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Model for the hybridization effect in disordered systems

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Within a tight-binding formalism, we present a Bethe-lattice-type approximation which can be applied to the whole Hamiltonian or to a hybridization part only and which is expected to be valid in disordered systems like liquids. In the first case, it gives simple scalar equations for the calculation of the densities of states and has been applied successfully to some transition-metal alloys. In the second case, it can be used to study the *sp*-*d* hybridization. We predict a Fano effect on the *sp* density of states which can lead to the creation of a pseudogap at the top of the *d* band. We recover an expression for the *sp* self-energy which is the basis for an explanation of positive Hall coefficients in amorphous transition metals and also implies the well-known *s*-*d* resistivity proportional to the *d* density of states at the Fermi level.

I. INTRODUCTION

In this paper, we are interested in disordered systems with a great number of nearest neighbors and by means of a Bethe-lattice-type approximation, we obtain an insight into two problems. The first is the calculation of densities of states (DOS's) for which our model gives simple scalar equations. The parameters are the atomic energies (charge transfer included) and the second moments of the Hamiltonian of coupling between the *s*, *p*, or *d* bands of the constituents which are easily calculated in terms of the pair correlation functions. We already have successfully used those equations in some transition-metal alloys. The second problem is that of hybridization which is somewhat more developed here.

It is well known that the hybridization of states of different bands can have important consequences on electronic characteristics such as the density of states or transport properties, in crystalline as well as in amorphous or liquid systems. In the crystalline state, band-structure calculations have shown the importance of *s*-*d* coupling in transition metals and particularly the reduction of the *s* density of states in the middle of the *d* band.[1] A simple theory of *s* and *p* densities of states for impurities in transition metals has been presented by Terakura,[2-4] the theory predicts a Fano effect and has been used recently to interpret some magnetic properties of alloys.[5,6] In numerous metallic crystalline compounds band-structure calculations have shown that the strong hybridization leads to repulsion of the bands and to the creation of a pseudogap.[7] For the composition of the compound, the Fermi level lies in the pseudogap, and this is the reason why we observe anomalies in physical properties such as the conductivity, the thermopower, the magnetoresistance, the Hall effect, etc. Lastly, let us recall that, in some disordered systems like noble metals, Mott[8] has shown the importance of the effect of *s*-*d* hybridization on conductivity. Recently, Weir *et al.*[9,10] argued that it could be the reason for the positive Hall coefficient observed in many amorphous and liquid alloys of transition metals; they used, however, a quite controversial reciprocal-space analysis.

These approaches to the study of hybridization effects in disordered systems have been applied to some peculiar cases and give a partial description. In our paper, we give a more general description of the main trends of the hybridization effects in disordered systems using a tight-binding formalism.

In the case of *sp*-*d* hybridization, we predict a Fano effect on the *sp* density of states and the appearance of a pseudogap at the top of the *d* band when the hybridization is sufficiently strong. It is worth noticing the similarity to the Fano effect described by Terakura for the case of an *s* or *p* impurity imbedded in a transition metal.[2-4] Our value of the self-energy due to the hybridization is also in agreement with that one used by Weir *et al.*[9,10] for their interpretation of positive Hall coefficients and implies an *s*-*d* resistivity proportional to the *d* density of states at the Fermi level.[8]

Our model for the DOS is based on a cluster-Bethe-lattice-method- (CBLM)-type that we call the scalar cluster Bethe-lattice method (SCBLM), and we establish its equations in Sec. II. The approximations involved are discussed and applications are briefly presented in Sec. III. In Sec. IV we discuss our approximation when it is applied to the hybridization only and present our results.

II. THE SCALAR CLUSTER BETHE-LATTICE METHOD (SCBLM)

The CBLM was developed ten years ago, and since that date it has been used successfully for alloys in its simplest version, that is to say by replacing the real lattice by a Bethe lattice with the same coordination number and geometrical atomic environment.[11,12] Among the applications are the studies of liquid alloys like Au-Cs,[13] of transition-metal-based solid alloys,[7,14] and of simple metal alloys.[15] In this section we first recall the basic quantities of the CBLM and the equations it leads to. Then we introduce a supplementary approximation well suited for

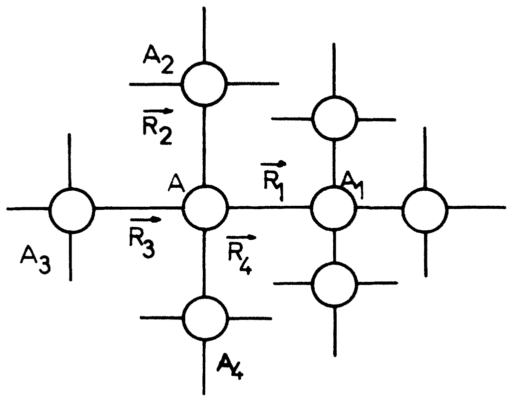

FIG. 1. Bethe lattice with four nearest neighbors.

disordered systems such as liquids, which allows us to write the equations in a much simpler form (see Sec. III). The aim of the method is the calculation of the Green's function (of an atom) $G(z)$; one can always write $G(z)$ as

$$G(z)=\frac{1}{z-H_0-\Sigma(z)}\ . \tag{1}$$

H_0 is the Hamiltonian of the atom with charge transfer and crystalline field included. $\Sigma(z)$ is the self-energy due to the coupling with the lattice. In a Bethe lattice, the self-energy of atom A is the sum of contributions of each branch starting from A in direction $\mathbf{R}_j$ (Fig. 1).

