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IMPURITY ELECTRONIC LEVELS IN A CLUSTER

Olev SILD

Füüsika Instituut (Institute of Physics), Riia 142, EE-2400 Tartu, Eesti (Estonia)

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Abstract. For a crystalline cluster of cubic symmetry, the electronic levels of an impurity in a cluster are calculated depending on the size of the cluster and on the impurity site in the cluster. The results of model calculations can be used in the analysis of the size-dependence and site-dependence mechanisms of the inhomogeneous variations of impurity electronic levels as well of inhomogeneous broadening of the corresponding spectral lines in the cluster systems.

Key words: crystalline cluster, impurity electronic levels, inhomogeneous broadening.

1. INTRODUCTION

Advances in the synthesis of nanocrystals or clusters in solid media (see e.g. [1]) have aroused interest in the study 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 [2], the impurity electronic levels in a one-dimensional cluster were calculated. In the present paper, a simple three-dimensional model of a 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 the Green's function method [3–5]. The Green's function method is applied to the present cluster model, too. However, here the Green's function of a perturbed Hamiltonian is calculated, whereas in [3–5] the Green's function of the unperturbed Hamiltonian was involved.

2. CLUSTER MODEL

Let us consider a crystalline cluster of cubic symmetry consisting of N identical atoms of spherical symmetry. All the distances between neighbour atoms are supposed to be equal to a. The atoms and atomic orbitals (AO) can be enumerated by three integer numbers, x, y, z, determining the site-vector of the atom $\vec{r} = (ax, ay, az)$.

For example, the simplest cluster of this type consists of a central atom and six neighbour atoms on the x, y, and z directions (see Fig. 1). Here the seven atoms are enumerated as follows: 000, 100, $\bar{1}00$, 010, $0\bar{1}0$, 001, $00\bar{1}$.

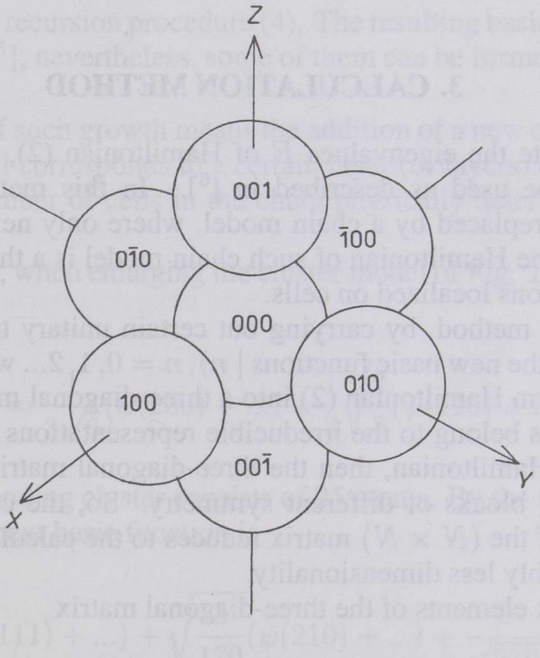

Fig. 1. The simplest crystalline cluster of a cubic symmetry.

In the basis of identical AOs $\psi(xyz)$, the $(N \times N)$ matrix of the electronic Hamiltonian of the cluster is

$$H = \begin{pmatrix} H(000,000) & H(000,100) & \dots \\ H(100,000) & H(100,100) & \\ \vdots & & \ddots \end{pmatrix}. \tag{1}$$

Further, the nondiagonal matrix elements are supposed to be nonzero only for the pairs of interacting nearest-neighbour atoms. As the atoms are identical, one can choose for all the diagonal elements $H(000,000) = H(100,100) = ... = 0$, and for all the nondiagonal (and nonzero) elements, $H(000,100) = H(100,000) = ... = 1$.

The replacing of the central atom of the number 000 by an impurity atom results in a perturbed Hamiltonian, $H + W$. The simplest perturbation matrix in the basis of AOs $\psi(xyz)$ is

$$W_{xyz,x'y'z'} = W\delta_{xyz,000}\delta_{x'y'z',000}$$

(W is a constant). Now the perturbed electronic Hamiltonian has the structure

$$H = \begin{pmatrix} W & 1 & 1 & 1 & \cdots \\ 1 & 0 & 1 & 0 & \\ 1 & 1 & 0 & 1 & \\ 1 & 0 & 1 & 0 & \\ \vdots & & & & \ddots \end{pmatrix} . \tag{2}$$

3. CALCULATION METHOD

To calculate the eigenvalues E of Hamiltonian (2), the chain model method can be used as described in [6]. In this method, the system considered is replaced by a chain model, where only neighbour cells are interacting. The Hamiltonian of such chain model is a three-diagonal one in basic functions localized on cells.

