

Institut Fizyki UMCS

E. TARANKO, R. TARANKO, M. PIŁAT

**Influence of the Next Nearest-neighbour-interactions  
on the Electrical Conductivity in Binary Alloys**

Wpływ oddziaływań z najbliższymi i dalszymi sąsiadami na przewodnictwo elektryczne  
stopów dwuskładnikowych

Влияние взаимодействий с ближайшими и дальнейшими соседями  
на электропроводность бинарных сплавов

Dedicated to Professor  
Stanisław Szpikowski on occasion  
of his 60th birthday

1. INTRODUCTION

Calculating the electronic energy band structure of solids by means of the linear-combination-of-atomic-orbitals one usually keeps interactions only up to nearest neighbours. Nevertheless, it is known, that for example, for the body centered cubic (bcc) crystal lattice the strength of the next-nearest-neighbour (nnn) interactions is not small in comparison with the nearest-neighbours ones [1]. In [2] it has been shown that inclusion of nnn interactions has greatly improved the accuracy of the calculated

(in tight-binding method) valence band structure and density of states for diamond and zincblende crystals. Kiwi M. et al. [3] have investigated the influence of nnn interactions and overlap between orbitals centered on neighbouring atoms on the band structure of the Bethe and diamond lattice. They showed, that inclusion of nnn interactions changed considerably the electronic structure of these solids.

The purpose of the present paper is the calculation of the density of states and electrical conductivity of disordered alloys with nnn interactions taken into account. The remainder of this paper is arranged as follows. In Sec. 2 we present a model alloy Hamiltonian and investigate the influence of nnn interactions on the density of states of a pure bcc crystal. Next, in Sec. 3, we introduce the nnn bcc lattice Green functions and give the recurrence equation for them. In Sec. 4 we present the formulas for dc and ac electrical conductivity with nnn interaction included. Numerical results for a density of states of a pure nnn bcc crystal and for a binary alloy crystal we present in Sec. 2 and 3, respectively, and numerical results for a dc electrical conductivity in Sec. 4.

## 2. THE ALLOY HAMILTONIAN

Let us consider a substitutionally disordered binary alloy  $A_x B_{1-x}$  with atoms A, B randomly distributed at sites of a cubic perfect lattice. The alloy is described by a single s-like conduction band and is assumed to be treated in the tight-binding approximation in Wannier's representation. The Hamiltonian reads:

$$H = \sum_n |n\rangle \epsilon_n \langle n| + \sum_{n \neq m} |n\rangle h_{nm} \langle m| = \quad (1a)$$

$$= \sum_n |n\rangle \epsilon_n \langle n| + h_1 \sum_{n \neq m} |n\rangle \langle m| + h_2 \sum_{n \neq m} |n\rangle \langle m| \quad (1b)$$

Here the  $|n\rangle$  are Wannier functions localized at the  $n$ -th site. The diagonal elements may be regarded as random atomic levels which take one of two possible values  $\epsilon_A$  or  $\epsilon_B$  depending on whether an atom of type A or B occupies the site  $n$ . As we can see from Eq. (1) we assume the hopping integrals  $h_{nm}$ , responsible for the propagation of electrons, to take on a non-zero value only when " $n$ " and " $m$ " are nearest-neighbours (nn) and next-nearest-neighbours (nnn). In general hopping integrals can take six possible values  $h_{AA}^{(1)}$ ,  $h_{AB}^{(1)}$ ,  $h_{BB}^{(1)}$ ,  $h_{AA}^{(2)}$ ,  $h_{AB}^{(2)}$ ,  $h_{BB}^{(2)}$  according to the occupation of sites " $n$ " and " $m$ ", but in the following we assume constant  $h_1$  and  $h_2$  values, independent on the nature of the atoms located at nearest or next-nearest-neighbour lattice sites. This means, we consider diagonal disorder, only. We assume the lattice of the alloy to be body centered cubic. The Hamiltonian of the ideal crystal composed, say of A-type atoms reads:

$$H_A = \epsilon_A \sum_n |n\rangle \langle n| + h_1 \sum_{n \neq m}^{(nn)} |n\rangle \langle m| + h_2 \sum_{n \neq m}^{(nnn)} |n\rangle \langle m| \quad (2)$$