$$\Sigma(z)=\sum_j \Sigma(z,\mathbf{R}_j)\ , \tag{2}$$

with

$$\Sigma(z,\mathbf{R}_j)=T^{\dagger}(\mathbf{R}_j)G(z,\mathbf{R}_j)T(\mathbf{R}_j)\ . \tag{3}$$

$T(\mathbf{R}_j)$ is the transfer matrix between A and the atom A_j in the direction $\mathbf{R}_j$. $G(z,\mathbf{R}_j)$ is the Green's function of the atom A_j located in the auxiliary Bethe lattice (Fig. 2) which is obtained from the initial Bethe lattice by removing the bond with A, placed in direction $-\mathbf{R}_j$. In the same way, one can calculate the self-energy of $G(z,\mathbf{R}_j)$ which gives

$$G(z,\mathbf{R}_j)=\frac{1}{z-H_0-\displaystyle\sum_{\mathbf{R}_k(\neq-\mathbf{R}_j)} T^{\dagger}(\mathbf{R}_k)G(z,\mathbf{R}_k)T(\mathbf{R}_k)}\ . \tag{4}$$

This self-consistent equation determines the Green's functions $G(z,\mathbf{R}_j)$ that are put in Eqs. (3), (2), and (1) to calculate $G(z)$.

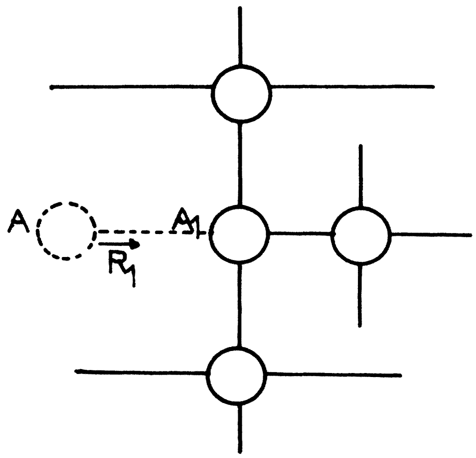

FIG. 2. Auxiliary Bethe lattice for the calculation of $G(z,\mathbf{R}_1)$.

In the CBLM, the environment of an atom is described by a mean field (here a mean self-energy) which is calculated from pair probabilities p_{ji}. p_{ji} is the probability that in a given direction $\mathbf{R}$ the neighbor of an atom of type i is an atom of type j. It is determined by the concentrations of the constituents and by the short-range order (SRO) parameter S:

$$p_{ij}=x_i+(1-x_i)S,\quad p_{i,j=i}=(1-x_i)(1-S)\ ,$$

with

$$\frac{-x}{(1-x)}<S<0\quad\text{for } x<\tfrac{1}{2}\ ,$$

$$\frac{-(1-x)}{x}<S<0\quad\text{for } x>\tfrac{1}{2}\ .$$

In a real system simulation, S is *a priori* unknown. Its value is that which minimizes the free energy $F(S)$.[13] The contribution of the bond $\mathbf{R}_k$ to the mean self-energy of an atom of type i is then calculated with a simple linear interpolation:

$$\Sigma_i(\mathbf{R}_k)=\sum_j p_{ji}T_{ji}^{\dagger}(\mathbf{R}_k)G_i(z,\mathbf{R}_k)T_{ji}(\mathbf{R}_k)\ . \tag{5}$$

$T_{ji}(\mathbf{R}_k)$ is the transfer matrix from an i atom to a j atom in direction $\mathbf{R}_k$, and $G_j(z,\mathbf{R}_k)$ is the mean Green's function of a j atom located on the auxiliary Bethe lattice defined above. So if one denotes by $G_i(z)$ the mean Green's function of atom i and by H_{0i} its Hamiltonian, (1)–(5) give the CBLM equations:

$$G_i(z)=\frac{1}{z-H_{0i}-\displaystyle\sum_{\mathbf{R}_k,j} p_{ji}T_{ji}^{\dagger}(\mathbf{R}_k)G_j(z,\mathbf{R}_k)T_{ji}(\mathbf{R}_k)}\ , \tag{6}$$

$$G_i(z,\mathbf{R}_k)=\frac{1}{z-H_{0i}-\displaystyle\sum_{j,\mathbf{R}_l(\neq-\mathbf{R}_k)} p_{ji}T_{ji}^{\dagger}(\mathbf{R}_l)G_i(z,\mathbf{R}_l)T_{ji}(\mathbf{R}_l)}\ . \tag{7}$$

(6) and (7) are equations between matrices, and it is not simple *a priori* to study qualitatively, from them, the effect of hybridization. We present now the approximation which allows to write (6) and (7) in a scalar form and leads to a simple analysis of some effects of hybridization (see Sec. IV).

