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# Local Order Dependent Impurity Levels in Alloy Semiconductors

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We develop a one band/may sites model for an isoelectronic impurity in a semiconductor alloy. The cluster-Bethe-lattice approximation is used to study the dependence of the impurity energy level upon the short range order (SRO) of the alloy. The Kikuchi parametrization is used to describe the latter. We take into account diagonal disorder only, with possible off-diagonal relaxation around the impurity site. All the inequivalent clusters of the impurity site and its first nearest neighbours are considered, thuc including the important short range alloy potential fluctuations. Results are presented for the local density of impurity states, for different degrees of SRO in the alloy.

Desenvolvemos um modelo de uma banda/muitos sitios para uma impureza isoeletronica em uma liga semicondutora. O método "cluster-Bethe-lattice" é utilizado para estudar a dependência da energia do nível de impureza com o grau de ordem de curto alcance (OCA) da liga, descrito pela parametrização de Kikuchi. Consideramos apenas desordem diagonal, com uma

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possível relaxação não-diagonal em torno do sitio da impureza. As flutuações de curto alcance do potencial da liga são consideradas através do estudo de todos os grupos inequivalentes de primeiros vizinhos da impureza. São apresentados resultados para a densidade local de estados para diferentes graus de OCA relevantes para a interpretação de experiências recentes de luminescência em ligas semicondutoras.

## 1. INTRODUCTION

The problem of impurity states in pure, ideal, semiconductors has been investigated extensively for many years, both experimentally and theoretically[1,2]. More recently, interest has been directed to the problem of iso-electronic impurities in alloy semiconductors, such as $GaAs_{1-x}P_x$ : N [3,4]. From the theoretical point of view, this is an open question, due to several difficulties: the host system is itself "impure", very little is known about local relaxation effects which are, in principle, dependent upon the local order in the alloy, and screening effects are not entirely understood[5]. Within the virtual crystal approximation for the host material, several models have been developed in the past fewyears to explain the properties of N impurities in Ga(As,P), which are more or less successful[4,6,7]. Recent experimental results for luminescence in the Ga(As,P): $N$ system[3,8] and for quaternary alloys (In,Ga) (As, P)[9] have shown that local order effects must be taken into account if one wants to fully explain the experimental data.

The aim of this work is to present a simple one band/many sites model of an iso-electronic impurity in an alloy semiconductor, which allows us to describe important effects of short range order (SRO) in the alloy upon the energy position of the impurity level. In spite of its simplicity, our model includes all the important features of a more realistic treatment, with the advantage of being quite transparent. We hope that it will serve to elucidate some of the questions connected with the impurity in an alloy problem. In Section 2 we present the model hamiltonian and discuss the method of solution. In Section 3 we discuss the alloy statistics and in Section 4 we present some numerical examples. Finally, in Section 5, we present our conclusions.

## 2. THE MODEL HAMILTONIAN

Let us start by describing the physical model of interest to us. We consider a ternary alloy semiconductor, for instance, In(As,P), with disorder restricted to one sub-lattice only. In addition, we consider one heavy iso-electronic impurity, e.g. Sb or Bi, which replaces an anion and which may produce a bound hole state. This particular choice of a model was dictated by our study of the quaternary alloy (In,Ga) (As,P)[9], but the results which we obtain are more generally applicable. In our one-band model, the valence band, derived mainly from anionic states, is represented by a tight-binding hamiltonian with one s-like state per site on a fcc lattice. We consider only diagonal disorder. Then, the hamiltonian may be written:

$$H = H_{vc} + H_A + H_I . \tag{2.1}$$

In eqn. (2.1):

$$H_{vc} = \sum_n E_0 |n\rangle \langle n| + V \sum_{(n,m)} |n\rangle \langle m| \quad , \tag{2.2}$$

where $E_0$ is the average atomic energy and the second sum is restricted to first nearest neighbor pairs on a fcc lattice. If we indicate the two anion species by A and $B$, and the concentration by $x(A_x B_{1-x})$, then:

$$E_0 = x\, E_A + (1 - x) E_B \quad . \tag{2.3}$$

The term $H_A$ corrects the virtual crystal approximation by re-introducing the proper alloy potential fluctuations:

$$H_A = \sum_n \delta_n \; |n\rangle \langle n| \; , \tag{2.4}$$

where, according to the site occupancy, $\delta_n = \delta_A = E_A - E_0 = (1-x)\,(E_A - E_B) =$ $= (1-x)\,.\Delta$ or $\delta_n = \delta_B = E_B - E_0 = -x\Delta$. Finally, the third term in eqn.(2.1) describes a single impurity placed at the origin:

$$H_I = \delta_I |0\rangle \langle 0| + V_I \sum_n{}' \left( |n\rangle \langle 0| + |0\rangle \langle n| \right) +$$

$$+ W \sum_{(n,m)}{}'' |n\rangle \langle m| \quad , \tag{2.5}$$

where $\delta_I = E_I - E$, $V_I$ is the hopping matrix element between the impurity orbital and its first nearest neighbor orbitals, and W describes possible relaxation effectsof the nearest neighbor clusterof the impurity[4]. The prime indicates that the summations are restricted to the 12-atoms nearest neighbor cluster of the impurity.

Our aim is to calculate the local density of states at the impurity site, taking into account the effects of the alloy potential fluctuations in the neighborhood of the impurity. To do this, we employ the cluster-Bethe-lattice approximation. Although it has been extensively discussed in the literature[10,12], we review briefly here the points of interest to us.

In Figure 1, we present the tree used as an approximation for the fcc lattice. The basic element is a tetrahedron, which allows us to take into account the fact that, in the fcc lattice, two atoms, nearest neihbors to a thirdatom, may also be nearest neighbors to each other. The immediate cluster around the impurity is described by four tetrahedra with one common vertex - the impurity site -. This is consistent with the statistical approximation used to describe short range order effects in the alloy, which is discussed in the next Section. The procedure for solving the dynamical problem, eqn. (2.1), is as follows. A particular distribution of A and B atoms in the 12 sites around the impurity is chosen and the

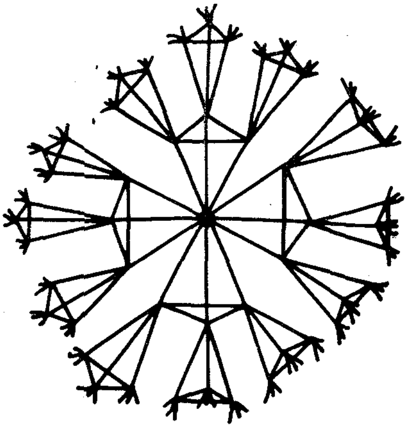

Figure I - The central cluster and the Bethe lattices in the tetrahedral approximation for the fcc lattice. The coordination number of all the atoms in the lattice is 12.

equations of motion for the matrix elements of the resolvent of (2.1) are written down. That is:

$$(Z - \varepsilon_I)\, G^I_{00} = 1 + V_I \sum_{j=1}^{12} G^\beta_{j0} \quad , \tag{2.6}$$

$$(Z - \varepsilon_\beta)\, G^\beta_{j0} = V_I G^I_{00} + W \sum_{i(j)} G^{\beta'}_{i0} + V \sum_{\ell(j)} G_{\ell 0} \; . \tag{2.7}$$

In (2.6), the summation over $j$ covers the 12 n.n. of the impurity, the superscript $\beta$ indicates the anion species occupying the $j$-th site ($A$ or $B$) and, as usual:

$$G_{n0} = \langle n | (Z - H)^{-1} | 0 \rangle \quad , \tag{2.8}$$

with H defined in (2.1). In (2.7), the 12 n.n. of the $j$-th atom are divided into three groups: the central (impurity) atom; 2 nearest neighbors to the impurity and to the $j$-th atom, which belong to the same tetrahedron (cf.Figure 1), indicated by the index $i$; and 9 nearest neighbors which belong to the Bethe lattice. To obtain a closed set of equations, we now make use of the Bethe-lattice approximation, <u>for the virtual crystal hamiltonian</u>, and write:

$$\sum_{\ell(j)} G_{\ell 0} = 9\, \phi\, G^\beta_{j0} , \tag{2.9}$$

where the trsnsfer function $\phi$ satisfies:

$$(Z - \varepsilon_0 - 2V)\, \phi = V + 9V\, \phi^2 \quad . \tag{2.10}$$

This is the standard solution to the Bethe lattice problem[10]. The justification for treating the crystal, further away than the nearest neigbor cluster, within the virtual crystal approximation is that, if the impurity state if fairly well localized, it is not very sensitive to potential fluctuations in distant regions of the crystal. Since the branch cut of the function $\phi$ determines the band edges for the virtual crystal, we have a very precise way of defining the energy position of localized levels. These are always determined with respect to band edges of the virtual host crystal. The solution of (2.10) is:

$$\phi(Z) = \frac{1}{18V}\left[Z - \varepsilon_0 - 2V \pm \sqrt{(Z - \varepsilon_0 - 2V) - 36V^2}\right] , \qquad (2.11)$$

where the sign is always chosen so that $\phi(Z = E + i0^+)$ tends asymptotically to zero outside the band limits and $\mathrm{Im}\,\phi(E + i0^+) > 0$ within the band.

Let $\tau = 1$ to $4$ label the four tetrahedra which have the impurity site as a common vertex and $\gamma_\tau$ the corrésponding anionic configuration. Then we can easily show that the sum over $j$ in (2.6), restricted to the three atoms belonging to the $\tau$-th tetrahedron may be written:

$$\sum_j G^\beta_{j0} = D(Z;\gamma_\tau)\, V_I\, G^I_{00} , \qquad (2.12)$$

where:

$$D(Z;\gamma_\tau) = \left[(\varepsilon_1)(\varepsilon_2)+(\varepsilon_2)(\varepsilon_3)+(\varepsilon_3)(\varepsilon_1)+2W((\varepsilon_1)+(\varepsilon_2)+(\varepsilon_3))+3W^2\right]$$

$$\left[(\varepsilon_1)(\varepsilon_2)(\varepsilon_3) - W^2((\varepsilon_1)+(\varepsilon_2)+(\varepsilon_3)) - 2W^3\right]^{-1} , \qquad (2.13)$$

and

$$(\varepsilon_i) = Z - \varepsilon_i - 9V\,\phi(Z) . \qquad (2.14)$$

The energies $\varepsilon_i$ take up the values $\varepsilon_A$ or $\varepsilon_B$ depending on the particular configuration $\gamma_\tau$.

Hence, for one particular distribution of atoms among the n.n. sites of the impurity, we may write:

$$G^I_{00} = \left[Z - \varepsilon_I - V_I^2 \sum_{\tau=1}^{4} D(Z;\gamma_\tau)\right]^{-1} \qquad (2.15)$$

In the next section we study the alloy statistics and define alloy average of $G^I_{00}$.

## 3. THE ALLOY STATISTICS

To define the alloy statistics we follow the work of Kikuchi who has analyzed in detail the problem of short-range-order in lattices, such as the one we consider, where it is necessary to go beyond the pair approximation[13]. We want to describe SRO effects in the cluster around the impurity site. Once this cluster is decomposed into 4 tetrahedra, we are left with three free sites per tetrahedron, the fourth being always occupied by the impurity. We may then define four probabilities $Q(IJK)$, with $I,J,K$ = A or $B$, such that:

$$Q(AAA) + 3Q(AAB) + 3Q(ABB) + Q(BBB) = 1 \,, \tag{3.1}$$

which describe the occupation of the three "free" vertices of one tetrahedron. Following Kikuchi, these probabilities are parametrized as follow:

$$\begin{aligned} Q(AAA) &= \tfrac{1}{2}\,(1 + \lambda - 3Z_2 - \xi_2) \\ Q(AAB) &= \tfrac{1}{2}\,(Z_2 + \xi_2) \\ Q(ABB) &= \tfrac{1}{2}\,(Z_2 - \xi_2) \\ Q(BBB) &= \tfrac{1}{2}\,(1 - \lambda - 3Z_2 + \xi_2) \end{aligned} \tag{3.2}$$

where $A = 2x-1$, $Z_2 = P(AB)$ is the pair probability and $\xi_2 = Q(AAB) - Q(ABB)$. To simplify the analysis, we restrict ourselves to a 50-50 alloy, for which $\lambda=0$. In Figure 2, we show the allowed variations of $Z_2$ and $\xi_2$, which guarantee that all $Q$'s lie between 0 and 1. The sum rule (3.1) is automati-