This Hamiltonian in " $k$ ", Bloch-like representation defined by

$$|k\rangle = \frac{1}{N} \sum_j e^{-ik R_j} |j\rangle \quad (3)$$

is diagonal, and the eigenvalue  $\epsilon(k)$  is given by

$$\begin{aligned} \epsilon(k) = & \epsilon_A - 8h_1 \cos \frac{ak_x}{2} \cos \frac{ak_y}{2} \cos \frac{ak_z}{2} - \\ & - 4h_2 \left[ \cos^2 \frac{ak_x}{2} + \cos^2 \frac{ak_y}{2} + \cos^2 \frac{ak_z}{2} \right] + 6h_2 \end{aligned} \quad (4)$$

So the pure A(B) component band is centered at  $\epsilon_A$  ( $\epsilon_B$ ) and has a width  $2W_A$  ( $2W_B$ ) =  $16h_1$  (the band extends from  $\epsilon_A$  ( $\epsilon_B$ ) -  $8h_1$  -  $6h_2$  to  $\epsilon_A$  ( $\epsilon_B$ ) +  $8h_1$  -  $6h_2$ ).

## 3. THE DENSITY OF STATES AND "nnn" LATTICE GREEN FUNCTIONS

The lattice Green functions for Hamiltonian with only nearest-neighbour hopping integrals included has been widely used [5-12]. Because of additional interactions included in the Hamiltonian (1) we must introduce the "nnn" lattice Green functions. They are defined in the following way:

$$G(lmn; E, a) = \frac{1}{\pi^3} \int_0^\pi \int_0^\pi \int_0^\pi \frac{\cos lx \cos mx \cos nx \, dx \, dy \, dz}{E^+ + \cos x \cos y \cos z + a(\cos^2 x + \cos^2 y + \cos^2 z)} \quad (5)$$

where  $E^+ = E + i0$ .

The density of states of the ideal crystal may be written in terms of these "nnn" lattice Green functions as:

$$D(E) = -\frac{1}{\pi} \frac{1}{8h_1} \operatorname{Im} G(000; \frac{E}{8h_1} - \frac{3}{4}k; k/2); \quad k = h_2/h_1 \quad (6)$$

Problem of calculations of the density of states for a pure bcc lattice with "nnn" transfer integrals included has been investigated in papers [13-15]. Nevertheless, for the sake of completeness and for latter discussion we calculate this density of states for several values of the ratio of transfer integrals  $h_1$  and  $h_2$  and present in Fig. 1. For a computational convenience we used the half bandwidth as an energy unit. The inclusion of the "nnn" transfer integrals in Hamiltonian (1) changes the shape of the density of states in a rather clearly way.

Firstly, the unphysical divergence in the middle of the band disappears. Secondly, the maximum moves in the upper energy band side (for  $h_2/h_1 < 1$ ) and simultaneously decreases and broadens. We can see, especially near the maximum of the curve  $D$  (Fig. 1) for  $h_2/h_1 = 0.5$  some similarity to the shape of the SC density of states (with "nn" transfer integrals in Hamiltonian included, only). This similarity increases with increasing ratio  $h_2/h_1$  and in limit  $h_2/h_1 \rightarrow \infty$  one can obtain the "nnn" sc tight-binding