As we mentioned above, the Bethe lattice is chosen such that geometrical arrangement of the neighbors of its sites is that of the real system. So, for the numerous amorphous systems whose local structure is that of a given crystalline system, the Bethe lattice possesses the point symmetries of that system. For those atoms which possess at most one level of each type, *sp* or *d*, the Green's functions $G_i(z)$ are scalar inside the invariant subspaces and do not couple them. If one denotes by α those subspaces and by P_α the projector on them, the Green's function of atom i is

$$G_i(z)=\sum_{\alpha(i)} P_\alpha G_\alpha(z) . \tag{8}$$

$G_\alpha(z)$ is a scalar and the sum is over the subspaces $\alpha(i)$ of atom i. In order to simplify (6) and (7), one can make a further approximation, discussed in Sec. III, and consider that $G_i(z,\mathbf{R}_k)$ possess the same symmetries as $G_i(z)$ but are calculated with an environment of $Z-1$ nearest neighbors:

$$G_i(z,\mathbf{R}_k)=\sum_{\alpha(i)} P_\alpha G'_\alpha(z) . \tag{9}$$

The equations are written in a simple form with some new notations. We call n_α the degeneracy of the subspace α and $g_{ij}(\mathbf{R})$ the pair correlation function between atoms of type i and j. One can then define the mean square of the matrix element between a state of the subspace α of atom i and a state of the subspace β of atom j.

$$T^2_{\alpha\beta}=T^2_{\beta\alpha}=\frac{1}{n_\alpha n_\beta}\frac{1}{Zp_{ji}}\int d^3\mathbf{R}\, g_{ji}(\mathbf{R}) \times \mathrm{Tr}[T^\dagger_{ji}(\mathbf{R})P_\beta T_{ji}(\mathbf{R})P_\alpha] . \tag{10}$$

From $T^2_{\alpha\beta}$ one can also define

$$\sigma^2_{\alpha\beta}=Zp_{ji}n_\beta T^2_{\alpha\beta} . \tag{11}$$

$\sigma^2_{\alpha\beta}$ is the part of the mean second moment of the DOS on a state α due to the coupling with states β of the neighbors. Finally, if one denotes by E_α the atomic energy of a state α (including charge transfer and crystalline field) and

$$(\sigma'_{\alpha\beta})^2=\frac{Z-1}{Z}\sigma^2_{\alpha\beta} ,$$

(6) and (7) give

$$G_\alpha(z)=\frac{1}{z-E_\alpha-\sum_\beta \sigma^2_{\alpha\beta}G'_\beta(z)} , \tag{12}$$

$$G'_\beta(z)=\frac{1}{z-E_\beta-\sum_\alpha (\sigma'_{\beta\alpha})^2 G'_\alpha(z)} . \tag{13}$$

III. DISCUSSION AND APPLICATION OF THE SCBLM

It is interesting to compare results obtained with the SCBLM and the usual CBLM for the same physical system. We have studied the DOS's of pure Co, pure Al, and $Co_{50}Al_{50}$ within the SCBLM [(12) and (13)] and the CBLM [(6) and (7)]. We took the same tight-binding parameters and short-range order in both cases and, following Moruzzi *et al.*[16] and Nguyen-Manh *et al.*,[17] we chose a bcc lattice for all those systems although Co and Al are fcc. Figure 3 gives a comparison of both methods for the alloy $Co_{50}Al_{50}$ whose chemical order is nearly complete $S(=-0.95)$. It appears that the SCBLM reproduces well some structures but gives neither the first peak of the DOS on the left nor the first pseudogap on the left. On the contrary, in the case of pure Co [Fig. 4(a)] and pure Al [Fig. 4(b)], the CBLM predicts DOS's which are not as structured as in the alloy and the SCBLM is a good ap-

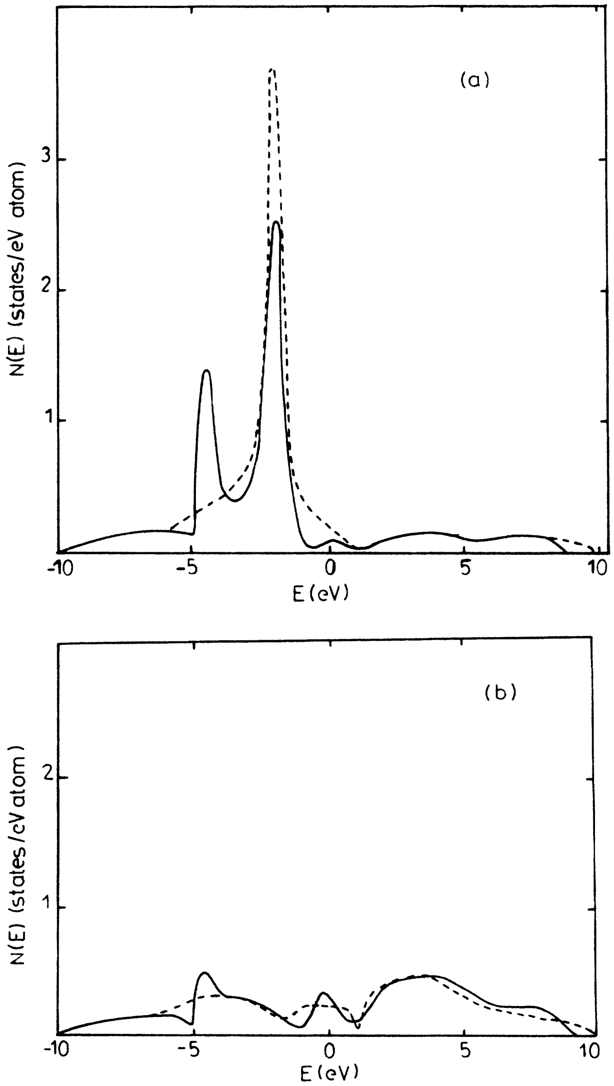

FIG. 3. Comparison between DOS calculated with CBLM (——) and SCBLM (— — —) for Co (a) and Al (b).

proximation. Note that in the case of Al, the tight-binding treatment cannot fit well the real electronic structure. We have also compared the two methods for the alloys Cu_xZr_{1-x} ($x=0.33,0.5,0.66$), whose local fcc structure is more compact than bcc and is *a priori* more suited for the use of the SCBLM. Figure 5 shows that the agreement is actually better, and this is important since the compactness of the fcc structure is typical of numerous amorphous. Thus our study confirms the validity of SCBLM in disordered systems whose DOS's presents few structures.