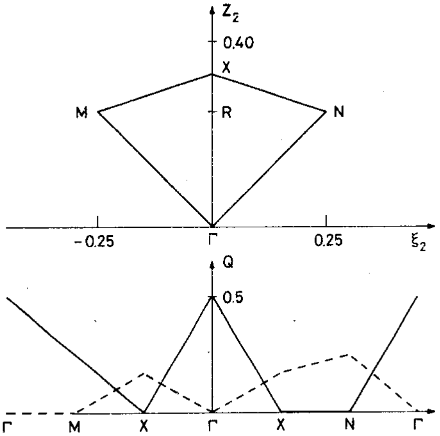

Fig.2 - Upper part: the allowed values of the $Z_2$ and $\xi_2$ Kikuchi parameters for a 50-50 alloy are contained within the solid lines. Lower part: values of $Q(AAA)$ (solid line) and $Q(AAB)$ (dashed line) along some directions in the $(Z_2,\xi_2)$ plane.

cally satisfied by the parametrization above. In Figure 3 we show the probability distribution for A atoms in the cluster for several allowed values of the pair $(Z_2,\xi_2)$. This Figure shows clearly that the pair probability $Z_2$ determines the width of the probability distribution and that $\xi_2$ determines its "skewness". We remark that all probability distributions obtained for allowed values of $(Z_2,\xi_2)$ yield and average value of 6 for the number of A (or *B*) atoms in the cluster. Since the concentration is not varied, the only freedom we have is to change the degree of SRO in the alloy.

We can now define an average value for the function $G^{I}_{00}$. In the tetrahedral approximation, the $2^{12}$ possible clusters are reduced to 35 inequivalent ones. These can be classified by the number of triangular units of type *AAA*, ***AAB***, ***ABB*** or ***BBB*** that they present. Numbering these sequentially from 1 to 4, the weight of a given cluster configuration is:

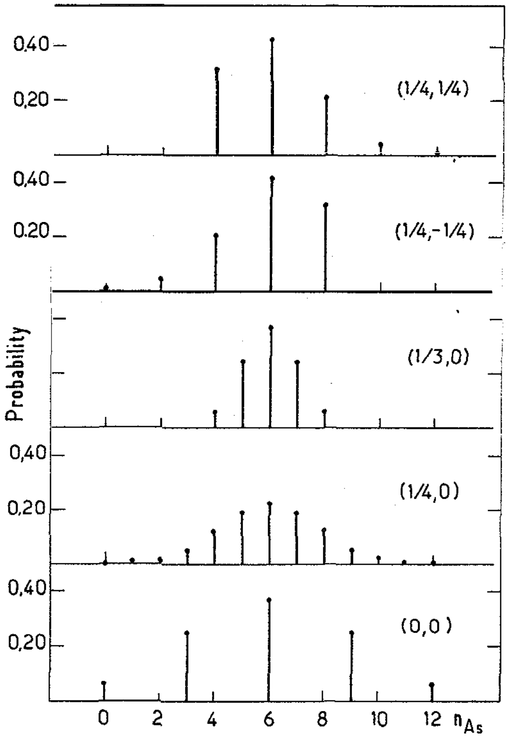

Fig.3 - Probability distribution for A atoms in the cluster of nearest neigbors of the impurity, corresponding to various special points on the $(Z_2,\xi_2)$ parameter space. The values of $(Z_2,\xi_2)$ are indicated and correspond, from bottom to top, to the points Γ, *R*, *X*, *M*, and N of Figure 2.