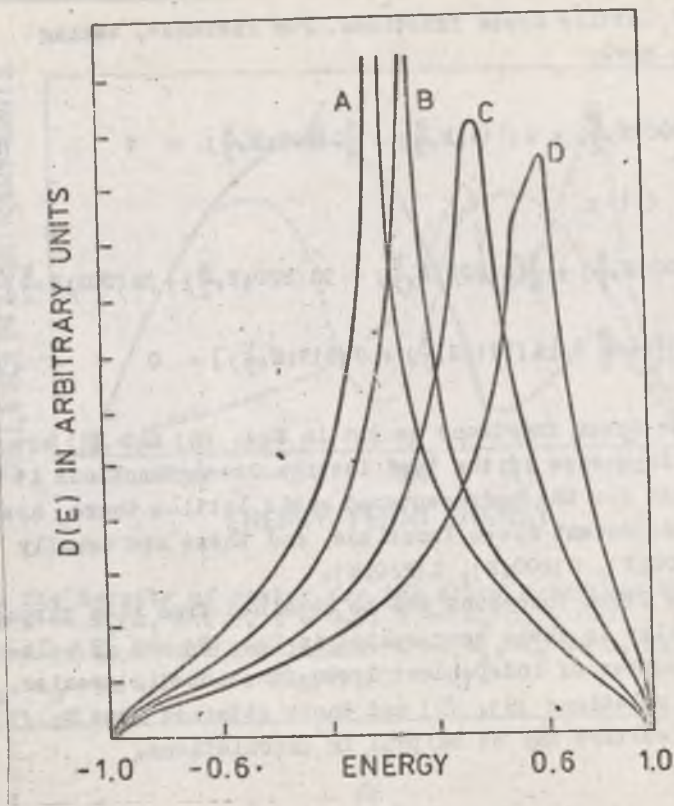


Fig. 1. The density of states for a pure "nnn" bcc crystal (in tight-binding representation). The parameters  $h_2/h_1$  are: A - 0.0, B - 0.1, C - 0.3, D - 0.5. Energy in units of half-bandwidth.

density of states (for s-like states) - see, for comparison [14, 15].

For a lattice Green functions defined in Eq. (5) we can write the following equation:

$$(E + \frac{3}{4}k)G(\vec{l}; E, \frac{k}{2}) + \frac{1}{8} \sum_{\vec{\delta}} G(\vec{l} + \vec{\delta}; E, \frac{k}{2}) + \frac{k}{8} \sum_{\vec{\delta}} G(\vec{l} + \vec{\delta}; E, \frac{k}{2}) = \delta_{\vec{l}, \vec{0}} \quad (7)$$

The first summation is performed over lattice vectors connecting nearest-neighbour atoms and the second one over the next-nearest-neighbour atoms. From this equation, taking various crystal vectors  $\vec{l}$  into consideration, we can obtain relations between dif-

ferent "nnn" lattice Green functions. For instance, taking  $\vec{l} = (000)$  we have:

$$(E + \frac{3}{4}k) G(000; E, \frac{k}{2}) + G(111; E, \frac{k}{2}) + \frac{3}{4}G(200; E, \frac{k}{2}) = 1 \quad (8)$$

and for  $\vec{l} = (111)$ :

$$(E + \frac{3}{4}k) G(000; E, \frac{k}{2}) + \frac{1}{8}[G(222; E, \frac{k}{2}) + 3G(220; E, \frac{k}{2}) + 3G(002; E, \frac{k}{2}) + G(000; E, \frac{k}{2})] + \frac{3}{8}k [G(111; E, \frac{k}{2}) + G(113; E, \frac{k}{2})] = 0 \quad (9)$$

Not all of the Green functions we get in Eqs. (8) and (9) are independent. In a case of the "nn" lattice Green functions it is known [21] that for the body-centered cubic lattice there are only three independent Green functions, and these are usually taken as  $G(000; E)$ ,  $G(200; E)$ ,  $G(220; E)$ .

The other Green functions can be obtained from them through relations similar to these represented in Eqs. (8) and (9). In our case the number of independent Green functions is greater, but still the relations (8), (9) and those obtained from Eq. (7) for other  $\vec{l}$  vectors may be helpful in calculations.

