On the Theory of Disordered Alloys*[1]

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In this work, the principal methods and results concerning the problem of disordered alloys are discussed on the basis of the Green operators formalism. The particular case of binary alloys is first analyzed. It is shown how Green's functions can be applied to the problem and how one can obtain physical results from them. Dyson's equation is established thus developing a perturbative series with the introduction of the proper self-energy operator. Then, some model calculations are presented in order to show how the different existing theories differ in the way the ensemble average of the Green's functions is performed. Generalizations that include the effects due to short range correlations responsible for the formation of clusters are introduced and also the relations between them and localized alloy states. In spite of the enormous effort expended, no theory exists that explains all the important observed phenomena, thus remaining many challenging problems open to theoretical investigation, some of them being discussed here.

Neste trabalho, os principais métodos e resultados relativos ao problema das ligas desordenadas são discutidos com base no formalismo dos operadores de Green. Analisa-se, primeiramente, o caso particular das ligas binárias e mostra-se com as funções de Green podem ser aplicadas ao problema, para a obtenção de resultados físicos. A equação de Dyson é então obtida desenvolvendo-se uma série perturbativa, com a introdução do operador de auto-energia. A seguir, são apresentados alguns modelos de cálculos, para mostrar como as teorias existentes diferem na maneira com que são feitas as médias sobre as configurações das funções de Green. São introduzidas generalizações que incluem efeitos devidos a correlações de curto alcance, responsáveis pela formação de "clusters", e também as relações destes com os estados localizados da liga. A despeito de enormes esforços, não existe ainda uma teoria que explique todos os fenômenos observados, sendo que muitos problemas permanecem abertos desafiando a investigação teórica, alguns desses problemas são aqui discutidos.

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1. Introduction

In this work, the principal methods and results concerning the problem of disordered alloys are discussed on the basis of the Green's operators formalism (the so called, resolvent method).

The problem of binary alloys, is first analyzed in Section 2. There, a perturbative treatment for the expansion of the resolvent is developed by introducing the self-energy operator and it is explicitly shown how physically important results, as the spectra and the density of states, can be obtained from the knowledge of the Greenian operator.

In Section 3, the analytical properties of the resolvent and the self-energy operator are discussed and the notion of "ensemble average" is introduced. Also, a collection of formulas to be used in the next Sections is derived.

Section 4 is devoted to the discussion of some of the zero order approximation properties of the problem and in obtaining the so called Coherent Potential Approximation. Other theories are also discussed, mainly to show how they differ in the calculation of the ensemble average of the Greenian operator.

In Section 5, the importance of Clusters and the relations between them and localized states are stressed. Some methods proposed to take them into account are analysed.

As a conclusion, one can say that, despite the enormous efforts of physicists working on the subject, no theory exists that explain all observed phenomena and so there remáins many challenging problems open to theoretical investigation.

It is interesting to mention here that the earlier papers on the subject were based on the Rigid Band Model of Jones and Mott[1]. Then, came the Virtual Crystal Approximation of Korringa[2] which was used for a long time because it provided a simple way to calculate energy bands and which is, presumably, a good zero order aproximation for the problem. In Section 4, it is shown that this is not exactly the case[3].

The theories based on the Multiple Scattering Theories of Beeby and Edwards[4], which do not make use of the concept of Bloch states, basically

differ from the ones mentioned above. The preliminary version of this theory had the inconvenience that the perturbation expansions used were only valid for small impurity concentrations and the results did not apply when the concentrations of the alloy components were of the same order.

The version due to Beeby[5], however, treated the alloy components in an equal footing and did not suffer from that limitation.

The theories that treat the alloy components symmetrically are the one of Yonezawa and Matsubara[6] and the so called Coherent Potential Model of Soven[7], extensively used for reasons which will be made clear in the following Sections.

