties, Materials Science Monographs 31, CMS, Belgrade, 1996
2. G.V.Samsonov, Problems of obtaining materials with definite properties, in Materials in Electronics, ed. M.M.Ristic and V.Mikijelj, International Institute for science of sintering and Institute of technical sciences of SASA, Belgrade 1977
3. V.Ya. Frenkel, Yakov Il'ich Frenkel: His work, life and letters, Basel-Boston-Berlin, 1996
4. Obituary: Yakov Il'ich Frenkel, Akad. Nauk SSSR Zurnal Eksper.Teoret.Fiz. 23 (1952) 613-618
5. S.L.Lopatnikov, H.Alexander, D.Cheng, J.Eng.Mech. ASCE, 2005

Садржај: *Јаков Иљич Френкељ је својим оригиналним и свестраним истраживањима у физици и физичкој хемији кондензованог стања, нуклеарној физици, електродинамици, науци о синтеровању, значајно допринео развоју савремене научне мисли, а његове научне идеје још увек служе као инспирација многим научницима. Имајући у виду богатство његових научних идеја, како у проучавању електропроводности у металима, истраживањима несавршености кристалне структуре, побуђених стања и фазних прелаза, тако и у заснивању науке о синтеровању. У овоме раду је приказан допринос појединих Френкељевих теорија које су од значаја за развој науке о материјалима.*
Кључне речи: *Френкељева теорија, наука о материјалима, наука о синтеровању.*