#### 4. DC AND AC ELECTRIC CONDUCTIVITY

In the random alloy problem many investigations have been devoted to the calculation of the electronic density of states, electric conductivity, Hall coefficient (see for example [16-19]). For these problems the coherent potential approximation (CPA) and its generalization (off diagonal disorder, cluster effects, short-range-order, long-range-order and so on) have been found useful. We use the coherent potential approximation formulated by Soven [20] (see also CPA method for ternary alloys [19]). The quantity we wish to determine first for the alloy is:

$$\langle G(E) \rangle \equiv G(E) = [E - W - \Sigma(E)]^{-1} \quad (10)$$

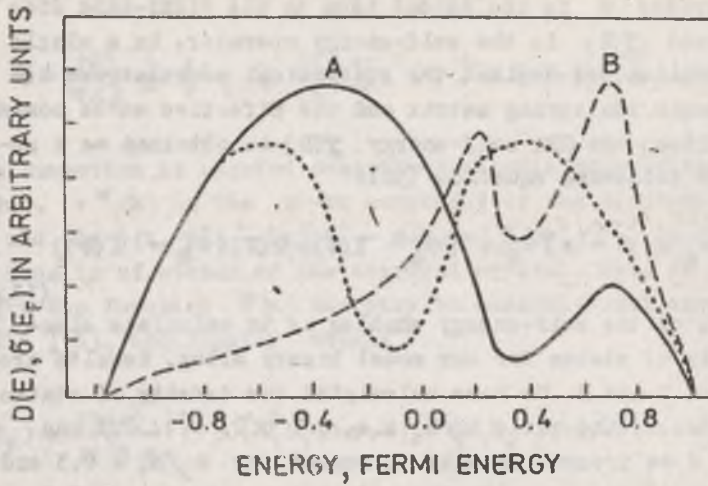


Fig. 2. The density of states for the alloy described by parameters: A —  $h_2/h_1 = 0.3$ ,  $x = 0.3$ ; B —  $h_2/h_1 = 0.3$ ,  $x = 0.5$ . Positions of an atomic levels are: A —  $\epsilon_A, \epsilon_B \rightarrow G, F$ ; B —  $\epsilon_A, \epsilon_B \rightarrow J, H$  (see fig. 3).

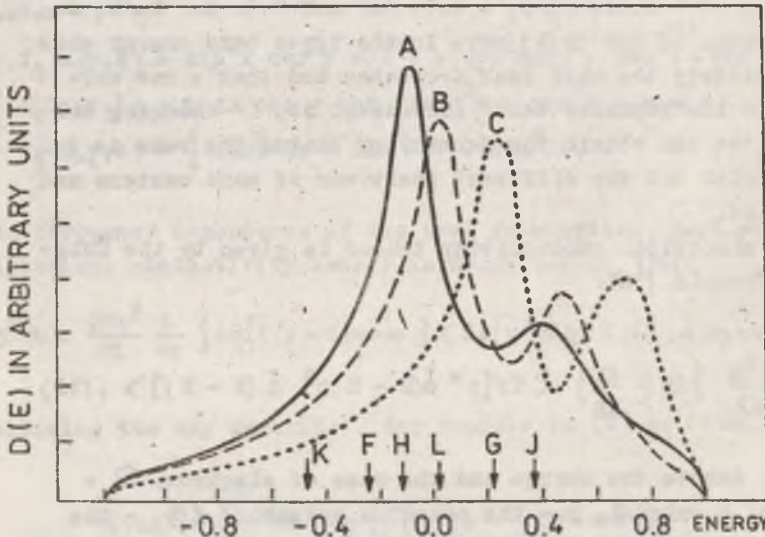


Fig. 3. The density of states for the alloy described by parameters:  $x = 0.3$  and  $h_2/h_1$  is 0.0, 0.3, 0.5 for curves A, B, C, respectively. Positions of atomic levels: A —  $\epsilon_A, \epsilon_B \rightarrow L, K$ ; B —  $\epsilon_A, \epsilon_B \rightarrow G, F$ ; C —  $\epsilon_A, \epsilon_B \rightarrow J, H$ .