Let us now apply it to the same alloys in the liquid phase. For those systems, the angle between the bonds of an atom and its neighbors varies, and one no longer has to consider that the local structure is that of a crystalline system. So we assume that the mean local environment is isotropic. Under this assumption, there exists a spherical point symmetry for our mean-field model and the invariant subspaces α are simply the s, p, or d bands of the constituents of the alloy. Figure 6 and 7 give the comparison of the DOS's calculated with and without this isotropic symmetry. It appears that the difference is rather small and the geometrical local environment does not play a major role in the electronic structure for our model. On the contrary, the chemical local environment (i.e., given by the short-range order parameter S) introduces strong modifications of the DOS.

Recently,[17] we have used this model to calculate the DOS's in $Ni_{40}Ti_{60}$, and Ni_xZr_{1-x} (with $x=0.35,0.5,0.65$) for which the number of nearest neighbors is about eleven and which are consequently good candidates. Combining it with a variational method and a hard-sphere Yukawa system[18] as a reference model we have been able to determine also partial structure factors in good agreement with experiment.

Let us finally point out that some of the features induced by the hybridization effect seem to be quite dependent on the crystallinity of the material. In the case of Co-Al alloys studied, for example, the pseudogap which occurs just at the Fermi level in the crystalline compounds does not exist in the liquid phase. Only the one that is in the unoccupied band appears.

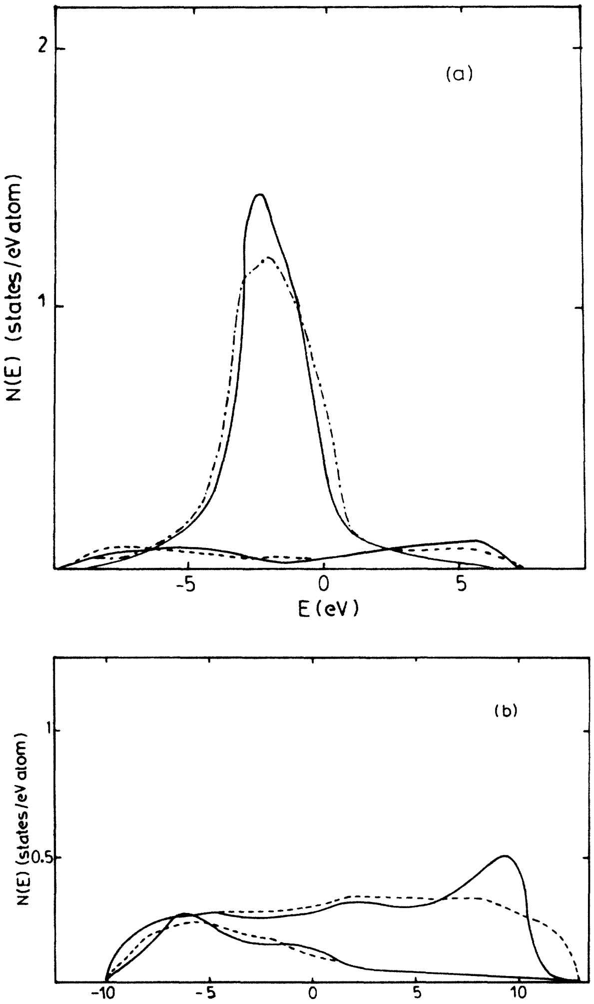

FIG. 4. (a) Comparison between s and d DOS of pure Co calculated with CBLM (——) and SCBLM (– – –). (b) Comparison between s and p DOS of pure Al calculated with CBLM (——) and SCBLM (– – –).

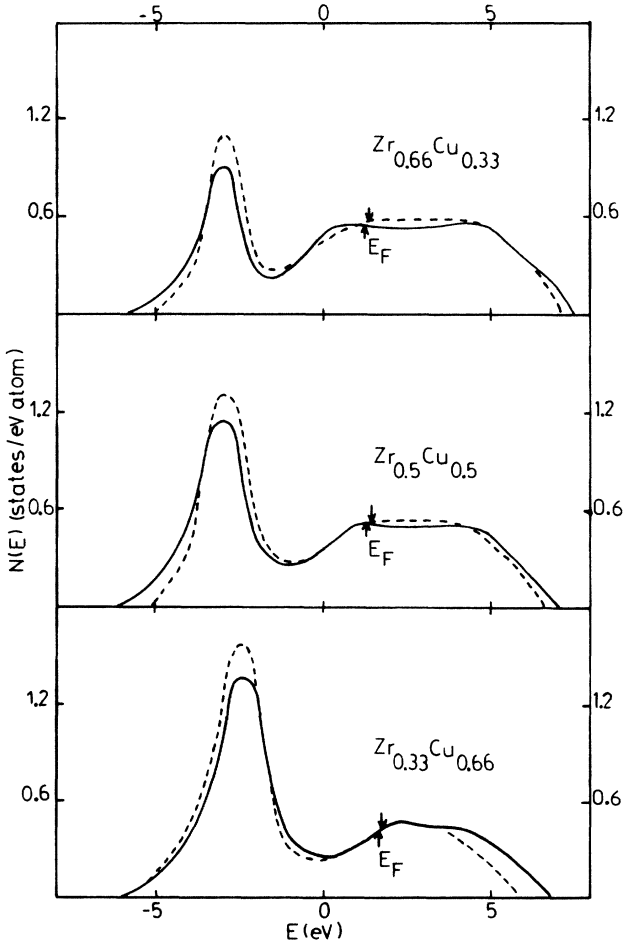

FIG. 5. Comparison between DOS calculated with CBLM (——) and SCBLM (– – –) for several amorphous Cu_xZr_{1-x} alloys.

