Density of States for a Three-dimensional Disordered Alloy

D. Pumpernik, B. Borštnik, M. Kertesz *, and A. Ažman
Chemical Institute Boris Kidrič, Ljubljana

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Densities of states for three-dimensional models of binary alloys are calculated with a method based on the negative eigenvalue theorem. Comparison is made with the densities of states obtained by diagonalizations of the Hamiltonian for a certain number of physically different clusters of impurities.

During the last years there has been a considerable interest in the study of disordered systems [1]. Various methods [1-6] have been used to evaluate the densities of states for one, two or three dimensional disordered systems. The purpose of this work is to study a three dimensional random binary alloy system with cubic symmetry using the negative eigenvalue theorem [2] (NET). The Hückel type Hamiltonian may be written as follows:

$$H = \sum_i \alpha_i \, |i\rangle \langle i| + \tfrac{1}{2} \sum_{ij} \beta_{ij} \left(|i\rangle \langle j| + |j\rangle \langle i| \right) \qquad (1)$$

where the sites i and j are nearest neighbours. We are interested not only in the site diagonal disorder but also in the site off-diagonal disorder. Two neighbouring sites i and j can be occupied by two A, two B or one A and one B atom. The corresponding values of the parameters α (site energy) and β (nearest neighbour integral) are α_{A}, β_{AA}, α_{B}, β_{BB} and β_{AB} respectively. In the general case all above mentioned parameters can be taken to be different. Since only neighbour interaction is taken into account, the H matrix is rather sparse. The distribution of non diagonal elements β_{ij} depends upon the enumeration of the lattice sites and upon the boundary conditions. If the system has the geometry of a regular three dimensional array consisting of $N_x N_y N_z$ atoms one can numerate in a simple way, where the index runs over N_x atoms in x direction than over subsequent N_y rows and than over N_z planes. In this case the parameters β are located on six off-diagonals which are dislocated from the main diagonal for 1 (connect the neighbours along x direction), N_x (neighbours along y direction) and $N_x N_y$ (neighbours in z direction).

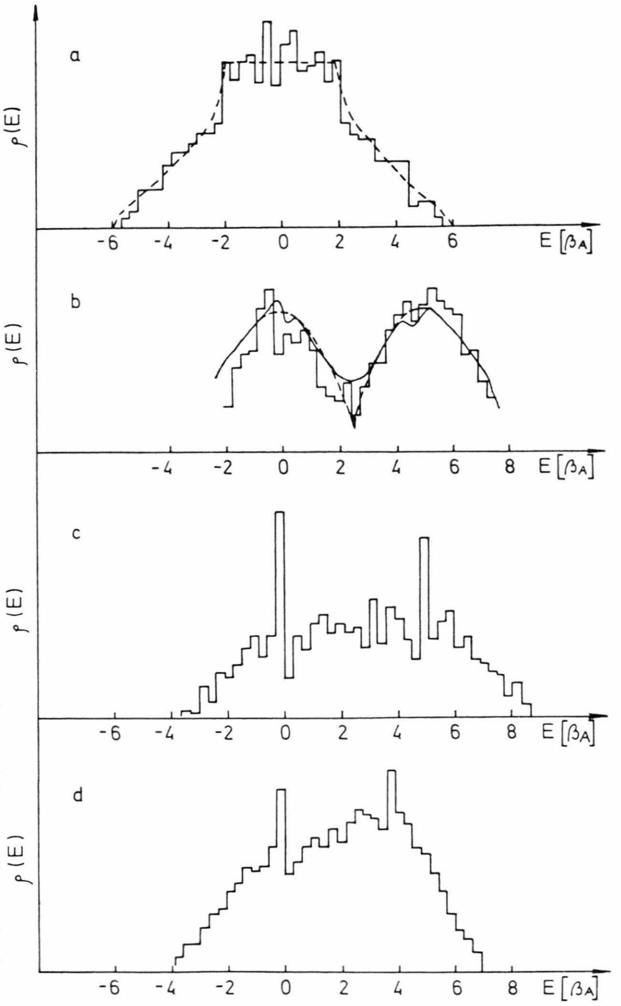

Fig. 1. Density of states. Solid curves give NET results. Plot 1a corresponds to a pure system, where the broken curve is the exact result. The parameters for 1b and 1c are the same except $\beta_{\mathrm{AB}} = 0.1 \, \beta_{\mathrm{A}}$ in 1c. Plot 1d has the parameters $\alpha_{\mathrm{A}} = 0$, $\alpha_{\mathrm{B}} = 3.6 \, \beta_{\mathrm{A}}$, $\beta_{\mathrm{B}} = 0.8 \, \beta_{\mathrm{A}}$, $\beta_{\mathrm{AB}} = 0.5 \, \beta_{\mathrm{A}}$. Plot 1b contains results from Ref. [6] (smooth curve-averages over phases and distributions of impurities) and CPA (broken curve).

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* Permanent address: Central Research Institute of Chemistry, Hungarian Academy of Sciences, Budapest.