the configuration average of the single-electron Green function. Here the operator  $\mathbb{W}$  is the second term on the right-hand side in Eq. (1a) and  $\Sigma(E)$  is the self-energy operator. In a single site approximation (we neglect the statistical correlations between the atomic scattering matrix and the effective waves coming from other sites) the CPA self-energy  $\Sigma(E)$  is obtained as a solution of the following equation [18]:

$$\Sigma(E) = x \epsilon_A + (1 - x) \epsilon_B + (\epsilon_A - \Sigma(E)) G(E) (\epsilon_B - \Sigma(E)) \quad (11)$$

The knowledge of the self-energy enables us to calculate electronic density of states for our model binary alloy. Results are shown in Figs. 2 and 3. We have calculated the density of states for four values of the ratio  $h_2/h_1$ , i.e. for 0.0, 0.1, 0.3 and 0.5. In Fig. 2 we present density of states for  $h_2/h_1 = 0.3$  and for two values of the concentration of A-type atoms:  $x = 0.3$  and  $x = 0.5$ . We can observe, that the peak's position do not depend on the concentration of various sorts of atoms, in contrast to the situation in the next Fig. 3. Here we have density of states curves for a constant concentration  $x = 0.3$  and for different values of a ratio  $h_2/h_1 = 0.0, 0.3$  and  $0.5$ . As  $h_2/h_1$  is raised the peaks of the  $D(E)$  move in the upper band energy side and simultaneously the main peak decreases and that's one corresponding to the "impurity band" increases. So, changing the ratio  $h_2/h_1$  we can obtain the density of states the same as for "nn" Hamiltonian but for different positions of band centers and concentrations.

The dc electrical conductivity tensor is given by the Kubo-Greenwood formula [16]:

$$\sigma^{ab} = \frac{2\pi e^2 \hbar}{m \Omega} \int dE \left( -\frac{df}{dE} \right) \langle \text{Tr} [p^a \delta(E - H) p^b \delta(E - H)] \rangle, \quad (12)$$

where  $e$ ,  $m$  denote the charge and the mass of electron,  $\Omega$  - the volume of a crystal,  $p$  - the momentum operator,  $f(E)$  - the Fermi-Dirac distribution function and  $H$  - the Hamiltonian of the system. The sign  $\langle \dots \rangle$  denotes the average over configurations. Since this method was described elsewhere [16, 18], we



quote here the final form of the formula

$$\sigma = \frac{2e^2}{\pi\Omega} \frac{1}{\pi} \int d\eta \left(-\frac{df}{d\eta}\right) \sum_k v^2(k) [\text{Im } G(k, \eta^+)]^2 \quad (13)$$

where summation is carried over the Brillouin zone of the bcc crystal,  $v^\alpha(k)$  is the  $\alpha$ -th component of the electron velocity and  $\text{Im } G(k, \eta^+) = \text{Im}[\eta^+ - \epsilon(k) - \Sigma(\eta^+)]^{-1}$  is the spectral density of states of the averaged crystal. Here we calculate exactly the function  $\bar{v}(k)$  contrary to commonly used approximate formula [16], and finally obtain

$$\sigma(E_F) = \frac{128e^2}{\pi^4 k_a} \int_0^{\bar{v}} \int \int [h_1^2 f_1(x, y, z) + 2h_1 h_2 f_2(x, y, z) + h_2^2 f_3(x, y, z)] \cdot \left\{ \frac{\text{Im } \Sigma(E_F)}{[E_F - \epsilon(k) - \text{Re } \Sigma(E_F)]^2 + [\text{Im } \Sigma(E_F)]^2} \right\}^2 dx dy dz \quad (14)$$

where:

$$\begin{aligned} f_1(x, y, z) &= \sin^2 x \cos^2 y \cos^2 z + \cos^2 x \sin^2 y \cos^2 z + \cos^2 x \cos^2 y \sin^2 z \\ f_2(x, y, z) &= \cos x \cos y \cos z (\sin^2 x + \sin^2 y + \sin^2 z) \\ f_3(x, y, z) &= \frac{1}{4} (\sin^2 2x + \sin^2 2y + \sin^2 2z) \end{aligned} \quad (15)$$

