

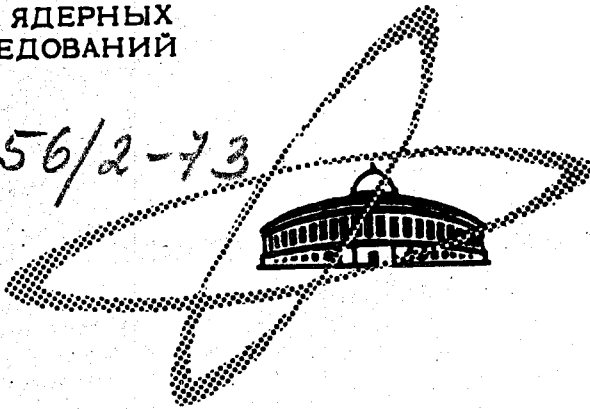
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MULTIPLE SCATTERING THEORY
AND PSEUDOGAPS IN AMORPHOUS
COVALENT SEMICONDUCTORS

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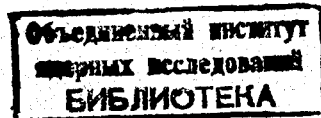
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**MULTIPLE SCATTERING THEORY
AND PSEUDOGAPS IN AMORPHOUS
COVALENT SEMICONDUCTORS**

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1. Introduction

The basic assumption of any band structure calculation of electronic states in crystals is the existence of an ideal long-range order because of the convenience of Bloch's Theorem. It is however well-known that the density of states is dominated by short-range order; only the fine structure depends on the type and degree of long-range order. An interesting example for this statement is the existence of amorphous covalent semiconductors like *Si* and *Ge*. In these materials the short-range order is similar to that found in the perfect crystal. Each atom is tetrahedrally coordinated with its four nearest neighbours. Small distortions of bond lengths and angles from the ideal values produce a structure without any long-range order ^{/1-3/}. Nevertheless recent experiments ^{/4-9/} indicate the existence of a pseudogap - a range of energy where the density of states is small if not zero - which is similar to the gap in the crystalline state. The basic problem which must be solved by a microscopic theory of amorphous materials is the understanding of the role of short-range order in producing an energy gap.

Investigations by Fletscher ^{/10,11/} and Ziman ^{/12/} indicate that the four-body distribution must have a short-range orientational order to produce a pseudogap. A suitable way to relate short-range order and density of states is the approach, which was first used by McGill, Klima and Ziman ^{/13-15/}. The authors describe the potential in the amorphous solid by nonoverlapping muffin-tin potentials. This has the advantage that, using multiple scattering theory, the density of states may be expressed analytically by a generalized Friedel sum in terms of phase shifts of muffin-tin potentials and their spatial

arrangement /16,17/ An appropriate expression for the density of states may be obtained by calculation of Friedel sums for clusters of few atoms and the neglect of the multiple scattering between these clusters. Indeed calculations for C , Si and Ge with clusters of only eight atoms clearly indicate the existence of a pseudogap. Calculations for clusters up to 30 atoms by Keller /18/ show a tendency to a perfect gap in the energy range where this gap is in the crystal. But the results show also that for clusters of 30 atoms intercluster contribution cannot be ignored. A further increasing of number of atoms in the clusters is questionable because of computational expense.

In this paper an alternative way to the cluster approach is investigated; it takes into account the topological connectivity of the system but considers only the nearest neighbour scattering processes between the atoms.

The idea is the following. From the viewpoint of molecular physics a semiconductor like Si or Ge is simply one enormous covalently bonded molecule. The bonding states form the valence band, whereas the antibonding states - separated by a gap - form the conduction band. A mathematical formulation of this simple picture is the tight-binding model of Weaire /19-24/. He was able to show that in this model a gap exists for a random network. In the sense of these considerations we assume, that in the multiple scattering approach the density of states is dominated by these nearest neighbour scattering processes which correspond to the well-known hybridized orbitals of molecular physics. In other words we transform the Weaire model into the multiple scattering formalism. In this approximation the Lloyd formula for the density of states may be reduced to an expression which separates the influence of the scattering properties of atoms from this of the topological connectivity. Using this model numerical calculations for amorphous C and Si show the existence of a pseudogap which is determined by short range order.

Section 2 gives a derivation of the density of state formula for the model based on the multiple scattering theory. Section 3 presents the numerical results for C and Si , and the main conclusions are summarized in Section 4.

2. Model

For noninteracting electrons, moving in an extended system of identical muffin-tin potentials, the integrated density of states per volume V may be expressed by [16, 17]

$$N(E) = N_0(E) - \frac{2}{\pi V} \text{Im Tr ln } D, \quad (1)$$

where $N_0(E)$ is the integrated free particle density of states. The second term describes the generalized Friedel sum for the solid. The matrix D is given in a mixed angular momentum-position (Ln) representation by

$$D_{LL'}^{nn'} \equiv (\text{ctg } \eta_L - i) \delta_{nn'} \delta_{LL'} + G_{LL'}^{nn'} \quad (2)$$

L stands for the quantum numbers of the angular momentum. The n -th muffin-tin potential is characterized by the phase shifts η_L and the position \vec{R}_n . G is, in the main, the free particle Green's function in the mixed angular momentum-position representation

$$G_{LL'}^{nn'} \equiv 4\pi(1 - \delta_{nn'}) \sum_{L''} i^{l-l'-l''} C_{LL'L''} h_{L''}(\vec{R}_n - \vec{R}_n) \quad (3)$$

with the abbreviations

$$h_L(\vec{r}) \equiv \{n_l(\kappa r) - i j_l(\kappa r)\} Y_L(\vec{n}), \quad \kappa = \sqrt{E},$$

$$C_{LL'L''} \equiv \int d\Omega Y_L(\vec{n}) Y_{L'}(\vec{n}) Y_{L''}(\vec{n}), \quad \vec{n} = \frac{\vec{r}}{r}. \quad (4)$$

$j_l(\kappa r)$ and $n_l(\kappa r)$ are the spherical Bessel and Neuman functions, respectively. The $Y_L(\vec{n})$ are real spherical harmonics.

