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HIGH-ENERGY BANDS OF POLYVALENT METALS AND ELEMENTARY SEMICONDUCTORS

1.Introduction

The most frequent calculations of energy bands are limited within the area of 10-20 eV around Fermi level in metals,or around the energy gap in semiconductors.Generally this is enough for the explanation of experiments such as:the form of Fermi surface,optical experiments,or photoemission.However,there is a class of experiments: the absorption of X-ray and low-energy electron diffraction /LEED/, for instance,which needs the knowledge of excited electron states in crystal $\sim$100 eV above the mentioned area.In this paper the results of calculations of high energy levels of polyvalent metals: Al,Pb and semiconductors:Si,Ge within the area up to $\sim$150 eV above the conduction band in metals that is, $\sim$100 eV from the bottom of valence band in semiconductors,are obtained by applying mVS pseudopotential[1/].

2.The difficulties emerged in energy bands calculations

The band structure can be obtained by solving the secular equation:

$$\det\left|\{(\vec{k}-\vec{g})^2-\varepsilon(\vec{k})\}\delta_{\vec{g}\vec{g}'}+S(\vec{g}-\vec{g}')\langle\vec{k}+\vec{g}|w|\vec{k}+\vec{g}'\rangle\right|=0 \qquad /1/$$

where $\varepsilon(\vec{k})$ is in Ryd.In /1/, $\vec{g}$ and $\vec{g}'$ are vectors of the reciprocal lattice /"recips"/,while $S(\vec{g}-\vec{g}')$ is the geometrical structure factor of the lattice and $\langle\vec{k}+\vec{g}|w|\vec{k}+\vec{g}'\rangle$ is the potential formfactor.

1/ Modified Veljković and Slavić pseudopotential [1] mVS

Solving of the equation /1/ is a complex problem which includes calculation of crystal potential, its matrix elements, diagonalization of the hamiltonian matrix and identification of eigenvalues of energy and eigenfunctions, according to the characteristics of crystal symmetry.

The problem of crystal potential is usually solved by means of using some of local crystal pseudopotentials.

The matrix elements calculations and matrix diagonalization is the technical problem, which needs a lot of computer time. For instance, in order to calculate excited levels in metals /Al/ up to 150 eV it is necessary to solve the equation /1/, of the order of 65x65 in every point in BZ[2/]. If we want to know density of levels, using the method of the paper [4], we must perform 2000 such calculations in points of IBZ. For this calculation 50 machine hours on CDC3600 are needed. Brust, while calculating $\varepsilon_2(\omega)$ -imaginary part of dielectric function for Si and Ge [5], has reduced the time of diagonalization by applying Löwdin's perturbation technique, that is, by supstituting the equation of the order of 90x90 by equation 20x20. Besides, 6 to 12 hours are spent, depending an the oscillator strength for interband transitions in expressions for $\varepsilon_2(\omega)$ [6] was treated.

The last of the previously mentioned problems is the identification of the energy eigenvalues and respective eigenfunctions according to the irreducible representations of the crystal point group. This problem, for high bands, is practically unsolvable without using the well symmetrised basis functions.

3. Symmetrisation

Further, we shall describe the procedure of "symmetrised plane wave /SPW's/" construction. First of all it is necessary to select the proper set of recips to generate the SPW's for expanding the crystal wavefunctions at some symmetry point.

2/ BZ is the first Brillouin zone and IBZ is the irreducible wedge of the BZ

From the set of recips we selected the "progenitors" having the following properties: acting by the group operators on progenitors one can get entire set of recips.

SPW functions of the progenitors and their equivalent vectors, are equivalent, so that the linearly independent basis can be formed by means of plane waves with progenitors.

Symmetrisation of these waves can be performed with the projection operator defined in [7] as

$$\hat{P}^{j}_{\mu\nu} = \frac{l_j}{l} \sum_{R} \Gamma^{j*}_{\nu\mu}(R)\, \hat{P}_R \qquad /2/$$

where $\Gamma^{j*}_{\nu\mu}(R)$ is conjugated metrix element j's irreducible representation, of dimension l_j of a point group, of order l. The sum is taken over all group operators.

If $\vec{k}+\vec{g}_n$ is progenitor, SPW function can be obtained on the basis of following formula:

$$SPW^{j}_{\mu\nu}(\vec{k}+\vec{g}_n) = \frac{1}{\sqrt{N^{nln}_{jl\mu\nu}}} \sum_{i} C^{nln}_{jl\mu\nu}(\vec{k}+\vec{g}_n)\, e^{i(\vec{k}+\vec{g}^{\,i}_n)\vec{r}} \qquad /3/$$

Vector $\vec{k}+\vec{g}^{\,i}_n$ is equivalent vector to the progenitor $\vec{k}+\vec{g}_n$. All necessary coefficients $C^{nln}_{jl\mu\nu}(\vec{k}+\vec{g}_n)$ and $N^{nln}_{jl\mu\nu}$ can be found in Luehrmann's paper [7]. There he has constructed a set of tables giving the coefficients of SPW's and matrix elements between them for all symmorphic space groups.

The formula for matrix element between two SPW's generated by the progenitors $\vec{k}+\vec{g}_n$ and $\vec{k}+\vec{g}_m$, respectively, is

$$\langle SPW^{j'}_{\mu'\nu'}(\vec{k}+\vec{g}_m) | w | SPW^{j}_{\mu\nu}(\vec{k}+\vec{g}_n) \rangle =$$

$$= \delta_{jj'}\, \delta_{\nu\nu'} \sqrt{M^{mln}_{jl\mu\nu}} \sum_{i} C^{mln}_{jl\mu\mu'}(\vec{k}+\vec{g}^{\,i}_n) \langle \vec{k}+\vec{g}^{\,i}_m | w | \vec{k}+\vec{g}^{\,i}_n \rangle \qquad /4/$$

The coefficients $C^{mln}_{jl\mu\mu'}$ and $M^{mln}_{jl\mu\nu}$, with appropriate explanations, can also be found in the tables of the mentioned paper.

