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IMPURITY ELECTRONIC LEVELS IN A ONE-DIMENSIONAL CLUSTER

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ПРИМЕСНЫЕ ЭЛЕКТРОННЫЕ УРОВНИ В ОДНОМЕРНОМ КЛАСТЕРЕ. Олев СИЛЬД

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Advances in the synthesis of nanocrystals or clusters in solid media (see e.g. [1, 2]) have aroused interest in the studying of size-dependent cluster properties including optical characteristics.

Like crystals a cluster can consist of impurity centres. Naturally, impurity quantum levels of the cluster and also the corresponding optical characteristics must be size-dependent.

In the present communication, a simple one-dimensional model of the cluster is considered to determine the size-dependent electronic levels of the impurity.

The theory of impurity centres in crystals has solved the problem of impurity electronic levels by Green's function method [3–5]. The Green's function method is applied to the present cluster model, too.

Let us consider a linear chain consisting of N identical atoms as a one-dimensional cluster. According to the LCAO method its electronic wave function is described as

$$\Psi = \sum_{i=1}^{N} C_i \Phi_i, \tag{1}$$

where Φ_i is the atomic orbital of the atom i.

If only neighbour atoms are interacting, the matrix of the electronic Hamiltonian in the basis of atomic orbitals is

$$H = \begin{bmatrix} H_{11} & H_{12} & 0 & 0 & \ldots \\ H_{21} & H_{22} & H_{23} & 0 & \\ 0 & H_{32} & H_{33} & H_{34} & \\ 0 & 0 & H_{43} & H_{44} & \\ \cdot & & & & \\ \cdot & & & & \\ \cdot & & & & \end{bmatrix}.$$

As the atoms are supposed identical, $H_{11} = H_{22} = \ldots = 0$ and $H_{12} = H_{21} = H_{23} = H_{32} = \ldots = 1$ can be chosen.

The eigenvector C_i $(i = 1 \ldots N)$ and the eigenvalue E are determined by the following system of equations

$$C_2 = EC_1,$$

$$C_3 + C_1 = EC_2, \quad C_4 + C_2 = EC_3, \ldots \tag{2}$$

$$C_N = C_{N-1}/E.$$

From system (2), the following recursion relation follows:

$$C_k = EC_{k-1} - C_{k-2}, \quad k = 2 \ldots N, \tag{3}$$

where $C_0 = 0$, $C_1 = 1$ can be chosen for an unnormalized eigenvector.

Due to the equality $C_N = C_{N-1}/E$ (see formula (2)) $C_{N+1} = 0$. The latter is considered as the eigenvalue equation

$$C_{N+1}(E) = 0.$$

Trying to find the eigenvalue in the form $E = e^{ix} + e^{-ix}$, recursion relation (3) is satisfied if

$$C_k = e^{i(k-1)x} + e^{i(k-3)x} + \ldots + e^{i(-k+1)x} = \sin kx / \sin x.$$

$C_{N+1}(E) = 0$ holds if $x = n\pi/(N+1)$, $n = 1 \ldots N$. Therefore, the eigenvalues are

$$E_n = 2\cos n\frac{\pi}{N+1}, n = 1 \ldots N \tag{4}$$

and the normalized eigenvectors are

$$\overline{C}_k = \sin\frac{kn\pi}{N+1} \Big/ \sqrt{\sum_{m=1}^{N} \sin^2 \frac{mn\pi}{N+1}}, \quad k = 1 \ldots N. \tag{5}$$

In the limit $N \to \infty$ the width of the energy band is 4 (here the matrix element $H_{12} = H_{23} = \ldots$ serves as the energy unit).

Further, we suppose that the atom of the number $i = f$ is replaced by an impurity atom. It results in a perturbed Hamiltonian, $H + W$. The simpliest perturbation matrix is

$$W_{jk} = W\delta_{jf}\delta_{kf} \tag{6}$$

(W – the constant).

In the case of localized perturbation the Green's function method is desirable to solve the eigenvalue problem. The corresponding equation can be written as follows [5]:

$$C = GWC.$$

Here C is the column matrix of the coefficients C_i and $G = (E - H)^{-1}$ is the Green's function.

Perturbation (6) results in the eigenvalue equation

$$WG_{ff}(E) = 1; \quad G_{ff}(E) = \sum_{n=1}^{N} \bar{C}_f^2 / (E - E_n), \tag{7}$$

where E_n and $\bar{C}_f$ are determined by (4) and (5).

From (7) the size-dependent (N-dependent) impurity levels E can be calculated, depending on the perturbation value W. This dependence is presented in Fig. 1, while the impurity is situated in the centre of the chain.