Figures 1 and 2 show the phase shifts for C_i and S_i , respectively. The energy range of the gap in the crystalline state is indicated by the arrows on the energy axis. In this energy range the muffin-tin potential is a strong scatterer both for s - and p -partial waves; the d -phase shifts are small (S_i) or negligible (C_i).

Taking into consideration the behaviour of the phase shifts and the short-range order we calculate the density of states (1) within the following approximations:

1. We restrict the consideration on s - and p -phase shifts only. The influence of the d -phase shift for S_i (Fig. 2) is calculated in the single site approximation.

2. Furthermore we take into account in (1) the nearest neighbour scattering only. This is an essential approximation but - taking into consideration the behaviour of phase shifts - it may be expected that this approximation gives a reasonable description of the density of states in the energy range of the gap.

3. The main contribution of the nearest neighbour scattering results from scattering processes which are typical for the covalent bond. To show this we transform the matrix (3) from the (L_n) representation into a mixed hybridized orbital-position (in) representation

$$G_{ij}^{nn'} = \sum_{L,L'} S_{iL}^n G_{LL'}^{nn'} (S^+)_{L'j}^n \quad (5)$$

The unitary matrices S^n produce a linear combination of angular momentum well-known from the theory of covalent binding

$$S \approx \frac{1}{2} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \end{pmatrix} \quad (6)$$

For different atoms the S^n differs from (6) by a suitable rotation of the coordination system in such a manner, that the hybridized orbitals i are always "directed" to the nearest neighbours. It may

be shown that in the interesting energy range the matrix elements $G_{ii}^{nn_i}$ - which describe the scattering between atoms n, n_i along the hybridized orbitals i which connect "directly" the atoms n and n_i - are the largest one. For the perfect tetrahedral coordination of the nearest neighbours the matrix elements $G_{ii}^{nn_i}$ are equal.

$$G_{ii}^{nn_i} = g \quad (7)$$

Now we take into account only these matrix elements (7) and obtain for the Green's function the final expression

$$G_{ij}^{nn'} = g \delta_{ij} \delta_{n'n_i} \quad (8)$$

With these approximations the model describes an ideal network of scatterers and allows one to investigate the influence of topological disorder on the density of states quite similar as for the tight-binding model of Weaire [21, 25]. In order to calculate the density of states from (1) we handle the matrix D in the same manner as the Hamiltonian of the Weaire model. D may be split in two parts

$$D = D_1 + D_2 \quad (9)$$

Then for the integrated density of states (1) we obtain

$$N(E) = N_0(E) - \frac{2}{\pi i} \text{Im Tr} \{ \ln D_1 + \ln (1 + D_2 D_1^{-1}) \} \quad (10)$$

D_1 describes the scattering within independent pairs of atoms

$$(D_1)_{ij}^{nn'} = (ctg \eta_1 - i) \delta_{nn'} + g \delta_{n'n_i} \delta_{ij} \quad (11)$$

D_1 is independent of the topological connectivity of the network and gives the contribution

$$-\frac{2}{\pi V} \text{Im Tr ln } D_1 = -\frac{4}{\pi V_0} \text{Im ln } \{(\text{ctg } \eta_1 - i)^2 - g^2\} \quad (12)$$

to the integrated density of states. (V_0 is the volume per atom). The last term in (9) takes into account the scattering between different hybridized orbitals at the same atom and may be written as

$$D_2 \equiv \tau P \quad (13)$$

with

$$\tau \equiv \text{ctg } \eta_0 - \text{ctg } \eta_1 \quad (14)$$

and the projection matrix P , which projects out the s -part in the (Ln) representation

$$P_{LL'}^{nn'} = \delta_{nn'} \delta_{LL'} \delta_{LO} \quad (15)$$

For the last term in (10) we obtain, using (13), (15) and the properties of the trace,

$$\text{Tr ln } (1 + D_2 D_1^{-1}) = \text{Tr ln } (1 + \tau P D_1^{-1} P) \quad (16)$$

An elementary calculation gives ^{/25/}

$$1 + \tau P D_1^{-1} P = \frac{\zeta - \tau g H}{(\text{ctg } \eta_1 - i)^2 - g^2} \quad (17)$$

with the parameter

$$\zeta \equiv (\text{ctg } \eta_1 - i)^2 - g^2 + \tau (\text{ctg } \eta_1 - i) \quad (18)$$

and the one band Hamiltonian

$$H_{LL'}^{nn'} \equiv \frac{1}{4} (1 - \delta_{nn'}) \delta_{LL'} \delta_{LO} \quad (19)$$

where n and n' are the nearest neighbours. As for the Weaire model /21/ the one band Hamiltonian (19) is independent of the potential. Its eigenvalues ϵ_ν are bounded by

$$-1 \leq \epsilon_\nu \leq 1 \quad (20)$$

and depend only on the connectivity of the network. With (12) and (16)-(19) we obtain for the integrated density of states (10) the expression

$$N(E) = N_0(E) - \frac{2}{\pi V_0} \text{Im} \ln \{ (\text{ctg} \eta_1 - i)^2 - g^2 \} - \frac{2}{\pi V} \text{Im Tr} \ln (\zeta - \tau g H) \quad (21)$$