$$W(\Gamma) = \frac{4}{n_1!n_2!n_3!n_4!}\left[Q(AAA)\right]^{n_1}\left[3Q(AAB)\right]^{n_2}\left[3Q(ABB)\right]^{n_3}\left[Q(BBB)\right]^{n_4} , \qquad (3.3)$$

where

$$n_1 + n_2 + n_3 + n_4 = 4$$

Thus:

$$< G^{I}_{00}(Z)> = \sum_{n_1 n_2 n_3 n_4} \delta_{n_1+n_2+n_3+n_4, 4} \, W(\Gamma) \cdot G^{I}_{00}(Z;\Gamma) , \qquad (3.4)$$

where:

$$G^{I}_{00}(Z;\Gamma) = \left[Z - \varepsilon_I - V_I^2 \left(n_1 D(Z;AAA) + n_2 D(Z;AAB) + n_3 D(Z;ABB) + n_4 D(Z;BBB)\right)\right]^{-1} . \qquad (3.5)$$

Once the dynamical problem is solved for each one of the 35 inequivalent clusters, as described in Section 2, eqns. (3.3) and (3.4) allow us to define the average local density of states at the impurity sites. We remark that, within the approximations made in eqs. (2.1), the solution of the dynamical problem, i.e., the determination of the energy of the localized impurity level (if any exists) for a given fluctuation ofthe alloy potential in the immediate neighborhood of the impurity, is indepen- of the statistical averaging of the fluctuations. This is due to the fact that we have assumed parameters to describe the impurity which are independent of the particular configuration of the cluster. In reality, relaxation and screening effects are dependent upon the local alloy composition.

## 4. NUMERICAL EXAMPLE

We apply the formalism developed in the two preceding Sections to a model $InAs_{0.5}P_{0.5}$ alloy with one isoelectronic impurity of Sb. The parameters of the hamiltonian consist of the three atomic energies $E_{As}$, $E_P$ and $E_{Sb}$, the valence band width (which is determined by $V$), and the impurity related hopping matrix elements $V_I$ and W. For the common valence band-width of InAs and InP we take 10eV, which yields in the Bethe lattice approximation $V = -0.83$ eV. The sign is chosen so as to place the maximum of the density of states near to the top of the band. The three atomic levels are determined by the ionisation energies of the three pure semiconductors: InP (5.72 eV), InAs (5.44 eV) and InSb (5.07 eV)[14]. Finally, we set simply $V_I = W = \alpha V$, in order to reduce the number of free parameters to one. The following remarks are in order: this is not a realistic description of the valence band of In(AsP); the ionization energies allow us to place the bands of the pure compounds with respect to each other, and hence to determine the "atomic" energy levels $E_{As}$, $E_P$ and $E_{Sb}$, but they do not provide either a realistic description of the potential fluctuations in the alloy or the impurity potential. However, given the simplicity of our basic model, this choice of parameters can be used to discuss quantitatively the results of alloy potential fluctuations in a specific case.

We can now determine, for different values of the parameters a, whether, for a given cluster configuration $\Gamma$ an impurity level is split-off the top of the valence band. The fluctuation of the cluster potential, with respect to the virtual crystal average, becomes more positive the more As atoms there are in the cluster. This means that the cluster formed by one impurity atom and 12 As atoms has the largest (positive) fluctuation and, as such, produces the highest lying impurity level. Similarly, the cluster of impurity and 12 P atoms produces the lowest lying impurity level. This may seem strange, when we consider that the size and electronegativity differences are smaller for Sb and As than for Sb and P, and hence that it is more likely that the latter cluster will produce a bound state, than the former. However, it must be kept in mind that the band edge is determined by the virtual crystal approximation and that P-rich clusters present an overall negative energy fluctuation with respect to the average. Hence, this may lead to the formation of virtual bound states i.e., resonances in the band of allowed states. However, in the present work we concentrate our attention upon localized states, completely split-off from the band. In Figure 4, we show the energies of split-off states associated with clusters of Sb + 12As and Sb + 12 P atoms, as a function of the relaxation parameter a. All other states have energies between the two extreme cases considered in the Figure. We see that below a certain critical value a, = 0.86 there are no split off impurity states. For 0.86 < a < 0.94 less than 35 clusters