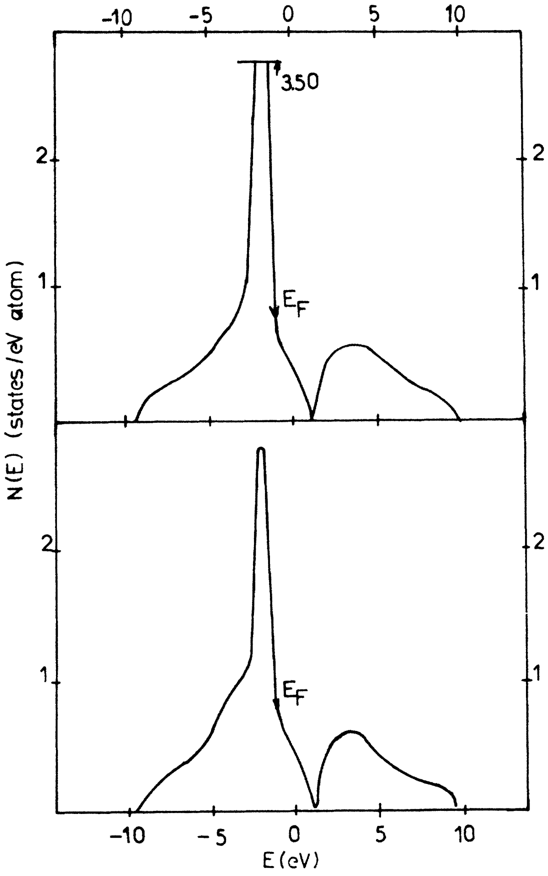

FIG. 6. Comparison between DOS of the alloy $Co_{50}Al_{50}$ calculated with the SCBLM for two symmetries. The upper figure corresponds to the symmetry of the bcc lattice. The lower figure corresponds to the spherical symmetry. The SRO parameter is $S=-0.95$.

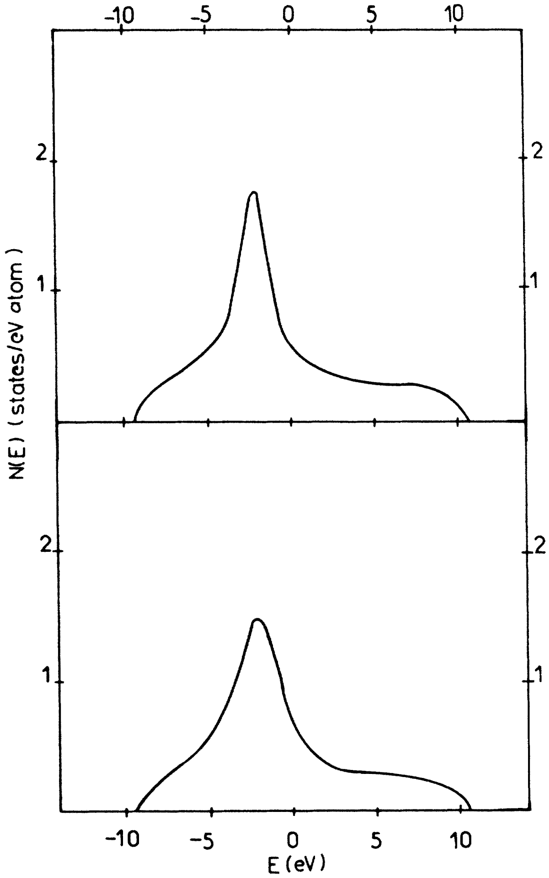

FIG. 7. Same comparison as in Fig. 6 for $S=0$.

IV. HYBRIDIZATION IN DISORDERED SYSTEMS

A. Expression of the self-energy

In order to study the effect of hybridization in disordered systems, it is possible to apply a Bethe-lattice-type approximation, analogous to the SCBLM, to the hybridization only, whereas the rest of the Hamiltonian is treated in a mean-field approximation (mean isotropic environment) on the real lattice. We show in the appendix and in Ref. 19 that, under this condition, the hybridization gives to each state of the α band a self-energy,

$$\Sigma_\alpha(z)=\sum_{\beta(\neq\alpha)}\sigma^2_{\alpha\beta}G_\beta(z)\ , \tag{14}$$

and that the Green's functions of the different bands obey

$$G_\alpha(z)=G_{0\alpha}[z-\Sigma_\alpha(z)]\ , \tag{15}$$

$$G_\alpha(z)=G_{0\alpha}\left[z-\sum_{\beta(\neq\alpha)}\sigma^2_{\alpha\beta}G_\beta(z)\right]\ . \tag{16}$$

$\sigma^2_{\alpha\beta}$ is defined in (10) and (11) and the α bands are *s*, *p*, or *d* bands of the constituents. $G_{0\alpha}(z)$ is the Green's function of the α band without hybridization which is *a priori* unknown in our formalism.