The density of states $\rho(E)$ is obtained simply by differentiating (21) with respect to energy and may be written as

$$\rho(E) \equiv \rho_1(E) + \rho_2(E) \quad (22)$$

with the structure independent part

$$\rho_1(E) = \frac{E^{1/2}}{2\pi^2} - \frac{2}{\pi V_0} \frac{d}{dE} \text{Im} \ln \{ (\text{ctg} \eta_1 - i)^2 - g^2 \} \quad (23)$$

and the structure dependent term

$$\rho_2(E) = \frac{2}{\pi V} \frac{d}{dE} \text{Im Tr} \ln (\zeta - \tau g H). \quad (24)$$

With the density of states $\mu(\epsilon)$ of the one band Hamiltonian H the expression (24) may be written as

$$\rho_2(E) = - \frac{2}{\pi V_0} \frac{d}{dE} \text{Im} \int d\epsilon \mu(\epsilon) \ln (\zeta - \tau g \epsilon). \quad (25)$$

Different functions $\mu(\epsilon)$ are shown in Fig. 3. The density of states for the diamond structure $\mu_2(\epsilon)$ were obtained by the method given in /21/ and the tabulated integrals in /26/. For the density of states of the Bethe lattice $\mu_3(\epsilon)$ a lattice without closed loops - we have used the results in /21/.

3. Numerical Results for the Density of States

The equations (23) and (25) has been evaluated numerically for amorphous covalent bonded *C* and amorphous *Si*. In order to compare the results with the cluster approach, the calculations are made with the same phase shifts * (see Figs. 1,2) used also by McGill, Klima and Ziman /13-15/. For the volume per atom V_0 is taken the crystalline value.

The results for *C* are shown in Figs. 4-6. In the single site approximation the density of states shows a peak at about 0.3 Ry, due to the weak resonance in the p -phase shift. The scattering along the hybridized bonds splits this peak in two peaks. Therefore the structure independent part has narrow peaks at about 0.1 Ry and 1.05 Ry and a low density region between these two peaks (see Fig. 4).

In order to investigate the influence of topological disorder on the density of states the structure dependent part $\rho_2(E)$ has been evaluated for different functions $\mu(\epsilon)$ (see Fig. 3). The results are plotted in Fig. 5 for the diamond structure $\mu_2(\epsilon)$, for the Bethe lattice $\mu_3(\epsilon)$ and for the density of states $\mu_1(\epsilon) = 2/\pi \sqrt{1-\epsilon^2}$. In the energy range 0.2-0.9 Ry $\rho_2(E)$ does practically not depend on the topological connectivity of the network. The variation of $\rho_2(E)$ with the functions μ_1 , μ_2 and μ_3 is of order of percents or smaller. This may be understand by consideration of equation (24). The parameter which controls the influence of the structure on the density of states is given by

$$a \equiv \frac{\tau B}{\zeta}. \quad (26)$$

In Fig. 5 is plotted $|a|^2$ as a function of energy. In the range 0.1-1.1 Ry $|a|$ is less than one and the logarithm in (24) may be expanded

The author is grateful to Dr. J.Klima for sending him the phase shifts for *C* and *Si*.

$$\rho_2(E) = -\frac{2}{\pi V_0} \frac{d}{dE} \operatorname{Im} \left\{ \ln \zeta - \sum_{m=1}^{\infty} \frac{1}{m} \alpha^m \mu^{(m)} \right\}, \quad (27)$$

where $\mu^{(m)}$ are the moments of the Hamiltonian (19)

$$\mu^{(m)} \equiv \operatorname{Tr} H^m = \int d\epsilon \mu(\epsilon) \epsilon^m. \quad (28)$$

From (19) follows directly $\mu^{(1)} = 0$ and - for any network with four nearest neighbours $\mu^{(2)} = 1/4$. The influence of topological connectivity is therefore of order $|\alpha|^3$ or smaller. We have evaluated $\rho_2(E)$ only for functions $\mu(\epsilon)$ which are symmetric about the origin (see Fig. 3). The variation of $\rho(E)$ with $\mu(\epsilon)$ is therefore of order $|\alpha|^4$.

The contribution $\rho_2(E)$ reduces the density of states between the two peaks of $\rho_1(E)$ (see Fig. 4) and is therefore important for the existence of the pseudogap. Calculations for different s -phase shifts showed that the behaviour of $\rho_2(E)$ and with it the density of states in the pseudogap region - depends sensitively on the s -phase shift. Figure 6 shows the result for the density of states $\rho(E)$. Its value in the region of the pseudogap is about one order of magnitude smaller than the free particle density. In comparison with the cluster calculations /13-15/ the gap is extended into the range of low energies. In order to obtain reasonable results for these energies, it is necessary to take into account further scattering processes which are neglected in (8).

Similar results were obtained for Si as shown in Figs. 7-9. The contribution of the d -phase shift is included in Fig. 9 in the single site approximation. As may be seen in Fig. 9 the calculated density of states has in the energy range 0.07-0.19 Ry a small negative value, due to the fact that the approximation made above do not conserve the positive definiteness of the density of states.

4. Conclusion

The main purpose of these calculations is to show that in covalent semiconductors the tetrahedrally coordinated nearest neighbours are able to produce a pseudogap. In correspondence with the results of the cluster approach /13-15/ the valence band and the conduction band are formed by resonance states. The behaviour of both the s - and

p -phase shifts is essential for the existence of the gap. The density of states within the pseudogap does practically not depend on the topological connectivity due to the existence of a small parameter, which controls the influence of long-range order.

The model gives only a simplified picture of the density of states. In comparison with the gap in the crystalline state and the results of the cluster approach the pseudogap is extended within the range of low energies. This is not surprising, since the approximation which is made in the model is questionable for this range of low energies. Nevertheless the model investigated above may be useful as a zero order approximation for more detailed numerical calculations. These calculations should take into account the in (8) neglected scattering processes by a cluster approach. Perhaps with such a "renormalized" cluster method - that is not based on independent scatterers but on the network model - a reducing of intercluster contribution may be obtained and in this way reasonable results for small clusters may be expected.