All the above mentioned theories, however, do not include the effects due to short range correlations responsible for the formation of clusters. This is one of the most important questions to be stressed out and many intrincate methods have been developed to take them into account. As mentioned before, these questions are treated in Section 5

2. Binary Alloys, the Greenian Operator and the Density of States

Let us start this Section giving a cristallographic description of binary alloys. A binary alloy is defined as a system consisting of two types of constituents, A and B (for example, closed shell positive ions), embedded in a medium of electrons and distributed in a random way at the lattice points. The lattice parameters have to be experimentally determined for a given concentration of the constituents. Random here means that no long or short range order correlations are present. As a consequence, clusters cannot be explained by the theory to be developed here.

If N is the total number of lattice points and N_A and N_B are respectively the number of the A and B constituents, then the concentrations are defined by

$$m_A = N_A/N, \quad m_B = N_B/N, \tag{2-1}$$

where obviously $m_A + m_B = 1$. We do not name A and B solute or solvent because we are interested in a theory valid for all possible concentrations of both constituents.

Our principal aim is to determine the electronic properties of the alloy and its transport properties. For that purpose, as a first step, we introduce a Greenian formalism for the problem in the one-electron approximation. We will use the vectors k in reciprocal space as one of the labels for the quantum mechanical states. This can be done because the alloy Hamiltonian is written as

$$H = H_0 + (H - H_0) = H_0 + H', \tag{2-2}$$

where H_0 is always periodic over the lattice and H' is always non periodic. No matter the functional form of H,, the real effects due to the random distribution of the constituents in the lattice will be described by H'. This is a very important remark because, as will be discussed[8] in Section 4, an arbitrary choice of H_0 and H' may lead to trivial results for the density of states.

The Greenian or resolvent operator, $G(z)$, of the Schrodinger energy equation[g],

$$H |1,\rangle = E |1,\rangle, \tag{2-3}$$

is defined as

$$G(z) = \frac{1}{z - H} \cdot \tag{2-4}$$

It is an analytic (operator-valued) function of the complex variable z, whose singularities constitute the spectrum of H. $G(z)$ is bounded in the whole complex plane except at the eigenvalues of H. If $\Delta(z)$ is the square of the distance from z to the closest eigenvalue of H, then

$$\| G(z) \| = \frac{1}{\Delta(z)} \cdot \tag{2-5}$$

Let us also define

$$G_0(z) = \frac{1}{z - H_0} \cdot \tag{2-6}$$

Then, using (2,-2), we obtain

$$G(z) = G_0(z) + G_0(z) \ H'G(z)$$
$$\equiv G_0 + G_0 H'G_0 + G_0 H'G_0 H'G_0 + \ldots \tag{2-7}$$

Suppose now that

$$H_0 |ak) = \varepsilon_{ak} |ak) . \tag{2-8}$$

Then,

$$\langle ak | G(z) | ak) \equiv G(z, k, a)$$

$$= \frac{1}{z - E\&} + \frac{1}{z - E\&} \ (ak \,|\, H' \,|\, ak) \ (ak \,|\, G(z) \,|\, ak)$$

$$+ \frac{1}{z - \varepsilon_{ak}} \sum_{a',\mathbf{k'}}' \ (ak \,|\, H' \,|\, a'k') \ (a'k' \,|\, G(z) \,|\, ak). \tag{2-9}$$

The primed sum, in Eq. (2-9), means that the term with intermediate state $|ak)$ has been excluded. On the other hand, for $|a'k') \neq |ak)$, we obtain

$$(a'k' \,|\, G(z) \,|\, ak) = \frac{1}{z - \varepsilon_{a'k'}} \ (a'k' \,|\, H' \,|\, ak) \ (ak \,|\, G(z) \,|\, ak)$$

$$+ \frac{1}{z - E\&,} \sum_{a'',\mathbf{k''}}' \ (a'k' \,|\, H' \,|\, a''k'') \ \langle a''k'' \,|\, G(z) \,|\, ak). \tag{2-10}$$