The question of the validity of the Bethe-lattice approximation for the hybridization is of course important and is well discussed in the formalism of Movagher *et al.*[20] that we intend to use in a further study. We show that for a system with $z\gg1$, in a mean-field theory, the effect of hybridization is to give a self-energy $\Sigma_\alpha(z)$ to the states of the α band [i.e., (15) remains valid]. However, expression (14) represents only the first term of $\Sigma_\alpha(z)$ in this formalism, and one must add corrections to it. In the case of amorphous Ni, we have a first estimation of this correction[21] which is 10—20% for the *s*-*d* hybridization. Finally the approximation (14) is expected to be better for *s*-*d* and *d*-*d* than for *s*-*s* hybridization.

Starting from (15), it is easy to calculate the DOS of the α band $n_\alpha(E)$ in terms of its DOS without hybridization $n_{0\alpha}(E)$:

$$n_\alpha(z) = -\frac{1}{\pi}\,\mathrm{Im}\left[G_{0\alpha}\left[z - \sum_{\beta(\neq\alpha)} \sigma_{\alpha\beta}^2 G_\beta(z) \right]\right] ,$$

$$n_\alpha(z) = -\frac{1}{\pi}\int n_{0\alpha}(E)dE\,\mathrm{Im}\left[\frac{1}{z - \sum_{\beta(\neq\alpha)} \sigma_{\alpha\beta}^2 G_\beta(z) - E} \right] ,$$

$$n_\alpha(z) = \int n_{0\alpha}(E) L_\alpha(z,E) dE , \tag{17}$$

$$L_\alpha(z,E) = \frac{\sum_{\beta(\neq\alpha)} \sigma_{\alpha\beta}^2 n_\beta(z)}{\left[z - \sum_{\beta(\neq\alpha)} \sigma_{\alpha\beta}^2 \mathrm{Re} G_\beta(z) \right]^2 + \pi^2 \left[\sum_{\beta(\neq\alpha)} \sigma_{\alpha\beta}^2 n_\beta(z) \right]^2} . \tag{18}$$

So the DOS of the α band, $n_\alpha(z)$, is the mean-value of the DOS without hybridization, $n_{0\alpha}(z)$, weighted by the Lorentzian $L_\alpha(z,E)$ whose width is

$$\Delta_\alpha(z) = 2\pi \sum_{\beta(\neq\alpha)} \sigma_{\alpha\beta}^2 n_\beta(z) , \tag{19}$$

and which is centered around the energy

$$Z_\alpha(z) = z - \sum_{\beta(\neq\alpha)} \sigma_{\alpha\beta}^2 \mathrm{Re} G_\beta(z) . \tag{20}$$

B. The mixing of states

Because of the hybridization a proper state of energy E has a nonzero amplitude in each α band and contributes simultaneously to all the DOS, $n_\alpha(E)$. From this, all bands fall in the same energy range and it is interesting for our simple model to verify this property.

In fact, if an α band has a nonzero DOS, $n_\alpha(z)$, for energy z, the width $\Delta_{\beta\neq\alpha}(z)$ [Eq. (19)] is also nonzero and the Lorentzian $L_\beta(z,E)$ overlaps $n_{0\beta}(E)$. So $n_\beta(z)$ [Eq. (17)] is nonzero which shows that the bands are of the same energy range.

C. The repulsion effect

We study now the hybridization of a band 1 situated below a band 2 in the limit of a weak coupling. Then, in (18), it is possible to replace $G_\beta(z)$ by $G_{0\beta}(z)$ and $n_\beta(z)$ by $n_{0\beta}(z)$. Inside the energy region around $n_{0\beta}(z)$, $\Delta_{\alpha\neq\beta}(z)$ is nonzero and (17) shows that $n_\alpha(z)$ is nonzero, which expresses the mixing of states. On the other, $\Delta_{\alpha\neq\beta}(z)$ is zero outside the energy region around $n_{0\beta}(z)$ and $L_\alpha(z,E)$ is a δ function which leads to

$$n_\alpha(z) = n_{0\alpha}(Z_\alpha(z)) . \tag{21}$$

So if z is below the band $n_{02}(E)$, $\mathrm{Re}G_{02}(z)$ is negative (Fig. 8) and $Z_1(z) > z$, which shows a repulsive effect on band 1. Similarly, outside the energy region around $n_{01}(E)$ band 2 feels a repulsive effect. So we find a well-known effect of hybridization which persists even when the coupling is stronger and can lead to the creation of a pseudogap between the hybridized bands.

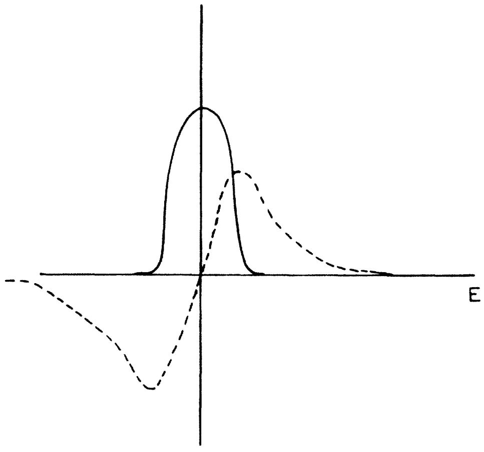

FIG. 8. Real (— — —) and imaginary part (——) for the Green's function of a band.