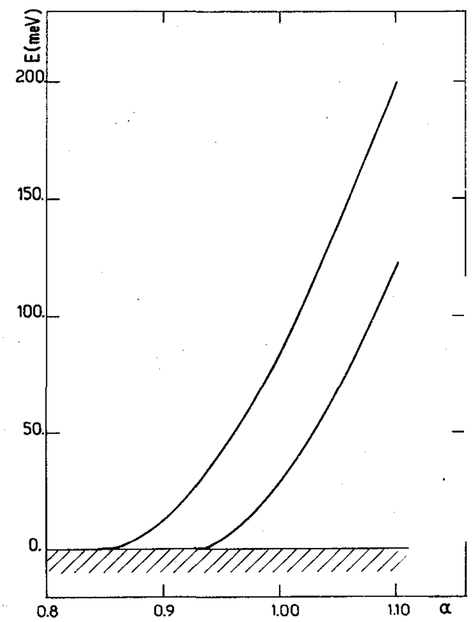

Fig.4 - Split-off impurity levels as a function of relaxation parameterafor cluster of 12 As atoms (upper curve) and cluster of 12 P atoms (lower curve). The top of the valence band is at 0 MeV. The intermediate clusters have impurity levels with energies between the two extremes plotted in the Figure.

present split-off states; for a > $\alpha_2$ = 0.94, all the 35 clusters present localized impurity levels. These are shown, for a = 0,96, on Figure 5. In it are given the energy position of a level, its weight on the central-impurity-site, the configuration which produces the level, specified by the four integers ($n_1 n_2 n_3 n_4$) and the total number of As atoms in the clusters. Configurations which produce almost degenerate levels (energy difference less than 1 MeV) are grouped together in this diagram.

In Figures 5 and 6, we present the average local density of states, in the energy interval of the impurity levels, for different parameters of SRO, corresponding to the probability distributions shown in Figure 3. The inipurity levels have been broadened by introducing an imaginary part of the energy of 0.5 MeV. In Figure 5, we consider the symmetric distributions, covering a high degree of SRO (lower part), the randomalloy (middle) and slightly less random alloy (top). In Figure 6, a sequence is presented which goes from clusters with a high probability for large numbers of P atoms (lower part), random alloy (middle), to clusters with a

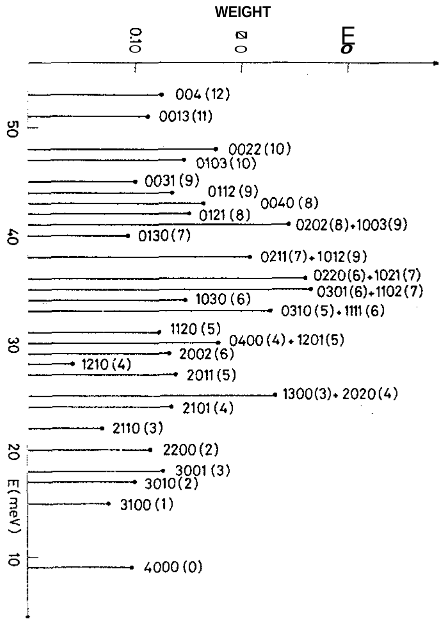

Fig.6 - Average local density of impurity states, broadened by 0.5 MeV, for three different degrees of SRO corresponding to the points Γ (lower part), R (middle) and X (upper) of Figure 3.

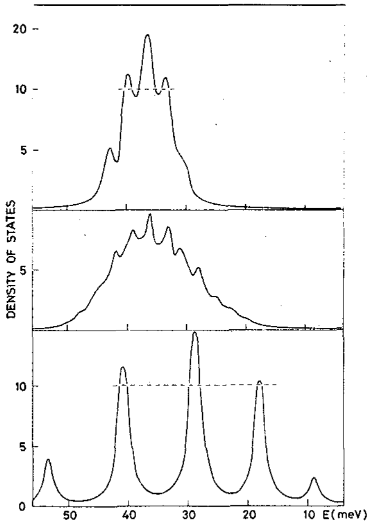

Fig.5 - Impurity levels for the 35 inequivalent clusters for α=0.96. Shown are the energy position of the levei (same convention as for Figure 4), the corresponding configuration of the cluster indicated by the 4 integers of eqn. (3.3), the number of As atoms in the clusters being given in parenthesis and, finally, the weight of the impurity level in the central all.

high probability of As atoms (top). Due to the almost uniform distribution of impurity levels for the various clusters (see Figure 5), the local density of impurity states (LDOIS) resembles closely the probability distributions shown on Figure 3. This is the case in part because we decoupled the dynamical and the statistical aspects of the problem. Taking into account a different relaxation for each cluster will produce a less uniform distribution in energy of the impurity levels.