Using this method, by carrying out certain unitary transformation of AOs $\psi(xyz)$, the new basic functions $\mid n\rangle, n = 0, 1, 2...$ will be calculated, which transform Hamiltonian (2) into a three-diagonal matrix. If the new basic functions belong to the irreducible representations of the symmetry group of the Hamiltonian, then the three-diagonal matrix is divided into noninteracting blocks of different symmetry. So, the calculation of the eigenvalues of the $(N \times N)$ matrix reduces to the calculation of matrices of a considerably less dimensionality.

The matrix elements of the three-diagonal matrix

$$H = \begin{pmatrix} a_0 & b_1 & 0 & \cdots \\ b_1 & a_1 & b_2 & \\ 0 & b_2 & a_2 & \\ \vdots & & & \ddots \end{pmatrix} \tag{3}$$

are calculated by using the following recurrence relation [6]:

$$\begin{gathered} \mid n+1\rangle = [(H - a_n) \mid n\rangle - b_n \mid n-1\rangle]/b_{n+1} \,, \\ a_n = \langle n \mid H \mid n\rangle \,, \\ b_n = \langle n \mid H \mid n-1\rangle \,, \quad b_0 = 0 \,. \end{gathered} \tag{4}$$

The choice of the starting basic function $\mid 0\rangle$ is free. It depends on what physics we are interested in. If we are interested in the electronic level of the impurity in the cluster, the impurity AO $\psi(000)$ must be chosen as $\mid 0\rangle$. Next $\mid n\rangle$ are calculated by relation (4) as linear combinations of the AOs

$\psi(xyz)$ of the cluster. If $\mid 0\rangle$ belongs to a certain irreducible representation, the next ones, $\mid 1\rangle, \mid 2\rangle \ldots$, are of the same symmetry.

For example, Hamiltonian (2) of the $N = 7$ cluster (see Fig. 1) is a (7×7) matrix. Suppose the central impurity atom in a state of spherical symmetry, i.e. $\psi(000)$ is full-symmetric. Then we are interested in the full-symmetric basic functions $\mid n\rangle$. There exist only two such functions: $\mid 0\rangle = \psi(000)$ and $\mid 1\rangle = 6^{1/2}[\psi(100) + \psi(\bar{1}00) + \psi(010) + \psi(0\bar{1}0) + \psi(001) + \psi(00\bar{1})]$. So, the problem of the impurity electronic level reduces to the eigenvalue problem of the (2×2) matrix.

Further, the minimum cluster must be enlarged to study the dependence of the impurity electronic levels on the cluster size. To enlarge the cluster, it is reasonable to add the atoms whose AOs would form the next $\mid n\rangle$ in accordance with recursion procedure (4). The resulting basic functions $\mid n\rangle$ are orthogonal [6]; nevertheless, some of them can be formed partly on the same AOs.

Every step of such growth means the addition of a new cell in the chain model. Each cell corresponds to a certain layer (or layers) of atoms in the cluster. The number of cells in the chain physically determines the bulk cluster size.

For example, when enlarging the cluster model of Fig. 1, the next basic function will be

$$\mid 2\rangle = \frac{1}{3\sqrt{6}}(\psi(200) + ...) + \frac{1}{3}\sqrt{\frac{2}{3}}(\psi(110) + ...)$$

and the corresponding cluster consists of 25 atoms. By the addition of one more layer, the next basic function is

$$\mid 3\rangle = \sqrt{\frac{6}{85}}(\psi(111) + ...) + \sqrt{\frac{3}{170}}(\psi(210) + ...) + \frac{1}{\sqrt{510}}(\psi(300) + ...)$$

and the cluster consists of 63 atoms. For this cluster the three-diagonal block of A_{1g} symmetry is

$$\begin{pmatrix} W & \sqrt{6} & 0 & 0 \\ \sqrt{6} & 0 & 3 & 0 \\ 0 & 3 & 0 & \sqrt{85/9} \\ 0 & 0 & \sqrt{85/9} & 0 \end{pmatrix} . \tag{5}$$

A chain model method enables a simple calculation of the Green's function of the system $G(E) = (E - H)^{-1}$ as a continued fraction. In the calculation, the elements of the three-diagonal matrix (block!) serve as the parameters of the continued fraction [6]. The continued fraction is just suitable for computing (as was demonstrated, e.g. in [7]).