The frequency dependence of the real (absorptive) part of the ac electrical conductivity tensor is described by [16]:

$$\sigma^{\alpha\beta}(\omega) = \frac{2\pi e^2}{\Omega} \frac{1}{\omega} \int d\eta [f(\eta) - f(\eta + \omega)] \langle \text{Tr} [v^\alpha \delta(\eta - H) v^\beta \delta(\eta + \omega - H)] \rangle \quad (16)$$

Following the way described, for example in [4] we obtain

$$\sigma(\omega) = \frac{e^2}{2\pi} \text{Re} \int d\eta \frac{1}{\omega} [f(\eta) - f(\eta + \omega)] \times$$

$$\cdot \left\{ \frac{\Phi(\Sigma(\eta^+ + \omega)) - \Phi(\Sigma(\eta^-))}{\Sigma(\eta^+ + \omega) - \Sigma(\eta^-)} - \frac{\Phi(\Sigma(\eta^+ + \omega)) - \Phi(\Sigma(\eta^-))}{\Sigma(\eta^+ + \omega) - \Sigma(\eta^-)} \right\} \quad (17)$$

Here the function  $\Phi$  reads (in terms of a "nnn" bcc lattice Green functions):

$$\begin{aligned} \Phi(z) = & \frac{a^2 h_1}{4h^2} [(1 + k^2)G(000; z_1, k_1) + G(200; z_1, k_1) - G(220; z_1, k_1) - \\ & - G(222; z_1, k_1) + 4kG(111; z_1, k_1) - 4kG(311; z_1, k_1) - \\ & - k^2G(400; z_1, k_1)]; \end{aligned} \quad (18)$$

$$z_1 = \frac{z}{8h_1} - \frac{3}{2} \frac{h_2}{h_1}, \quad k_1 = \frac{1}{2} \frac{h_2}{h_1}, \quad k = \frac{h_2}{h_1}.$$

Numerical results of the dc electrical conductivity are presented in Figs. 4 and 5. The conductivity is plotted as a function of the Fermi energy  $E_F$ , and half of the bandwidth of the pure material is taken as a unit of energy. In Fig. 4 we show  $\sigma$  for  $x = 0.3$  and for two values of ratio  $h_2/h_1$  equal to 0.3 - curve A and 0.5 - curve B. We can see that conductivity depends on a value of the next-nearest neighbour transfer integral, it is greater for greater ratio  $h_2/h_1$ . This is consistent with the physical picture of the motion of electrons in systems described by Hamiltonian (1), namely, electrons have an additional possibility for propagation in crystal.

In order to give a simple and transparent picture of the influence of "nnn" transfer integrals on dc conductivity we present in Fig. 5 conductivity curves for the alloy described by concentration of A atoms equal 0.5 and  $h_2/h_1 = 0.5$  - curve A and  $h_2/h_1 = 0.0$  - curve B. In a case of "nn" Hamiltonian a conductivity is a symmetrical curve (and density of states, too). For the "nnn" Hamiltonian situation is quite different. Now conductivity is a strongly asymmetric function of  $E_F$  and an "impurity" part of this curve has a smaller value in comparison with the "host" part, although is located in energy region of increased values of a density of states.

