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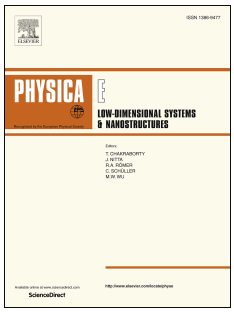

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Mechanism of the order-disorder transition in ultra-small metal nanoparticles

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Abstract – This paper reviews advances in physical modelling and experimental studies of order-disorder transition in ultra-small metal nanoparticles. The interrelation of temperature hysteresis and order-disorder transition in nanoparticles is analysed in detail. The recently discovered dynamic structure of ultra-small nanoparticles is also discussed in this paper. In addition, the mechanism of the order-disorder transition in the ultra-small metal nanoparticles has been established. The transition occurs due to the vacancy formation in nanoparticles. It implies that the transition occurs in a nanoparticle if the vacancy spanning cluster is formed in it. The position and dimensions of the spanning cluster change due to the exchange of energy with the environment or with the external sources. This can cause the continuous change in the structure of nanoparticles due to their ultra-small size. The calculation of the nanoparticle critical sizes at which the order-disorder transition occurs was performed. The critical diameters of the studied nanoparticles lay in the interval 1 – 6 nm and depend on the transition temperature. The critical diameters decrease with increasing the transition temperature. It was found that the transition of Au nanoparticles from a metallic state to non-metallic state was due to the formation of vacancies in them. All model predictions have been compared with experimental observations and reported data.

1. Introduction. – It was established recently that ultra-small nanoparticles (USNs) with characteristic dimensions of 1−3 nm have the physical properties that differ from those of free molecules, and those of nanoparticles of larger size [1, 2]. Their unique properties have been already applied and used to create new technologies [1–3]. It was reported that Au USNs with the characteristic size less than 1.5 nm are of enhanced catalytic activity [4]. Au and Ag USNs gives a fluorescence spectrum instead of surface plasmon resonance [5, 6]. The optical properties of metal USNs also attract wide interest because they give information about the formation of metallic state. The metal USNs are a promising material for the manufacture of sensors, solar cells, water purification, imaging and diagnostics [7]. The study of the thermodynamics properties of the USNs have revealed that crystalline nanosolids become disordered if their characteristic size becomes less than a critical one [8]. Nanosolids of the critical size undergo order-disorder phase transition instead of ordinary melting [8]. But this theory does not give us a description of the transition mechanism. The purpose of the present article is to give a description of the order-disorder transition in nanoparticles of the critical size.

In macroscopic solids, the order-disorder transition also attracts scientist's attention. It was shown that crystalline defects may cause this transition [9–11]. The transformation occurs if the defects quantity surpasses its critical value. The crystal-glass transformation was investigated in quasi-two-dimensional binary colloidal suspensions [9]. Radiation of bulk materials conducts to accumulation of defects of their crystal structure. When the quantity of defects becomes more than its critical value, the structure of the materials becomes disorder [10, 11]. It was observed in some metallic glasses [12] that electron irradiation induced the crystal-to-amorphous-to-crystal transition. Under the influence of the electron beam irradiation, the graphene monolayer became disordered [13]. The disorder increased gradually in graphene, while the material remained in the solid state. It was observed that a crystalline mono-layer graphene had a solid-state transition into a 2D carbon glass during the exposure of electron