Reprint requests to Dr. A. Ažman, Chemical Institute Boris Kidrič, University of Ljubljana, Murnikova 6 — P. predal 537, *Ljubljana*, Jugoslawien.

The density of states dN/dE of the above mentioned Hamiltonian can be obtained exactly using the negative eigenvalue theorem (NET). This procedure is rather time consuming and we tried to find out what is the smallest size of the model giving resonable results without consuming extravagant quantities of computer time. We found that elongated models $N_x = N_y < N_z$ which give matrices with low bandwidths (small $N_x N_y$) are more appropriate than cubes ($N_x = N_y = N_z$). Taking $N_x = N_y = 6$ or 7 and $18 \leqq N_z \leqq 36$ one obtains reasonable agreement with the exact result (Fig. 1 a) for a pure system; and with the results obtained by other methods for disordered systems. Two types of boundary conditions were examined: periodic boundary conditions and free-end boundary conditions. The results show that periodic boundary conditions overemphasise the contribution of the semiperiodic "resonance" states whose wave vectors are integer multiples of $2\pi/(N_x a)$ and $2\pi/(N_y a)$ where a is the lattice constant.

Figure 1 b gives density of states for $\alpha_A = 0$, $\alpha_B = 4.8\,\beta_A$, $\beta_A = \beta_B = \beta_{AB}$ with the concentration of the impurity (atoms B) $r = 0.5$. This is the case when two well resolved bands should appear[6]. The effect of the inclusion of the off-diagonal disorder ($\beta_{AB} \neq \beta_A = \beta_B$, Fig. 1 c) is to flatten the bands. Figure 1 d corresponds to the general case ($\beta_{AB} \neq \beta_A \neq \beta_B$) where the substructures of the spectrum are quenched. In Fig. 2 the density of states is given for $\alpha_A = 0$, $\alpha_B = 9\,\beta_A$, $\beta_A = \beta_B = \beta_{AB}$ and $r = 0.1$ representing the case where two systems of atoms are well separated. In this case two well separated bands appear. In the minority band (Fig. 2) a three-peaked structure is evident. The physical meaning describing these substructures was given previously[7]. Recently a very efficient method[6] was described and applied to the Hamiltonian [Eq. (1)] with site diagonal disorder on a system with 7980 sites. In Figs. 1b and 2 densities of states predicted by the method from Ref.[6] and by the coherent-potential approximation[1] (CPA) are included. The comparison shows that NET applied on models of the above mentioned size (~1000) reproduces the results of the method introduced by Alben et al.[6] quite well. The application of NET on adsorption phenomena is very attractive. A model for this consists of one layer of atoms B while the rest is the semiinfinite bulk with atoms of type A. In Fig. 3 the density of states from NET is given for $\alpha_B = 0.2$, $\beta_B = 0.2$, $\alpha_A = 0$, $\beta_A = 1$ and $\beta_{AB} = 0.2$ with the ratio $N_B : N_A = 1:5$. The spectrum is spread around $E = 0$. The maximum is at $E = 0.2$ where a sharp band corresponds to the density of states of adsorbed atoms.

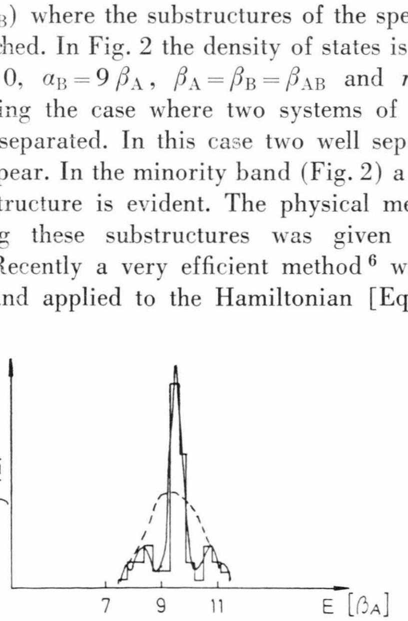

Fig. 2. Density of states (only the minority band) for two well separated systems $\alpha_A = 0$, $\alpha_B = 9\,\beta_A$, and the results from Ref.[6] (smooth curve) and of CPA (broken curve).

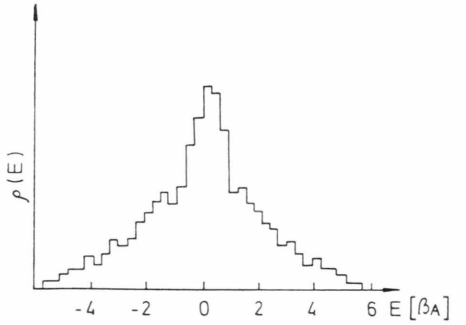

Fig. 3. Density of states for model system of adsorption.