For block (5), the Green's function presented as a continued fraction is as follows:

$$G(E) = \cfrac{1}{E - a_0 - \cfrac{b_1^2}{E - a_1 - \cfrac{b_2^2}{E - a_2 - \cfrac{b_3^2}{E - a_3}}}} =$$

$$= \cfrac{1}{E - W - \cfrac{6}{E - \cfrac{9}{E - \cfrac{85}{9E}}}} . \qquad (6)$$

$G(E)$ has poles at the energy eigenvalues E.

The number of eigenvalues equals the number of cells in the chain. By enlarging the cluster size, i.e. the corresponding number of cells, the spectrum of eigenvalues will approach the energy band of the crystal.

The cluster model described above is an analogue of the tight-binding model of a crystal. For the latter the bandwidth of the electronic energy spectrum is $12 \mid H(000, 100) \mid$ [8]. Thus, enlarging the unperturbed ($W = 0$) cluster model, the boundary levels E_{bl} of the spectrum of its eigenvalues will approach the energy values $E_{\mathrm{bl}} = \pm 6$, since $H(000, 100) = 1$ has been chosen in our calculation (Section 2).

4. SIZE-DEPENDENCE OF IMPURITY ELECTRONIC LEVELS

By using the calculation method of Section 3, the impurity electronic levels were calculated depending on the perturbation constant W and on the number l of the cells in the chain model. The number l determines the cluster size as described in the previous section, e.g. for the cluster of Fig. 1, $l = 2$. Figure 2 presents the upper boundary levels E_{bl} of the eigenvalues spectrum, depending on W and l ($l = 3 \ldots 10$). At $W = 0$, $E_{\mathrm{bl}} = \sqrt{15}$ for $l = 3$ and $E_{\mathrm{bl}} \to 6$ for crystal limit, $l \to \infty$. At $W < E_{\mathrm{bl}}$, naturally, the impurity electronic levels are strongly mixed with host atom levels and only at $W > E_{\mathrm{bl}}$ the boundary levels can be called the impurity ones.

In the ensemble of clusters with different sizes the variations of impurity electronic levels have spread to intervals of values decreasing with the growth of W, as the growth of W means a gradual withdrawal of the impurity level from its resonance with the host atom levels. In an ensemble of small clusters with $l = 3 \ldots 10$ the variation intervals in the case of $W = 5, 6, 7, 8, 9$ are 0.152, 0.063, 0.030, 0.016, 0.009, respectively, $H(000, 100)$ being the energy unit.

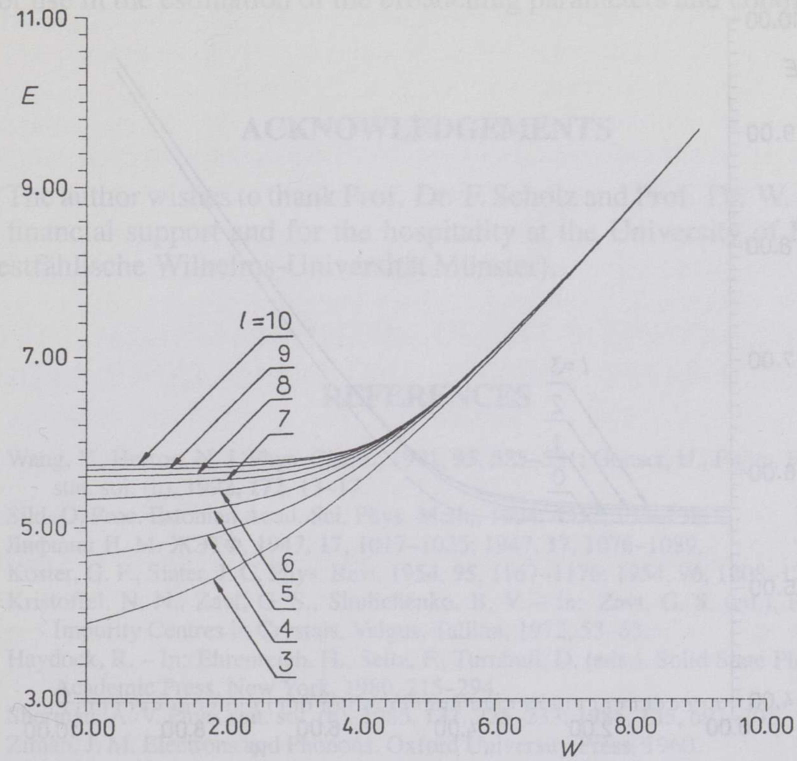

Fig. 2. Impurity electronic levels of the cluster, depending on the perturbation constant W and on the number l of cells in the chain model of the cluster.