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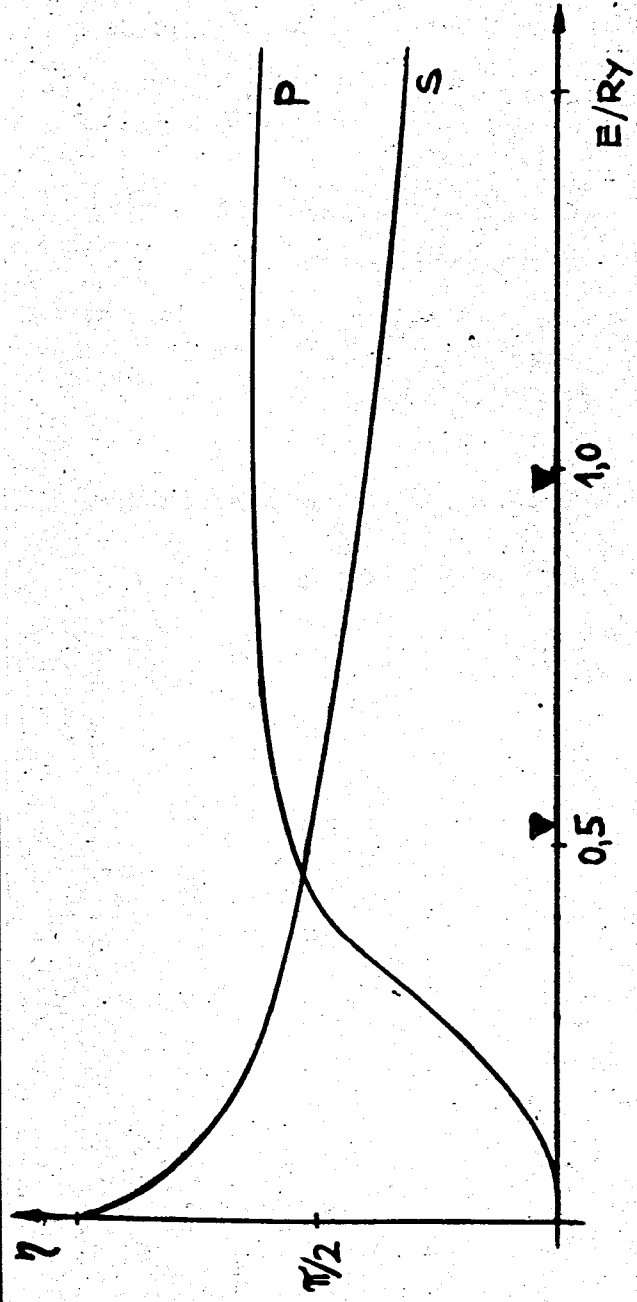


Fig. 1. Phase shifts for C as a function of energy.

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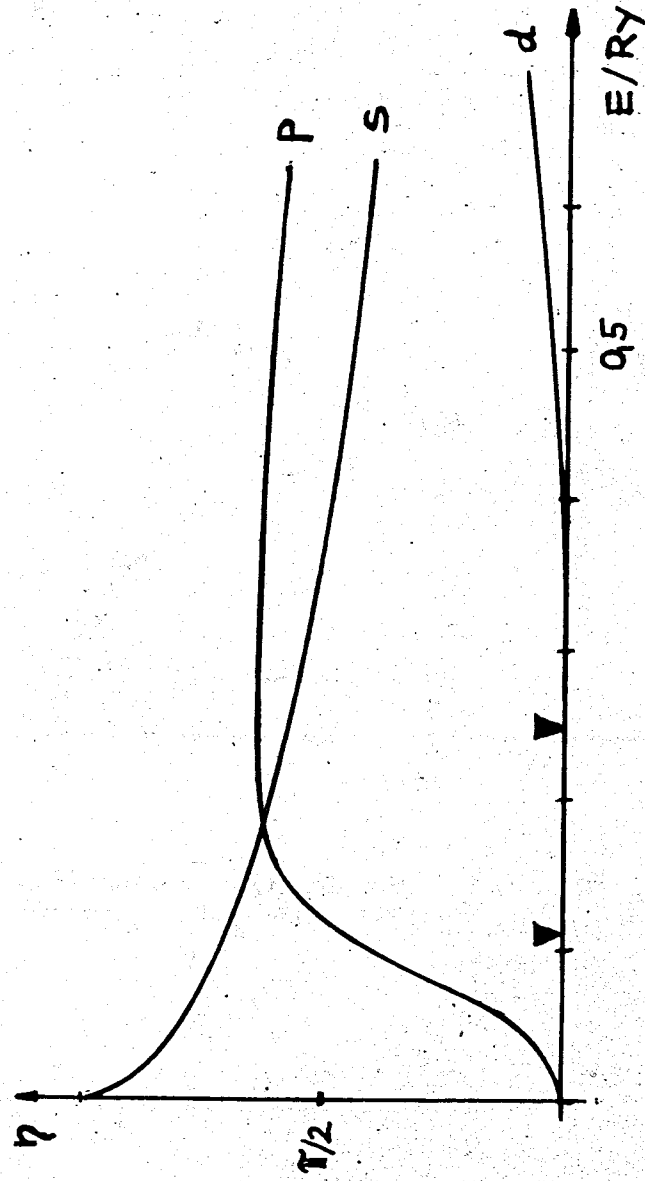


Fig. 2. Phase shifts for Si as a function of energy.

