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PROBLEM ON THE EFFECTIVE ELECTRON MASS IN NANOCLUSTERS

V. N. Nikiforov,[1] B. L. Oksengendler,[2] N. N. Turaeva,[2] and M. B. Marasulov[2] UDC 621.382+539.293

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Numerous investigations of nanoclusters (for example, see [1]) have convincingly demonstrated that their properties differ significantly from the properties of bulk crystals genetically related to the nanoclusters. These differences are dual:

– radically new effects can be observed,

– properties can be analogous, but values of the parameters can differ significantly.

The problem on the value of the electron mass in a nanocluster belongs to problems of the second type. Indeed, in numerous works where the quantum nanocluster chemistry was studied (for example, see [2, 3]), the electron mass m was set equal to the free electron mass in vacuum. This value was used to calculate the energy characteristics [3], magnetic properties [2], etc. On the second side, there were calculations by the pseudo-potential method [4] where the effective mass (m^*) was used to analyze concrete effects (for example, the effect of cascade electron ionization). On the third side, there were works devoted to phenomenological nanocluster modeling [5] where the optical properties were also studied based on the effective electron mass (according to Shockley and Pekar [6]).

The present work is aimed at determination of the character of the effective electron mass dependence on the nanocluster size. Let us consider a nanocluster with radius R much greater than the interatomic distance a, i.e., $R > a$. The number of atoms in the nanocluster is $N \propto \left(\frac{R}{a}\right)^3 >> 1$. This means that the notion of the effective mass m^* is applicable to an analysis of the electron structure of such cluster. Hence, we can take advantage of the method of $\boldsymbol{k} \times \boldsymbol{p}$ analysis [6]. This means that the electron wave function is the Bloch wave $\psi_{n\boldsymbol{k}} = u_{n\boldsymbol{k}} e^{i\boldsymbol{kr}}$, and the modulating multiplier $u_{n\boldsymbol{k}}$ reflects the existence of a periodic field and obeys the perturbed Schrödinger equation [7]

$$\left(H_{\boldsymbol{k}_0} + H'_{\boldsymbol{k}}\right) u_{n\boldsymbol{k}} = E_n(k) u_{n\boldsymbol{k}}, \tag{1}$$

where $H'_{\boldsymbol{k}} = \frac{\hbar^2}{m}(\boldsymbol{k} - \boldsymbol{k}_0)\,\boldsymbol{p} + \frac{\hbar^2}{2m}\left(\boldsymbol{k}^2 - \boldsymbol{k}_0^2\right)$, n is the serial number of the electron band, $\boldsymbol{k}_0$ specifies a point of the Brillouin zone, and the operator is $\boldsymbol{p} = -i\nabla$.

Near the bottom of the conduction band (at point $\boldsymbol{k}_0$), where $\boldsymbol{k} - \boldsymbol{k}_0$ is small, the second-order perturbation theory ($\boldsymbol{k} \times \boldsymbol{p}$ perturbation) can be used, and the equation

[1]M. V. Lomonosov Moscow State University, Low Temperature Phys. Dpt., Moscow, Russia; [2]Institute of Polymer Physics and Chemistry of the Uzbekistan Academy of Sciences, Tashkent, Uzbekistan, e-mail: nvn@lt.phys.msu.ru. Translated from Izvestiya Vysshikh Uchebnykh Zavedenii, Fizika, No. 12, pp. 109–111, December, 2012. Original article submitted June 18, 2012.

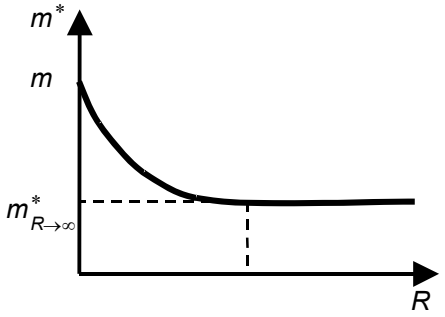

Fig. 1. Dependence of the effective electron mass in the nanocluster on its radius.

