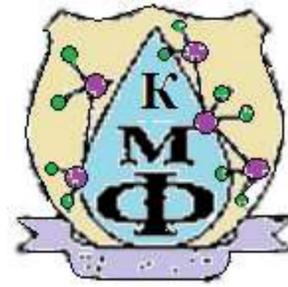# Melting mechanism of a nanocrystal

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1. Introduction

In this work the classical theory of phase transformations is shown to be inapplicable for describing the melting of nanocrystals. For this purpose, one uses the theory of non-classical vacancies. When a nanocrystal is heated to the critical temperature, its lattice becomes defect-free. When this temperature is exceeded, thermal expansion leads to the appearance of vacancies in the lattice. These vacancies are conventionally called non-classical. The energy of a nanocrystal containing defects of the indicated type is calculated. It was found that at a certain temperature the lattice of such a nanocrystal loses its mechanical stability. The process of loss of stability is identified with melting, and the temperature is considered as the melting point of the nanocrystal. This temperature increases with decreasing nanocrystal size.

2. Methods

The theory of melting of nanocrystals is developed accordingly to the following assumptions.

Let us assume that the nanocrystal has a simple cubic lattice and that at the temperature $T = 0$ the lattice is ideal. The unit cell size for this case is denoted by a_0. The same size at $T>0$ is denoted by a. The lattice nodes contain particles that are power centers. It is also assumed that only particles that are nearest neighbors interact. We write the interaction energy of a pair of such particles in the form:

$$U = \varepsilon \left(\frac{q}{m-q} \lambda^{-m} - \frac{m}{m-q} \lambda^{-q} \right)$$

where ε is the energy of the interparticle bond, and λ is the degree of deformation of this bond, determined by the formula
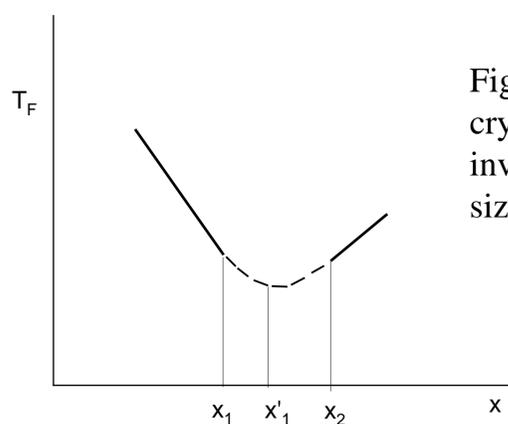
$$\lambda = a / a_0$$

Fig. 1. Dependence of the crystal melting point on the inverse value of the crystallite size.

3. Results

The formula which describes melting process of nanocrystals is shown below:

$$\int_0^{T_F} \alpha(T')dT' = \frac{1}{2A}\left[1 + \frac{9}{mq} \frac{\left(\frac{\varphi}{3}-1\right)+\frac{2}{3}N^{-1/3}}{1-N^{-1/3}} \right] \qquad (1)$$

where α is a coefficient of thermal expansion and φ the average number of broken links per one of the nodes that are occupied by vacancies.

In its meaning, the physical quantity $N^{-1/3}$ is a size characteristic of the crystallite. As it is seen from formula mentioned above, the melting temperature increases with decreasing nanocrystal size. This tendency is confirmed by the experimental data of [12], where the melting point of Al nanocrystals was found to increase with a decrease in the number of atoms in the nanocrystal from 62 to 55(see Fig.2).
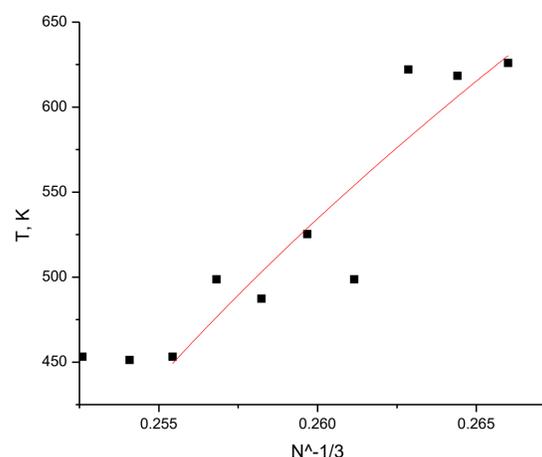

Fig. 2. The approximation of the dependence of the melting temperature of Al clusters on the inverse cluster size by the formula (1)[1].

4. Conclusions

The concentration of nonclassical vacancies increases with increasing deformation of thermal expansion according to a linear law. In this case, the bulk elastic modulus of the nanocrystal decreases, and the ability of the lattice to resist stretching caused by thermal expansion decreases. Therefore the nanocrystal lattice loses its mechanical stability at a certain temperature. The loss of stability manifests itself in the fact that, at the certain temperature an increasing in deformation is accompanied with a decrease of the stress in the nanocrystal. This decrease is caused by the breaking of bonds that survived after the formation of vacancies. Eventually the absence of a lattice makes it possible to classify this phase as a liquid phase, considering the described process of loss of stability as a kind of melting process and calling it the melting point.

5. References

1. Breaux, G. A., Neal, C. M., Cao, B., & Jarrold, M. F. (2005). *Physical review letters*, *94*(17), 173401.