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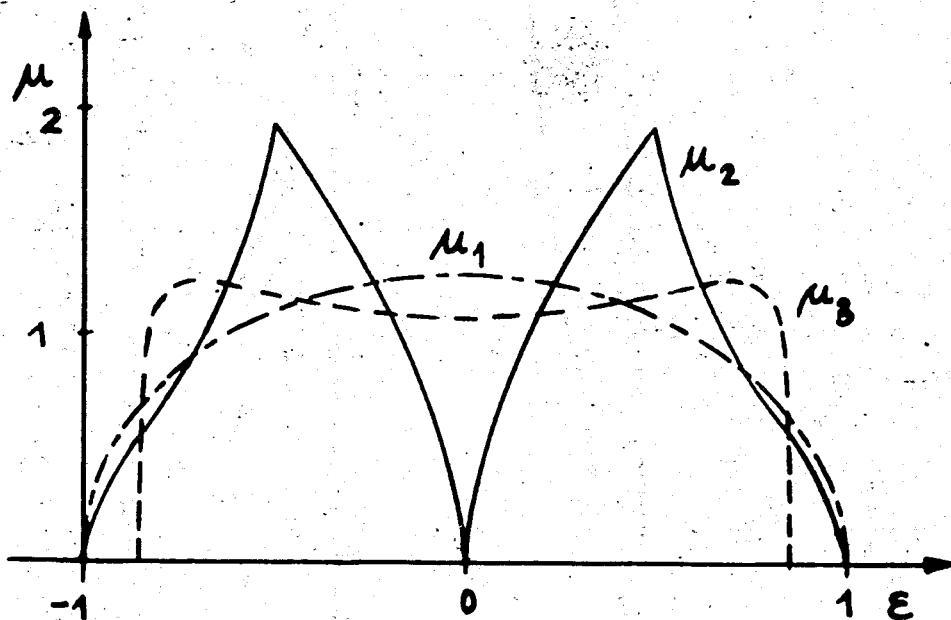


Fig. 3. Density of states $\mu(\epsilon)$ for the tight-binding Hamiltonian (19). $\mu_1 = 2/\pi \sqrt{1 - \epsilon^2}$, μ_2 diamond structure μ_3 Bethe lattice.

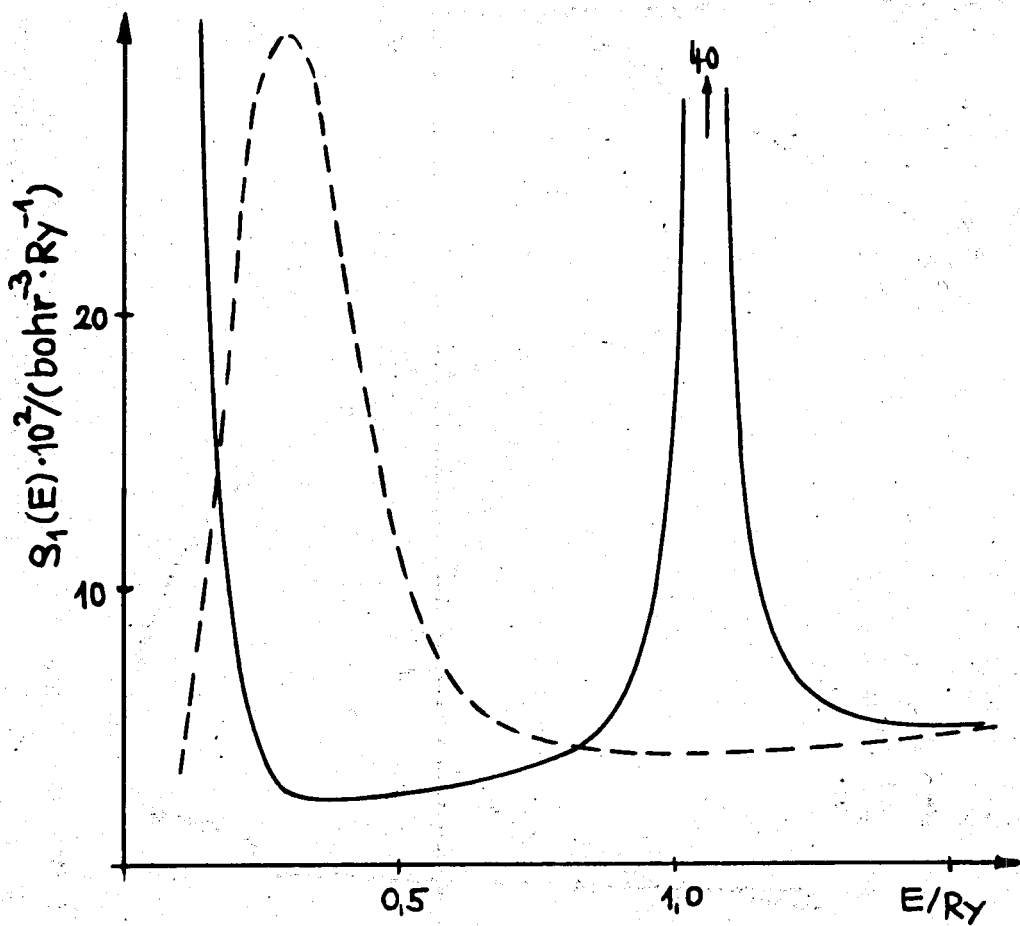


Fig. 4. Density of states for C. Structure independent part $\rho_1(E)$
 Single site approximation - dashed line.