D. The *sp*-*d* hybridization

When an *s* or *p* band hybridizes with a *d* band in an amorphous metal, one can consider in a first approximation that the *d* band is weakly perturbed:

$$G_d(z) \simeq G_{0d}(z) .$$

Then (16) shows that the *s* or *p* states acquire a self-energy,

$$\Sigma_{sp}(z) = \sigma_{spd}^2 G_{0d}(z) , \tag{22}$$

which is analogous to the expression obtained by Weir *et al.*[9,10] in a random-phase approximation and by a perturbation calculation,

$$\Sigma_s(z,\mathbf{k}) = \sigma_{sd}^2(k^2) G_{0d}(z) . \tag{23}$$

However, Weir *et al.* treat the nonhybridized *s* electrons as free electrons, and the coupling between a state $\mathbf{k}$ and the atomic *d* states has a dependence on the energy k^2 which does not exist in our tight-binding treatment. This introduces a dependence of σ_{sd}^2 on the energy of the conducting state. As for (23), the imaginary part of (22) expresses a finite lifetime of the *sp* states and implies a resistivity due to the *sp*-*d* hybridization proportional to the *d* DOS at the Fermi level.[8] If one applies (22) to free electrons, it can lead also to an S-shaped dispersion curve for $E(\mathbf{k})$ which is the basis for the explanation given by Weir *et al.*[9,10] of the positive Hall coefficient observed in numerous amorphous and liquid alloys of transition metals.

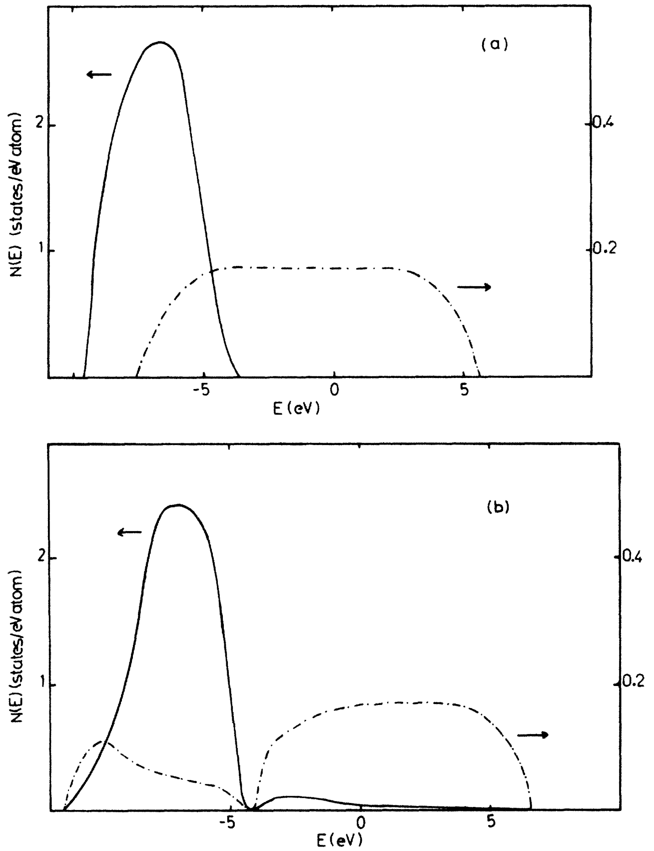

FIG. 9. *s* and *d* DOS without (a) and with (b) hybridization. The two densities of states are not at the same scale.

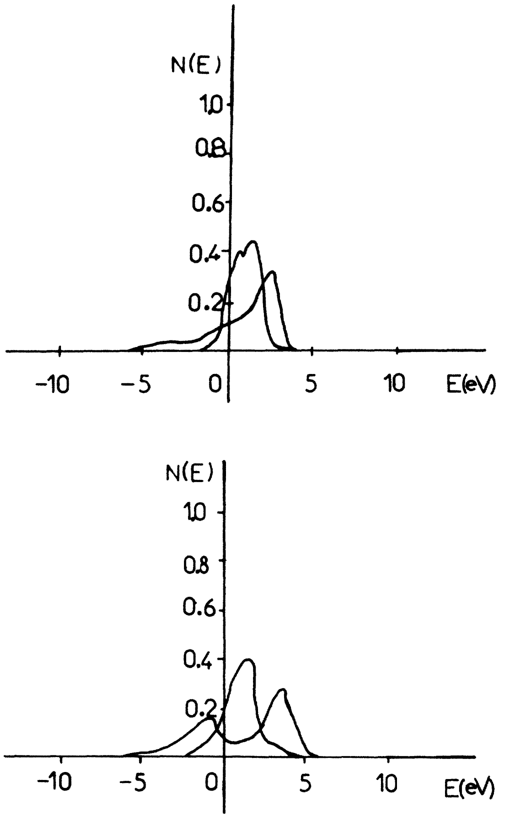

FIG. 10. *s* and *d* DOS in simulated amorphous Ni without (upper figure) and with (lower figure) hybridization. The two densities of states are not at same scale. Those figures are taken from Ref. 9.