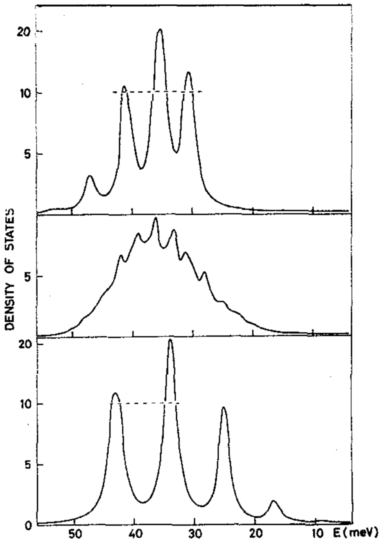

Fig.7 - Average local density of impurity states, broadened by 0.5 MeV, for three different degrees of SRO, corresponding to the points *M* (lower part), *R* (middle) and N (upper) of Figure 2.

## 5. DISCUSSION AND CONCLUSIONS

In this paper we have studied the effect of SRO upon the local density of states in an alloy semiconductor. We have taken as a specific model that of an isoelectronic impurity in a single band/many sites approximation. Although the model is not realistic enough to allow us to make precise quantitative predictions, some qualitative remarks of importance can be made. In completely random alloys, the heterogeneous broadening can be appreciable (tens of meVs). In alloys presenting a certain degree of SRO, the LDOS of the impurity levels acquires a structure, which may reflect that of the alloy probability distribution around the impurity site. In extreme cases, well defined peaks are produced, the widths of which can be considerably smaller than the overall width of the inhomogeneous broadening.

The question of the observation of such effects remains open. On the one hand, there is the possibility of selectively exciting impurity levels within a spectral interval[8], which would allow at least an indirect probing of the LDOIS. On the other, luminescence spectra may provide evidente for the importance of SRO effects in alloys, as in the study of $In_{1-x}Ga_xAs_yP_{1-y}$ by Etienne et *al.*[9]. In such a case, thermalization effects lead to a partial occupation of the impurity levels and shifts of the luminescent line may be observed, for an alloy of uniform composition,as the degree of SRO changes. With the increasing technological importance of semiconducting alloys, it is clear that, in the future, many more studies of the role of impurities in these systems will be performed. For those interested in the properties of disordered systems, semiconductors alloy offer an unique opportunity, because, unlike their metallic conterparts, very powerful optical techniques can be employed to elucidate their properties.

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## REFERENCES

1. See the review by S.T.Pantelides, in Rev.Mod.Phys. 50, 797 (1978) and references therein.
2. M.Jaros, Adv.in Phys. 29, 409 (1980).
3. D.J.Wolford, B.G.Streetman, S.Lai and M.V.Klein, Solid State Commun. 32, 51 (1974).
4. W.Y.Shu, J.D.Dow, D.J.Wolford and B.G.Streetman, Phys.Rev. B*16*, 1597 (1977).
5. A.Baldereschi, J.Lumin. 7, 79 (1973).
6. R.A.Faulkner, Phys.Rev. *175*, 991 (1978).
7. G.G. Kleiman and M.Fracastoro-Decker, Phys.Rev.B*21*, 3478 (1980).

8. D.J.Wolford, B.G.Streetman and J.Thompson, Int.Conference on Semiconductors, Kyoto 1980 (to be published).

9. B.Etienne, R.Nahory, E.V.K.Rao, M.A.Pollack and M.Voos (private communication).

10. J.D.Joannopoulos and F.Yndurain, Phys. Rev. B*10*, 5164 (1974).

11. B.Koiller, B.Maffeo and H.S.Brandi, Phys.Rev. B18, 1966 (1978).

12. J.B.Salzberg, C.E.T. Gonçalves da Silva and L.M.Falicov, Phys. Rev.B*14*, 1314 (1976).

13. R.Kikuchi, Phys. Rev. 81, 988 (1951).

14. J.A.Van Veohten, Phys. Rev.*187*, 1007 (1969).