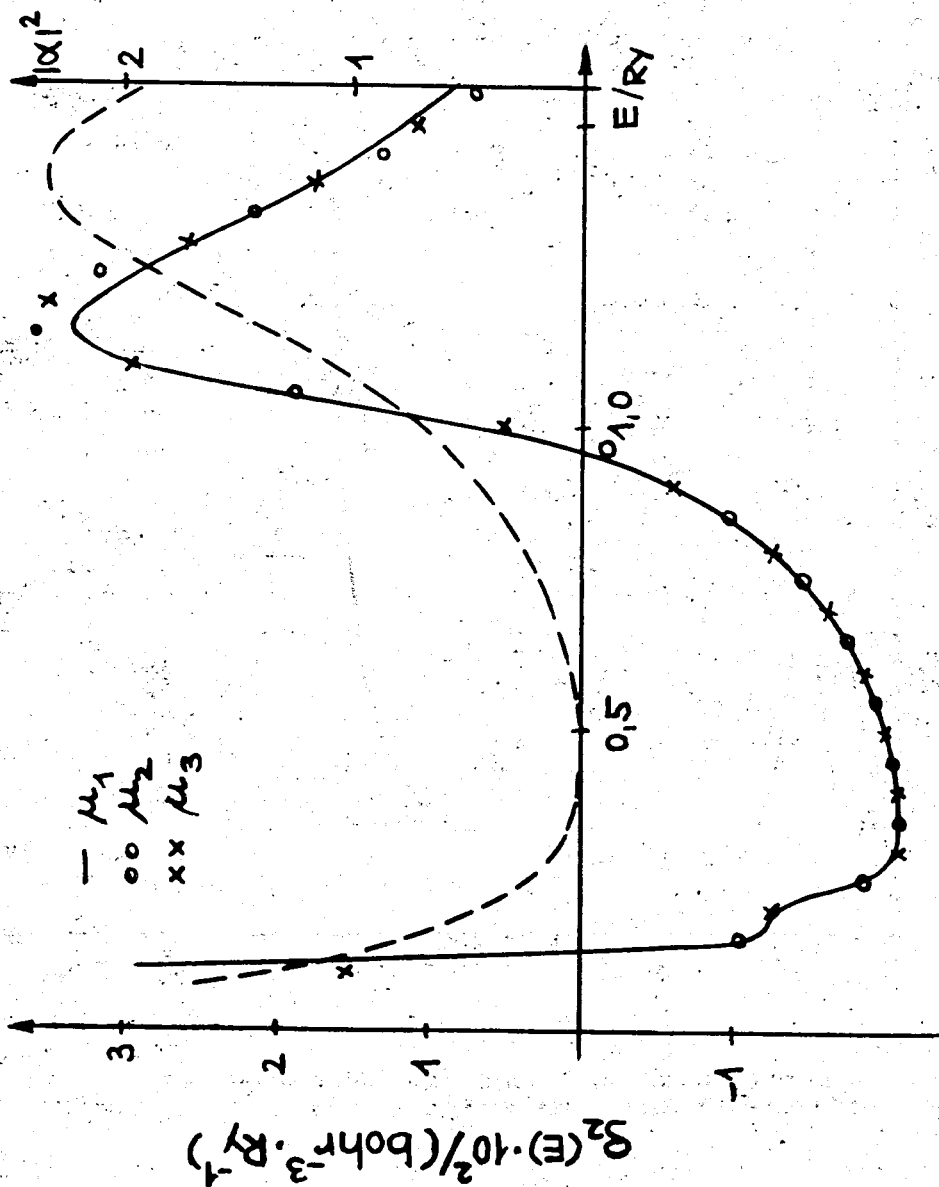


Fig. 5. Density of states for G . Structure dependent part $\rho_2(E)$ for μ_1 , μ_2 and μ_3 . Structure parameter $|a|^2$ -dashed line.