5. SITE-DEPENDENCE OF IMPURITY ELECTRONIC LEVELS

The cluster model considered in the previous section supposed the impurity atom being situated in the centre of the cluster. In real clusters the impurity atoms can replace also the host atoms near the 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 edge.

Such site-dependence has been calculated for the cluster consisting of atoms with $x \geq 0$, y, z – arbitrary integers, i.e. for the cluster with plane edge. In this cluster the impurities 000, 100, 200, 300..., having the distances fa ($f = 0, 1, 2, 3...$) from the cluster edge, are considered. As a matter of fact, the impurity electronic levels at the crystal surface are calculated.

Figure 3 presents the boundary levels E_{bl} of the eigenvalues spectrum, depending on W and f ($f = 0....3$). It demonstrates a considerable level variation only for the impurities in the two-atomic outer layer of the cluster. For nonplane edges, naturally, the variation values are different and only the variation interval can be used for estimations.

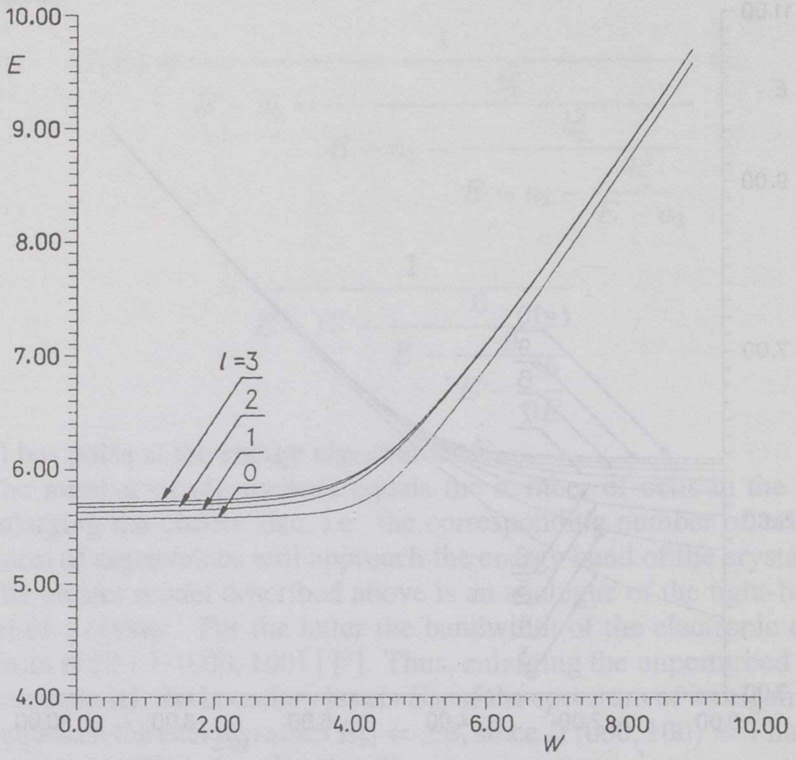

Fig. 3. Impurity electronic levels of the cluster, depending on the perturbation constant W and on the distance fa (a – lattice constant) of the impurity from the cluster edge.

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

6. CONCLUSIONS

In the present contribution, a chain model method was developed for the calculation of the electronic levels of an impurity in a cluster, depending on the size of the cluster and on the impurity site in the cluster.

In an ensemble of clusters with different sizes 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 has been performed [9]. So, the size- and site-dependence mechanisms of the inhomogeneous broadening can be effective in spectral hole burning. The outlined chain model method can be of use in the estimation of the broadening parameters and conditions.

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LISANDI ELEKTRONNIVOOD KLASTRIS

Olev SILD

On arvutatud kuubilise sümmeetriaga kristallilise klastri lisandiaatomi elektronnivood sõltuvalt klastri suurusest ja lisandi asukohast klastris. Arvutustulemused on kasutatavad lisandiaatomi elektronnivoode mittehomogeensete variatsioonide klastermehhanismide hindamisel, samuti klastersüsteemide spektrijoonte mittehomogeense laienemise analüüsimisel.