ISSN 1063-7842, Technical Physics, 2014, Vol. 59, No. 10, pp. 1573–1575. © Pleiades Publishing, Ltd., 2014.
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SHORT COMMUNICATIONS

Role of Electron Confinement in the Formation of Tamm Surface Levels in Nanoparticles

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Received March 31, 2014

Abstract—We study the effect of electron confinement in a nanoparticle on the parameters of Tamm's levels. It is shown using the combination of the Tamm model and the Kronig–Penney model that an increase in the gap width in the electron spectrum of the crystal leads to an increase in the energy of the Tamm state and a decrease in the degree of localization of the wavefunction of the Tamm state. Some applications of the results on the properties of the Tamm level (e.g., the effect on the surface tension of a nanocluster, the manifestation of modifications considered here in the multiple exciton generation effect in quantum dots, the possible role of the shape of a nanoparticle during its growth, and the role of varying Tamm states in catalysis by nanoparticles) are indicated.

DOI: 10.1134/S1063784214100235

INTRODUCTION

In 1932, I.E. Tamm demonstrated for the first time on the basis of quantum mechanics that apart from the band states of electrons in a crystal known at that time, electron states of a completely different type can exist at the crystal surface [1]. These surface electron states have a discrete energy spectrum and wavefunctions exponentially decaying with increasing distance from the surface to the bulk and towards vacuum. During more than 80 years that elapsed since then, the theory of surface states was considerably developed as regards the computational technique and analysis of manifestations of such states in various crystals [2, 3]. Due to the evolution of science of nanoobjects, the problem of surface states has become even more topical. However, general analysis of the problem of surface states shows that basically new factors that were not reflected in the proposed model should be taken into account as applied to nanoclusters. The concepts of the role of the surface curvature (nonplanar surface), the sharpness of the potential barrier simulating the width of the surface region (diffuse nature of the interface), and finiteness of the nanocluster size (in contrast to the case of a semi-infinite crystal) should be introduced into the theory. At the same time, nanoparticles have a characteristic that describes the above properties in an integrated manner; we are speaking of confinement of elementary excitations in a nanoparticle. The most important property determined by the confinement of electrons is the discretization of their electron spectrum, which accompanies the increase in the gap width in the spectrum; the broadening of the gap increases upon a decrease in the characteristic size of a nanoparticle [4]. Therefore, it is reasonable to consider the features introduced into the characteristics of Tamm surface states of nanoparticles by a fundamental property like the electron confinement.

1. MODEL

We construct our analysis on the combination of three models: the Tamm model of surface states [1], the well-known Kronig–Penney model of a solid [5], and the results obtained by the Efros brothers on the electron structure of a nanosphere [4]. For this purpose, each model will be slightly developed.

The basic scheme of Tamm's analysis [1] is shown in Fig. 1. Tamm presented the wavefunction of the surface electron state outside the crystal (for $x < 0$) in the form

$$\psi = A\exp\left[\frac{\sqrt{2m(U_0 - E)}}{h^2}x\right], \qquad (1)$$

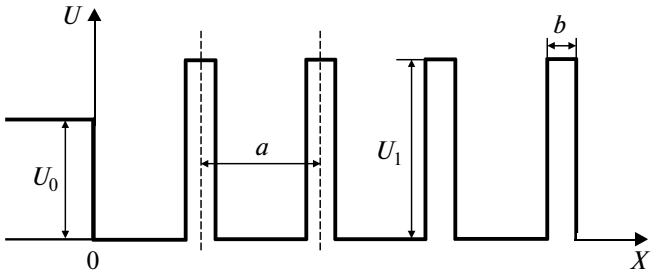

Fig. 1. Potential energy of a crystal with a surface in the Tamm– Kronig–Penney model.