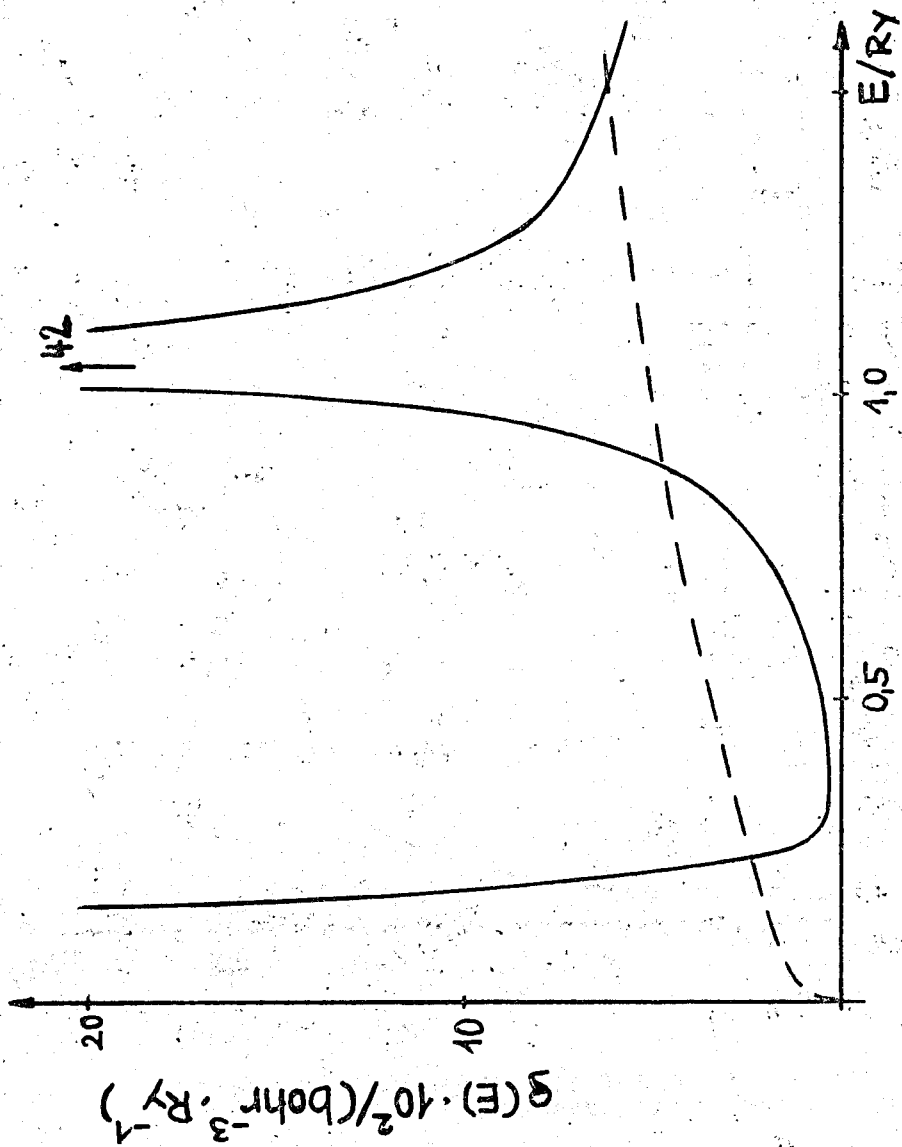


Fig. 6. Density of states $\rho(E)$ for C as a function of energy. Free particle density - dashed line.

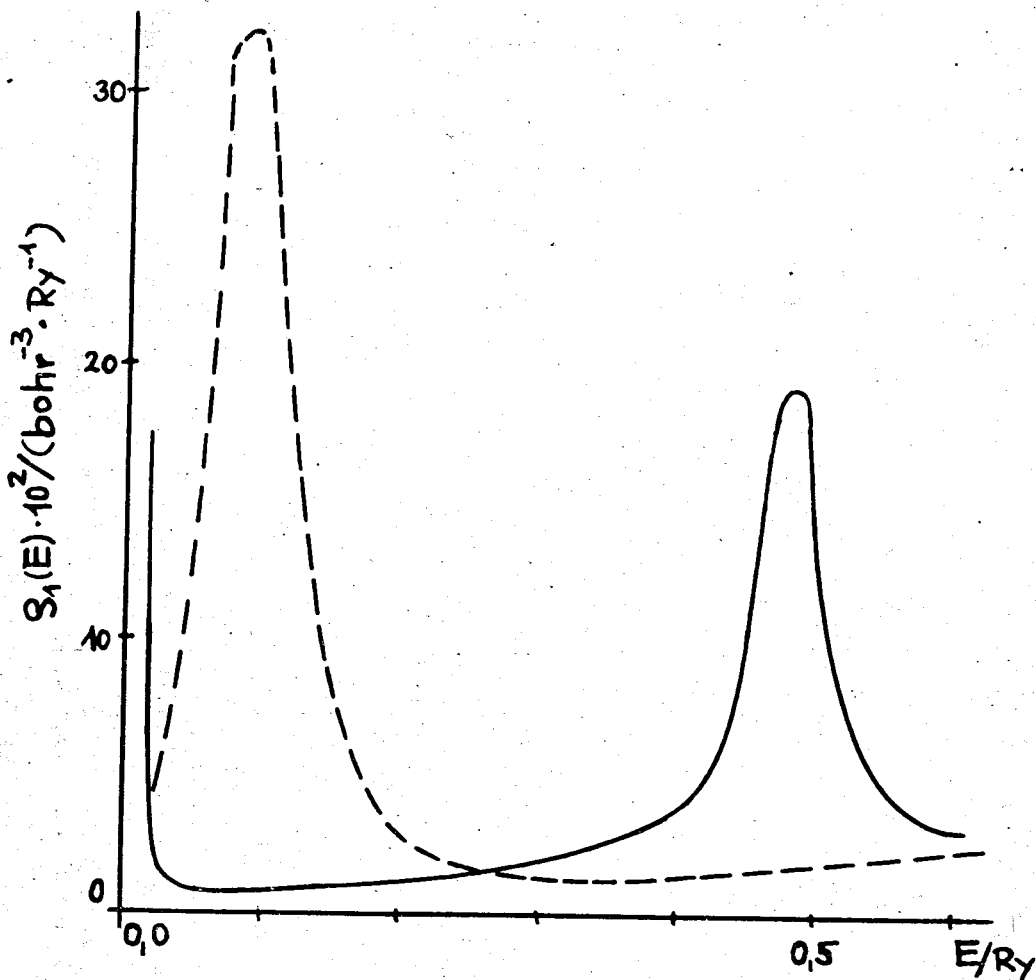


Fig. 7. Density of states for Si. Structure independent part $\rho_1(E)$
 Single site approximation - dashed line.