The formula /4/ shows all the advantages which fully applied crystal symmetry offers: Matrix elements of two SPW's are different from zero only if both SPW's belong to the same column

and to the same irreducible representation.In that way the secular equation is reduced to block-diagonal form and calculated energy eigenvalues and eigenfunctions are immediately classified according to irreducible representations.

4.Results

A great number of authors have examined the band structure of metals and semiconductors.Their investigations are mainly directed towards the examination of Fermi surface forms in metals and optical transitions in semiconductors.That is why there is only a small number of papers in which high levels are given.The best known papers for high Al are:Connoly's[8]and Hoffstein-Boudreaux's[9],for Si and Ge Brust-Kane[10].We have no information about excited levels of Pb.

The band structure for f.c.c. lattice Al,Pb,Si and Ge is calculated along the direction (001) in BZ by applying mVS pseudopotential. The programme for symmetrisation of wave functions and diagonalization of matrix is made according to the instructions of Hoffstein-Moller[11] The input data are:recips and label of representation,while the programme automatically constructs appropriate SPW waves and matrix elements between them according to the equation /4/.The energy levels are calculated by means of 50 SPW's.The results are shown in the Fig.1 only for Δ_1 irreducible representation.Our results agree well with the results in [8,9,10],especially with the results of Hoffstein-Boudreaux [9] for Al.

Note that these results will be used to calculate LEED spectra Al for surfaces: (001) ,(111) , (110) ,and will be reported in one of the following papers.

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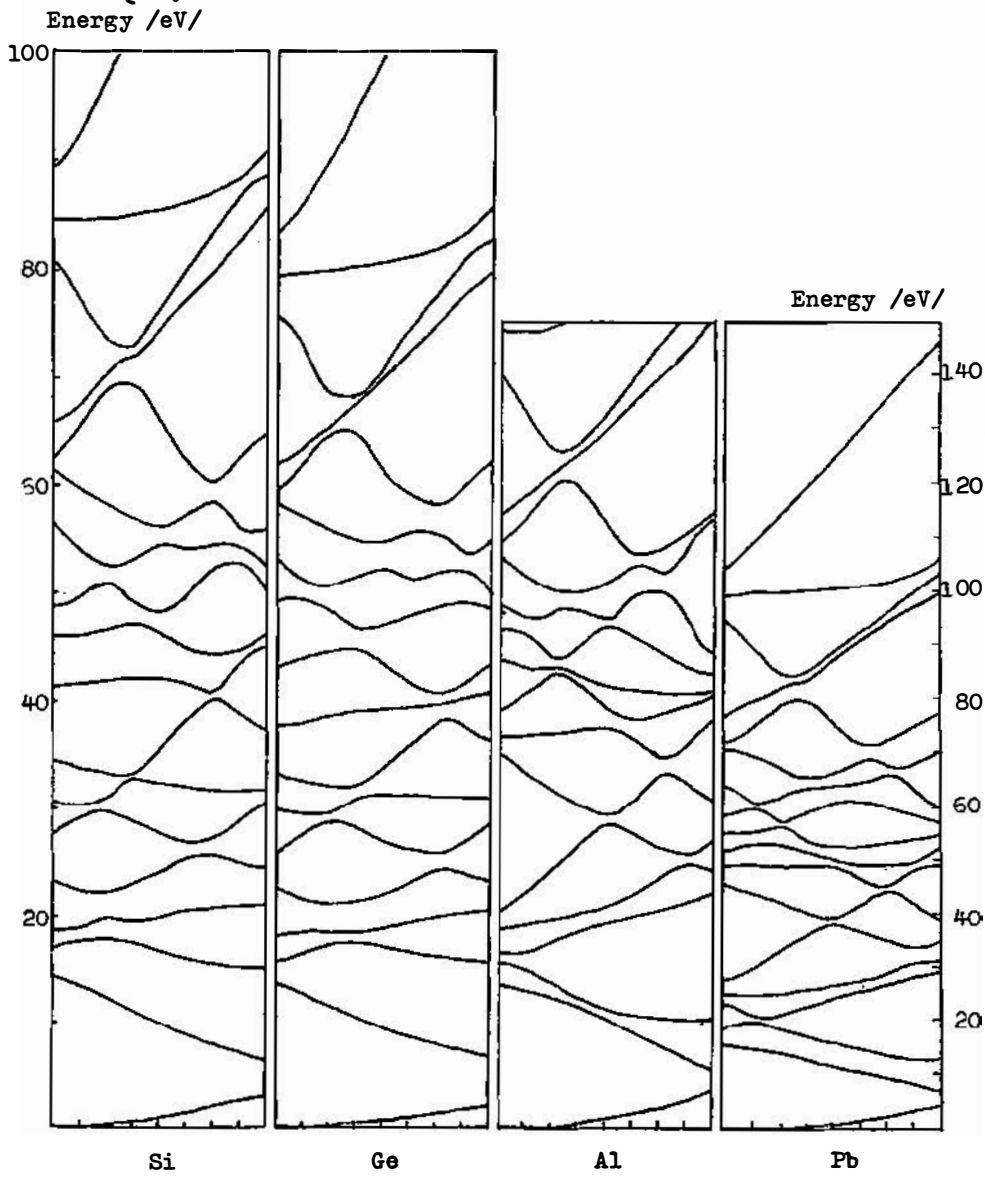

Fig.1.Center-symmetrical bands Δ_1 along (001) direction