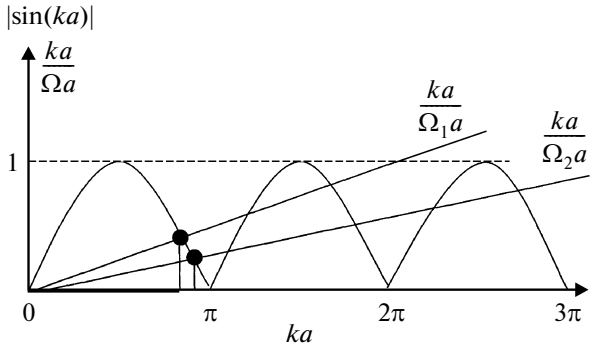

Fig. 2. Plot for determining the boundaries of allowed and forbidden bands (bullets); $\Omega_1 < \Omega_2$.

where E (energy of Tamm's state) satisfies the condition $0 < E < U_0$. Introducing the parameters (see Fig. 1)

$$\xi = \frac{a}{h}\sqrt{2mE}, \quad q = \frac{a}{h}\sqrt{2mU_0}, \qquad p = ab\frac{mU_1}{h^2}. \tag{2}$$

Tamm obtained the following equation for energy E:

$$\xi\cot\xi = \frac{q^2}{2p^2} - q\sqrt{1-\frac{\xi^2}{q^2}}. \tag{3}$$

Let us simplify this expression for low energies ($\xi \ll 1$):

$$E\left(qa^2 - \frac{2m}{h^2}\right) = q - \frac{q^2}{2p^2}. \tag{4}$$

Thus, we obtain the dependence of energy E on dimensionless parameter p appearing in the Kronig–Penney model [5]. This model can also be represented in Fig. 1 if we consider the range of $X \gg 0$. The equation for allowed values of energy in the Kronig–Penney model has the form (in notation used in [5])

$$\left\{\begin{array}{l}\left|\cos\left(ka - a\cot\left(\dfrac{\Omega a}{ka}\right)\right)\right| \le \dfrac{1}{\sqrt{1+\left(\dfrac{\Omega a}{ka}\right)^2}} \\ E = \dfrac{h^2}{2ma^2}(ka)^2\end{array}\right\}. \tag{5}$$

Here, Ωa characterizes the dimensionless barrier penetrability. For low energies ($\Omega a/ka \gg 1$), Eq. (5) is transformed to

$$|\sin(ka)| \le \frac{ka}{\Omega a}. \tag{6}$$

Expanding $\sin(ka)$ (for $ka < 1$), we obtain the first two solutions $E = f(\Omega a)$:

$$E_1 = 0, \quad E_2 = \frac{h^2}{2ma^2}6\left(1-\frac{1}{\Omega a}\right)^2. \tag{7}$$

The graphical form of Eq. (6) is shown in Fig. 2. Combining Fig. 2 with Eq. (7), we obtain penetrability parameter Ωa as a function of the first band gap:

$$E^1_{\text{gap}} = E_2 - E_1: \qquad \frac{1}{\Omega a} = 1 - \sqrt{\frac{E^1_{\text{gap}}}{h^2/2ma^2}}/6. \tag{8}$$

Matching the Kronig–Penney model and the Tamm model by the condition $p = \Omega a$, we obtain from expressions (8) and (4)

$$\frac{E}{h^2/2ma^2} = 2\sqrt{\frac{U_0}{h^2/2ma^2}} - \frac{U_0}{h^2/2ma^2} - \left[1 - \frac{1}{6}\sqrt{\frac{E^1_{\text{gap}}}{h^2/2ma^2}}\right]^2. \tag{9}$$

Let us now take into account the dependence of gap width E^1_{gap} on radius R of a nanosphere [4]:

$$E^1_{\text{gap}} = E^0_g + \frac{A}{R^2}, \quad A \equiv h^2\pi^2/2m, \tag{10}$$

where E^0_g is the gap width for the bulk material. Substituting expressions (10) into (9), we obtain the following dependence of the position of the Tamm level on nanoparticle radius R:

$$E = \frac{h^2}{2ma^2}\varphi(R). \tag{11}$$

Here,

$$\varphi(R) \equiv \left\{2\sqrt{\frac{U_0}{h^2/2ma^2}} - \frac{U_0}{h^2/2ma^2} - \left[1 - \frac{1}{6}\sqrt{\frac{E^0_g + A/R^2}{h^2/2ma^2}}\right]\right\}. \tag{12}$$