Equations (17) and (18) lead also to a simple interpretation of the effect of hybridization on the *sp* DOS in some typical cases. We consider the situation represented in Fig. 9. When z is below the *d* band, $\mathrm{Re}G_d(z)$ is negative (Fig. 8) and

$$Z_{sp}(z)=z-\sigma_{sp\text{-}d}^2\mathrm{Re}G_d(z)$$

is greater than z. So $n_{sp}(z)$ is the mean value of $n_{0sp}(z)$ in a region where it is greater than $n_{0sp}(E)$ and the hybridization reinforces the *sp* density of states (Fig. 9 and 10). On the other hand, if z is above the *d* band $\mathrm{Re}G_d(z)$ is positive (Fig. 8) and $n_{sp}(z)$ is the mean value of $n_{0sp}(E)$ in a region where it is weak and possibly zero. So when the hybridization is sufficiently strong, a pseudogap appears at the top of the *d* band [Fig. 9(b)]. It is worth noticing that we obtain results analogous to the Fano effect described by Terakura[2] in the very different case of an *s* or *p* impurity in a transition metal. In order to study the *sp* DOS inside the *d* band, one has to take into account the finite width of the *sp* band. When one calculates the *sp* DOS in the middle of the *d* band [$\mathrm{Re}G_d(z)=0$], one weights the nonhybridized *sp* DOS by a Lorentzian centered on z whose width is $2\pi\sigma_{sp\text{-}d}^2 n_d(z)$. If the hybridization is sufficiently strong the width of the Lorentzian is greater than that of the nonhybridized *sp* DOS, and an important part of the Lorentzian does not contribute to (17) which leads to a decrease in the *sp* DOS inside the *d* band (Figs. 4 and 10).

V. CONCLUSION

In summary, we must recall that our Bethe-lattice-type approximation has been developed within a tight-binding scheme. On one hand, it can be applied to the whole Hamiltonian (SCBLM) and gives simple equations to calculate DOS's in liquid systems including both charge transfer and chemical order. On the other hand, it can be used to study *sp-d* hybridization. It appears that the *sp* electrons acquire a self-energy whose imaginary part indicates a finite lifetime and a resistivity proportional to the *d* density of states and whose real part can lead to negative group velocity at the Fermi level and consequently to a positive Hall coefficient. We also predict a creation of a pseudogap at the top of the *d* band for strong hybridization.

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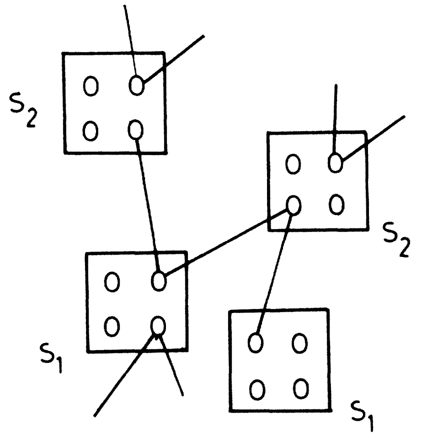

FIG. 11. Bethe approximation for the *s*-*d* hybridization. Each circle in S_1 represents the *s* orbital of an atom. Each circle in S_2 represents the five *d* orbitals of an atom.

APPENDIX

We consider an ensemble of systems S_i, constituted of orthogonal orbitals $|i\nu\rangle$ which can be either different orbitals (s,p,d) of a given type of atom, or orbitals of different atoms. For example, in the case of the *s*-*d* hybridization in a pure liquid, we consider the system S_1 of the *s* orbitals and the system S_2 of the *d* orbitals. The systems S_i are described by the Hamiltonian H_{0i} and are coupled together by the hybridization Hamiltonians V_{ij}. We now apply the Bethe approximation to the hybridization terms so that the systems S_i formally play the role of the atoms in the usual Bethe lattice (Fig. 11). Each orbital $|i\nu\rangle$ is coupled to the orbitals $|j\mu\rangle$ of systems S_j which belong to uncoupled subspaces $E_{i\nu,j\mu}$. Each subspace $E_{i\nu,j\mu}$ itself represents the system S_j which is coupled by the hybridization to the other systems (inducing S_i), but without the hopping integral between $|j\mu\rangle$ and $|i\nu\rangle$. The calculation of the Green's function of this lattice is identical to that of the usual Bethe lattice with a spherical point symmetry. The effect of hybridization is to give a supplementary self-energy $\Sigma_i(z)$ to the $|i\nu\rangle$ orbital of S_i [$\Sigma_i(z)$ is the same for all $|i\nu\rangle$ because of the mean-field approximation]:

$$\Sigma_i(z)=\sum_{j,\mu}|\langle i\nu|V_{ij}|j\mu\rangle|^2G_{i\nu,j\mu}(z) ,$$

where $G_{i\nu,j\mu}(z)$ is the diagonal element of the Green's function of the lattice over the state $|j\mu\rangle$ but without the hopping integral between $|j\mu\rangle$ and $|i\nu\rangle$. When the number of nearest neighbors is not too small, a given hopping integral has a small influence (in the case of *s*-*d* hybridization it corresponds to the coupling of one *s* orbital of an atom with all the *d* orbitals of a neighbor) and one can consider that

$$G_{i\nu,j\mu}(z)=G_j(z) .$$

$G_j(z)$ is the diagonal element of the Green's function over a state $|j\mu\rangle$. Finally,

$$\Sigma_i(z)=\sum_{j(\neq i)}\sigma_{ij}^2G_j(z) ,$$

where σ_{ij}^2 is the second moment of V_{ij} and is given in the main text in (10) and (11).

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