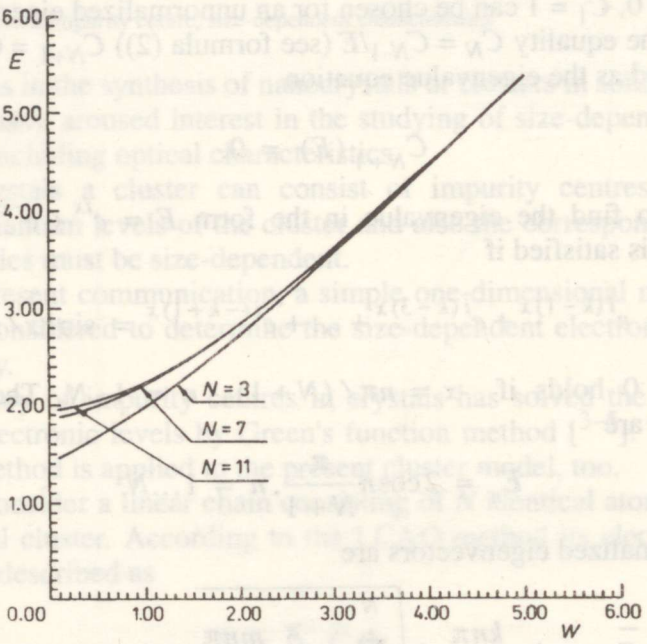

Fig. 1. Size-dependence of impurity electronic levels; N is the number of atoms in a one-dimensional cluster.

The present model calculation demonstrates that a considerable size-dependence of impurity levels occurs i) at the energy distances of the impurity levels from the energy band up to the bandwidth and ii) at cluster sizes up to about ten lattice constants.

In finite clusters a part of impurities are situated near the end (edge) of the cluster. It is interesting to find out the variation of the impurity levels depending on the distance of the impurity from the cluster's end (edge). Formula (7) enables the calculation of such site-dependence. Fig. 2 presents the electronic levels of the impurity replacing the atom of the number f = 1,2,...6 in the linear cluster with N = 11. The Fig. 2 demonstrates a considerable level variation only for the impurities replacing two edge atoms.

In bulk clusters, the percentage of the volume of the two-atomic outer layer is $P = 100(1 - (R-2)^3/R^3)$; the cluster radius is R lattice constants. Such percent of impurities are responsible for the site-dependence of impurity levels. For example, P = 48; 35; 27 for R = 10; 15; 20, respectively.

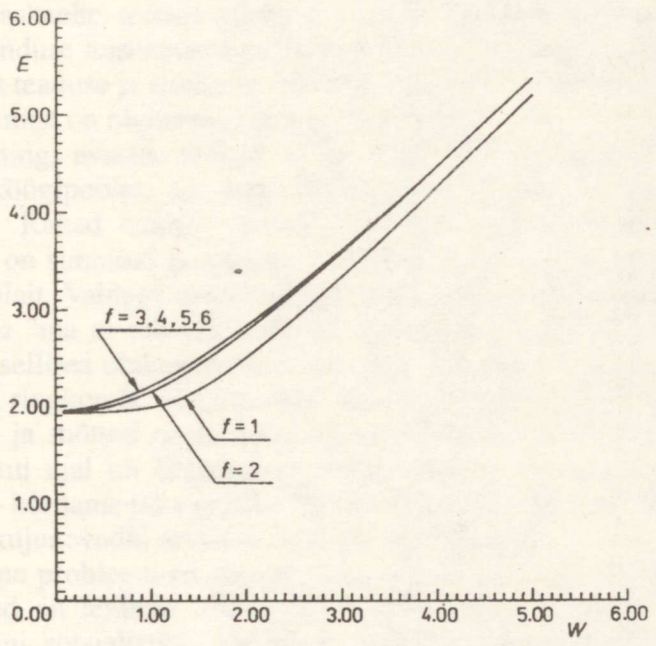

Fig. 2. Site-dependence of impurity electronic levels; f numbers the impurities beginning from the cluster edge.

In the ensemble of the clusters with different sizes (different N of one-dimensional clusters) the size- and site-dependent variations of impurity electronic levels will result in the variations of the corresponding spectral line frequencies. It is the so-called inhomogeneous broadening of the spectral line.

In inhomogeneous systems spectral hole burning was performed [6].

So, the size- and the site-dependence mechanisms of the inhomogeneous broadening can be effective in spectral hole burning. The present consideration can be useful in the estimation of the broadening parameters and conditions.

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