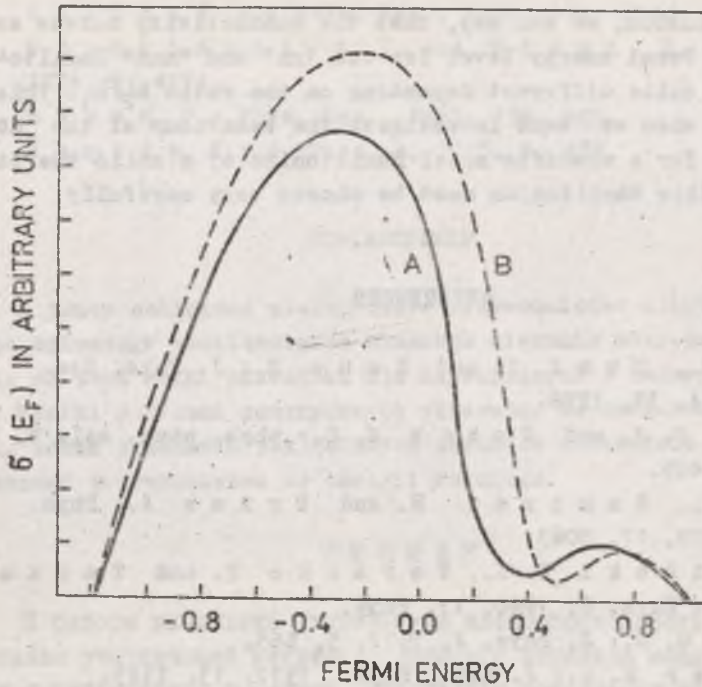


Fig. 4. The dc electrical conductivity for the alloy described by parameters:  $x = 0.3$  and  $h_2/h_1$  equal to 0.3, 0.5 for curves A and B, respectively.

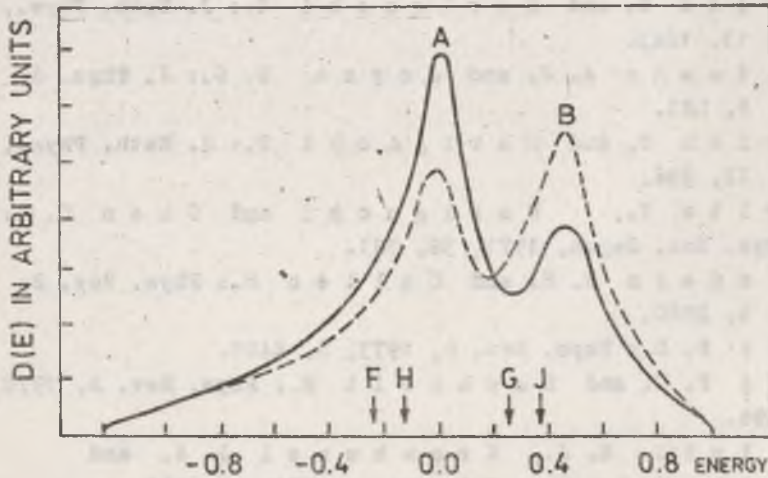


Fig. 5. The dc electrical conductivity (curve A) and density of states (curve B) of the alloy described by parameters:  $x = 0.5$ ,  $h_2/h_1 = 0.5$ . Curve C - dc conductivity for "nn" Hamiltonian - for comparison.

In conclusion, we can say, that the conductivity curves as functions of Fermi energy level for the "nn" and "nnn" Hamiltonians may be quite different depending on the ratio  $h_2/h_1$ . This means, that when we want investigate the behaviour of the dc conductivity for a specific model Hamiltonian of a solid the parameters of this Hamiltonian must be chosen very carefully.

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## STRESZCZENIE

W pracy obliczono stałoprądowe przewodnictwo elektryczne stopu opisanego hamiltonianem ciasnego wiązania zawierającym różne od zera całki przeskoku dla najbliższych i dalszych sąsiadów. Wyniki obliczeń numerycznych wskazują, że dołączenie do opisu całek przeskoku dla dalszych sąsiadów całkowicie zmienia zależność przewodnictwa od energii Fermiego.

## Р Е З Ю М Е

В работе вычислено статическую электропроводность сплавов в модели учитывающей матричные элементы перехода между ближайшими и дальнейшими соседями. Результаты показывают как функция фермиевской энергии сильно зависит от величины этих параметров.