It is well known that the calculation of the wave function from NET is cumbersome. Therefore such an approach can not be used to find the correspondence between the density of states and the local configuration of impurity atoms. A simple approach to solve this problem is introduced here. The idea is based upon the findings[2] in one and two dimensional calculations of vibrational properties of disordered systems, that the wave vectors are strongly localized inside the clusters which possess some translational symmetry. Contributions of these clusters to the overall density of states will be close to the density of states of infinite systems with the same translational symmetry. The corresponding eigenvectors are attenuated on the boundaries of the clusters. The variety of the shapes of the unit cells is inexhaustive, but their weights depend upon the concentrations of the impurity atoms. To obtain an approximation to the density of states of the disordered alloy with a certain concentration of impurities, one can take into account only a finite number of distinct unit cells. Let us consider only cubic unit cells containing N^3 atoms. The overall density of states can be obtained as a weighted sum over the contributions of all distinct configurations of atoms A and B in the unit cell. If there are k impurity atoms in the unit cell the number of permutations giving different configurations of atoms in the unit cell is $(N^3)!/k!(N^3-k)!$. Only a limited number of these configurations has a distinct density of states. If the symmetry is taken properly into account, these configurations and the corresponding weights can be easily found and the density of states can be written

$$S(r,w) = \sum_{k=0}^{N^3} \frac{g(r,k)\,k!\,(N^3-k)!}{(N^3)!} \cdot \sum_{\substack{\text{subgroups}\\ \text{of } O_h}} \frac{\dim O_h}{\dim p} \sum_i S_i(p,k,w)\,. \tag{2}$$

Here $\dim O_h$ is the dimension of the group O_h which is the symmetry group of the ordered system and $\dim p$ is the dimension of the subgroup of O_h which belongs to the particular configuration of impurity atoms in the unit cell. $\Sigma S_i(p,k,w)$ is the sum over the density of states of those configurations of impurity atoms which belong to the symmetry subgroup p. $g(r,k)$ is proportional to the probability of occurence of clusters with k impurity atoms in the unit cell if the impurity concentration has the value r. $S_i(p,k,w)$ has been determined by numerical evaluation of the dispersion relations and by counting the states in the space wave vectors.

This analysis was performed for the unit cell with $N=2$ and compared with the results obtained by NET for parameters values as in Figure 1b. In Figs. 4a and 4b are depicted the densities of states of two particular configurations with $N=2$, $k=4$. One can see that the appearence of the gap is strongly correlated with the number of mixed bonds in spite of the fact that the nearest neighbour transfer integrals are all equal. The contributions of the configurations with $k \neq r N^3$ (in our case $k \neq 4$) cannot be evaluated since one should know the average number (M) of unit cells in the cluster. $g(r,k)$ can be expressed by a Poisson distribution $g(r,k) = C^{Mk}_{MN^3}\, r^{Mk} (1-r)^{M(N^3-k)}$ where the C^n_m are binomial coefficients. Even for moderate values of $M\,(>10)$, $g(r,k)$ is a strongly peaked function and one can transform it into a δ-function. In this case the resulting overall density of states can be approximated by the last two sums of Eq. (2) and is depicted in Figure 4c. The density of states (compare Fig. 4c and Fig. 1b) determined in the prescribed way shows two well separated bands with some substructure which might be the result of the unsufficient number of atoms in the unit cell.

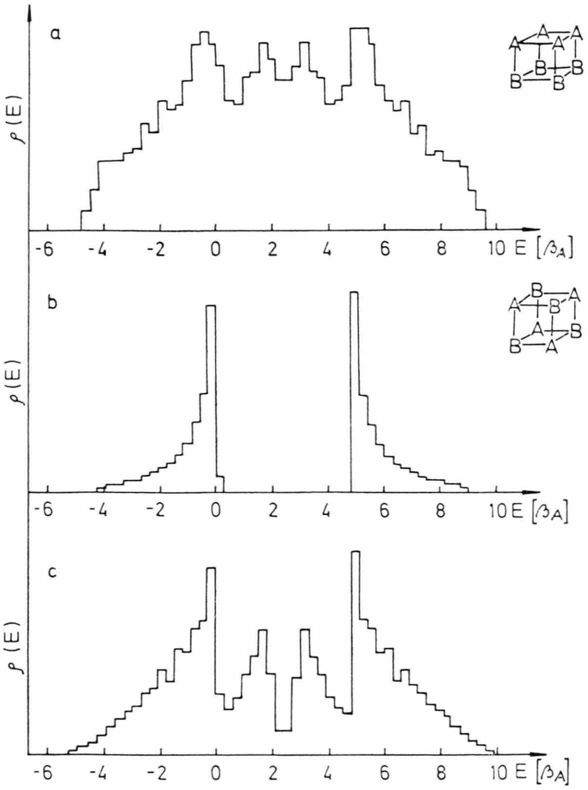

Fig. 4. Densities of states for two particular configurations (a, b) and the overall density of states (c).

The general conclusion from all results is that NET is a convenient method to treat electronic properties of random alloys. The critical factor in its application is the computer time. The total number of arithmetical operations increases as the product $(N_x^2\, N_y^2\, N_z^2)$. Therefore we can not avoid some effects in the density of states which are the consequence of the finite size (e.g. sharp peaks in Fig. 1c) of the system. Nevertheless it is surprising that a relatively small number of atoms reproduces the behaviour of the disordered alloy quite well.

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