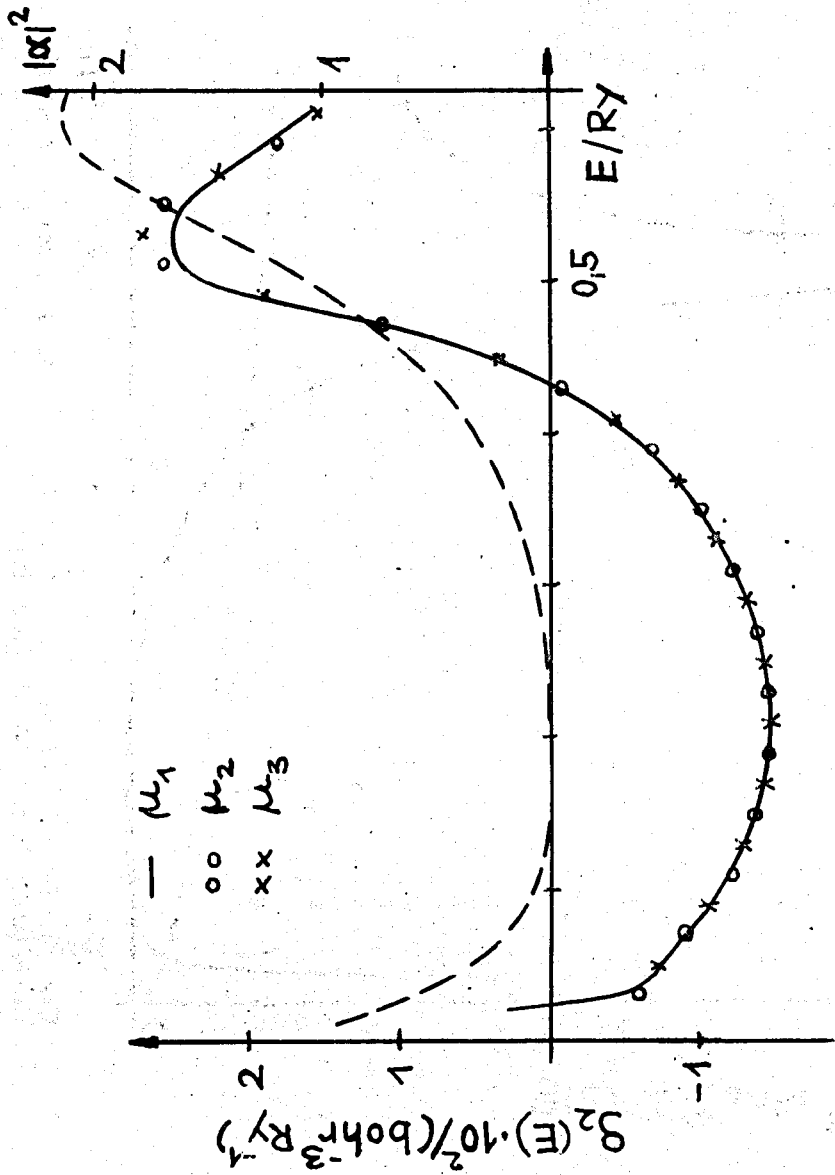


Fig. 8. Density of states for Si. Structure dependent part $\rho_2(E)$ for μ_1 , μ_2 and μ_3 . Structure parameter $|a|^2$ -dashed line.

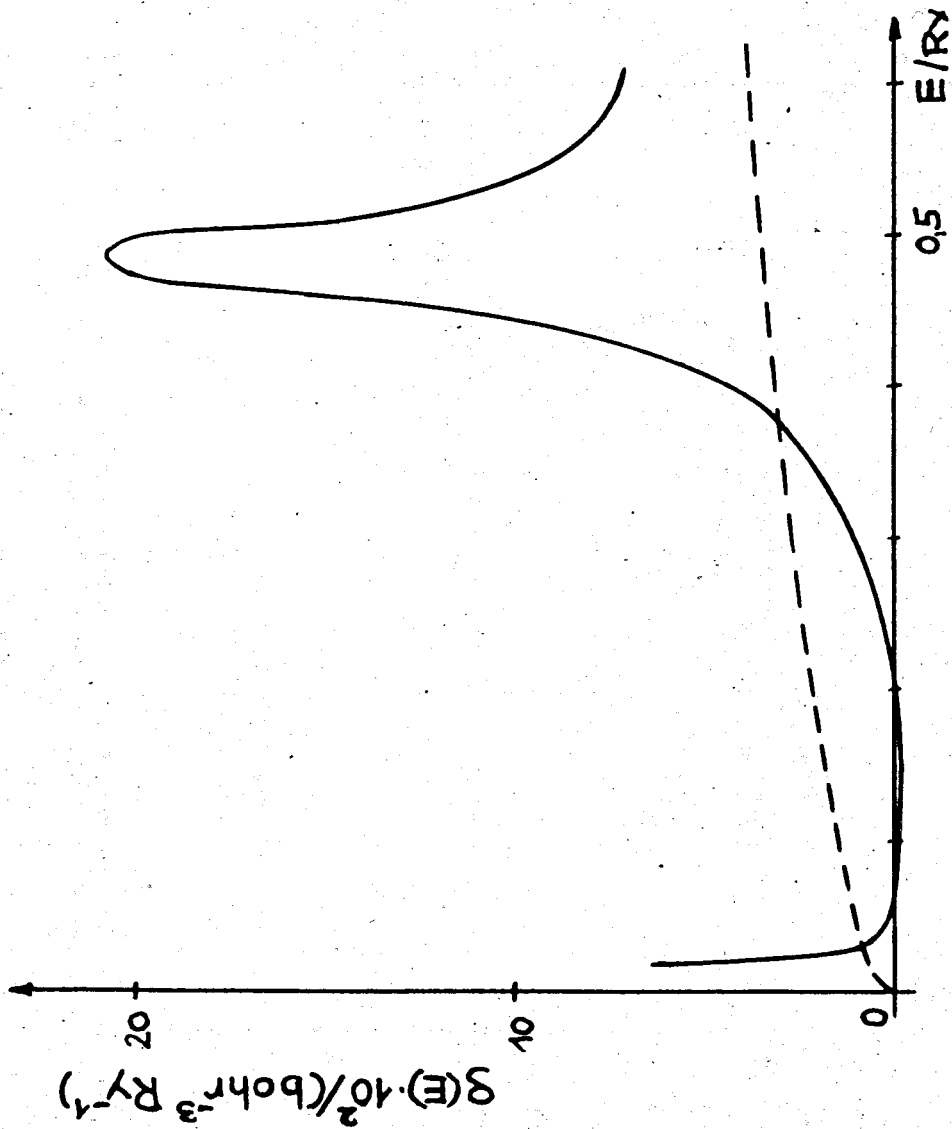


Fig. 9. Density of states $\rho(E)$ for Si as a function of energy. Free-particle density-dashed line.