$$\left(\frac{1}{m^*}\right)_{ij} = \frac{1}{\hbar^2}\left(\frac{\partial^2 E_c}{\partial k_i \partial k_j}\right)_{\boldsymbol{k}=\boldsymbol{k}_0} = \frac{1}{m}\delta_{ij} + \frac{2}{m^2}\sum_{n\neq c}\frac{\left\langle u_{c\boldsymbol{k}_0}\left|p_i\right|u_{n\boldsymbol{k}_0}\right\rangle\left\langle u_{n\boldsymbol{k}_0}\left|p_j\right|u_{c\boldsymbol{k}_0}\right\rangle}{E_c(\boldsymbol{k}_0) - E_n(\boldsymbol{k}_0)} \tag{2}$$

can be derived for the effective mass m^* [6]. Thus, the effective electron mass m^* is expressed through the electron mass m in vacuum, matrix elements $\langle 0|-i\nabla|\alpha\rangle$, and energy bandgap $\Delta E_g = E_c - E_n$. What new feature brings such object as a nanocluster to this pattern? First, it changes values of wave functions $\psi_{n\boldsymbol{k}} = u_{n\boldsymbol{k}} e^{i\boldsymbol{kr}}$ (especially in the expression for $u_{n\boldsymbol{k}}$ as well as the choice of the electron wave functions in the form of the Bloch wave). Second, because of the confinement phenomenon for the electron, the bandgap itself depends on the nanocluster size: $\Delta E_g = \Delta E_g^0 + \frac{A}{R^2}$, where $A = \frac{\hbar^2\chi^2}{2m}$ and χ denotes zeros of the spherical Bessel function [5]. Hence, according to Eq. (2), the m/m^* value depends on the nanocluster radius R. We now estimate this dependence having simplified Eq. (2). We set $\left\langle u_{c\boldsymbol{k}_0}\left|p\right|u_{n\boldsymbol{k}_0}\right\rangle \approx \hbar / a$. Then

$$\frac{m}{m^*} \approx 1 + 2\frac{\dfrac{\hbar^2}{ma^2}}{\Delta E_g^0 + \dfrac{\hbar^2\chi^2}{2mR^2}}. \tag{3}$$

It can be seen that for $R \to \infty$ (i.e., for infinite crystal), we obtain

$$m^*_{R\to\infty} = m\left[1 + 2\frac{\dfrac{\hbar^2}{ma^2}}{\Delta E_g^0}\right]^{-1}, \tag{4}$$

that is, we obtain the effective mass for the bulk materials. With decreasing R, the effective mass increases, that is, tends to the free electron mass (Fig. 1). Thus, for $R \to 0$, we obtain $m^* \to m$. It is interesting to note that pattern (3) showing similarity in the effective mass m^* and bandgap $\Delta E_g = \Delta E_g^0 + \frac{\text{const}}{R^2}$ in the nanocluster, was established long time ago

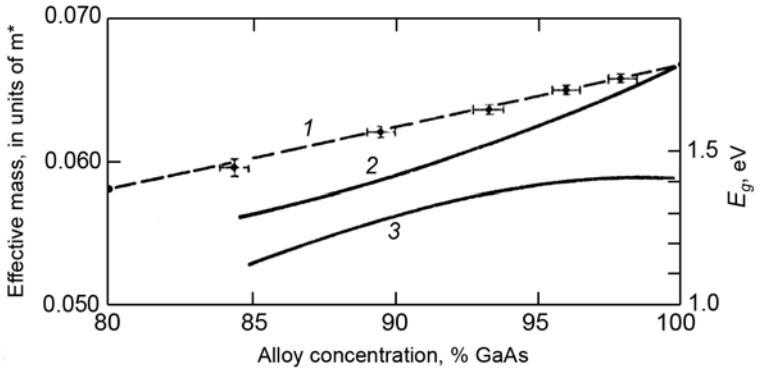

Fig. 2. Experimental values of the effective mass with correction for nonparabolicity (points). Here curve *1* shows the linear mass change between GaAs and InAs, curve *2* shows the effective mass change at the band edges predicted by the *k-p* method, and curve *3* shows the corresponding change of the fundamental bandgap *E* [8].

for a group of bulk GaAs–InAs semiconductor alloys [8] (Fig. 2). It is essential that for these objects, the $\boldsymbol{k}-\boldsymbol{p}$ method is applicable to the examined problem even with allowance for such fine effect as spin-orbital splitting of the valence band Δ, since the formula that demonstrates the similarity in m_c^* and ΔE_g^0 for the alloys has the form

$$\frac{m}{m_c^*} = 1 + \frac{P^2}{3}\left(\frac{2}{\Delta E_g^0} + \frac{1}{\Delta E_g^0 + \Delta}\right). \tag{5}$$

Here $P^2 \approx 19.6$ eV. Qualitative agreement of Eq. (5) with Fig. 2 is quite obvious.

Thus, the examined dependence $m^*(R)$, undoubtedly, must be taken into account both in an experiment (for example, on nanomagnetism phenomena [1, 9]) and in theoretical analysis of various effects (for example, as in the theory of multiple exciton generation at a quantum dot, but on a heuristic basis [10, 11]).

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