It should be noted that $d\varphi(R)/dR < 0$. Thus, exponent α in the wavefunction $\psi(x) = A\exp(\alpha x)$, $x < 0$, for the Tamm electron has the form

$$\alpha = \frac{1}{a}\sqrt{\frac{U_0}{h^2/2ma^2} - \varphi(R)}. \tag{13}$$

Analyzing this expression, we can easily see that the value of α decreases with R:

$$\frac{d\alpha}{dR} > 0. \tag{14}$$

Consequently, we obtain two important results (Fig. 3) [6]: (i) upon a decrease in nanoparticle radius R, the Tamm level increases, approaching U_0 from below; and (ii) the degree of localization of Tamm wavefunction α decreases upon a decrease in radius R.

2. SOME APPLICATIONS

It is well known that the problem of matching of two phases (surface and bulk) naturally appears in

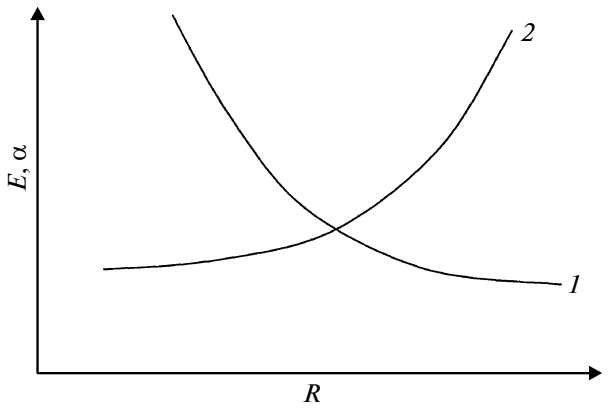

Fig. 3. Schematic qualitative dependence of the energy of Tamm's level (*1*) and damping factor of the wavefunction of a Tamm electron (*2*) on the nanoparticle radius.

experiments with nanoparticles. This problem is known as the core–shell problem [6–8]. The natural explanation of this problem is the notion that the surface of nanoparticles is characterized by a more complex defect structure as compared to the bulk. At the same time, it is clear that this idea becomes less productive upon a decrease in temperature. The concept proposed in this communication indicates that the core–shell idea is more fundamental and is associated with the basic characteristic, viz., the change in the range of the Tamm state, which is due to confinement of electron excitations. Unfortunately, this most fundamental circumstance has not been manifested in experiments. We believe that a number of such manifestations have already been discovered or can naturally be expected. Let us list these facts.

1. With decreasing R, the surface tension that is directly connected with Tamm's states changes, leading to an increase in the surface activation of nanoclusters [6].

2. The effect of multiple generation of excitons in quantum dots [9] depends in the arrangement of Tamm's levels, which in turn leads to its dependence on the nanocluster radius.

3. The effect of UV radiation on the shape (spherical, ellipsoidal, or quasi-linear) of a growing nanocluster in a solution [10] is probably associated with different depths (and, hence, the extent of charging) of a Tamm level in different parts of the nanocluster surface differing in curvature $1/R$.

4. The experience gained in operation with magnetic nanoclusters indicates that it is expedient to speak of nanomagnetism depending on R [11].

5. There exists a trend, viz., nanocatalysis, this has been considered only in particular chemical model up until now [12]. The application of the concept of Tamm's levels (e.g., in the problem of conversion of gold nanoparticles into a very active catalyst whose effectiveness increases in proportion to the decrease in the third power of the nanoparticle diameter [13]) appears as absolutely essential.

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Translated by N. Wadhwa