Iterating (2-10), we obtain

$$(a'k' \,|\, G(z) \,|\, ak)$$

$$= \frac{1}{z - \varepsilon_{a'k'}} \left\{ \langle a'k' \,|\, H' \,|\, ak) + \sum_{a'',\mathbf{k''}}' \langle a'k' \,|\, H' \,|\, a''k'' \rangle \frac{1}{z - \varepsilon_{a''k''}} \ \langle a''k'' \,|\, H' \,|\, a\mathbf{k} \rangle \right.$$

$$\left. + \dots \right\} G(z, \mathbf{k}, a). \tag{2-11}$$

Now, since

$$|a''k''\rangle \frac{1}{z - \varepsilon_{a''k''}} \ \langle a''k'' \,| = \frac{1}{z - H_0} |a''k''\rangle \ \langle a''k'' \,|, \tag{2-12}$$

we can write (2-11) as

$$\frac{1}{z - \varepsilon_{a'k}} \ (a'k' \,|\, \{ H' + H' \frac{1}{z - H_0} \ H' + \dots \}' \,|\, ak) \ G(z, \mathbf{k}, a), \tag{2-13}$$

where $\{ \quad \}'$ means that, for all complete sets to be used in the expression, the state $|ak)$ is missing.

Using (2-13), Eq. (2-9) can be written as

$$G(z, \mathbf{k}, a) = \frac{1}{z - \varepsilon_{ak}} +$$

$$+ \frac{1}{z - \varepsilon_{ak}} \ (ak \,|\, \{ H' + H' \frac{1}{z - H_0} \ H' + \dots \} \,|\, ak) \ G(z, \mathbf{k}, a). \tag{2-14}$$

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Now, the proper self-energy, $\Sigma(z, \mathbf{k}, a)$, is introduced. By definition,

$$\Sigma(z, \mathbf{k}, a) = \langle a\mathbf{k} \mid \{H' + H' \frac{1}{z - H_0} H + \ldots\}' \mid a\mathbf{k}). \qquad (2\text{-}15)$$

Then, Eq. (2-14) can be written as

$$G(z, \mathbf{k}, a) = \frac{1}{z - \varepsilon_{ak}} + \frac{1}{z - \varepsilon_{ak}} \Sigma(z, \mathbf{k}, a) \ G(z, \mathbf{k}, a)$$

or

$$G(z, \mathbf{k}, a) \equiv (a\mathbf{k} \mid G(z) \mid a\mathbf{k}) = \frac{1}{z - \varepsilon_{ak} - \Sigma(z, \mathbf{k}, a)} \qquad (2\text{-}16)$$

We first observe that $(a'\mathbf{k}' \mid G(z) \mid a\mathbf{k})$ has a pole at $z = E_{ak}$, where $E_{,,}$ is the pole of $G(z, \mathbf{k}, a)$, i.e., it satisfies

$$E_{ak} - \varepsilon_{ak} - \Sigma(z, \mathbf{k}, a) = 0. \qquad (2\text{-}17)$$

We can now construct the state vector

$$\mid 1, a\mathbf{k}) = C \lim_{z \to E_{ak}} (z - E_{ak}) \ G(z) \mid a\mathbf{k}), \qquad (2\text{-}18)$$

where C is a normalization constant. Taking the identity

$$E_{ak} - H = (z - H) + (E_{ak} - z), \qquad (2\text{-}19)$$

and applying it to $C(z - \varepsilon_{ak}) G(z) \mid a\mathbf{k})$, we obtain

$$(E_{ak} - H) \ C(z - E_{ak}) \ G(z) \mid a\mathbf{k}\rangle$$

$$= C(z - H)(z - E_{ak}) \frac{1}{z - H} \mid a\mathbf{k}\rangle - C(z - E_{ak})^2 \ G(z) \mid a\mathbf{k}\rangle. \qquad (2\text{-}20)$$

In the limit $z \to E_{ak}$, both terms, on the right-hand side of Eq. (2-20), vanish and we are left with

$$(H - E_{ak}) \mid 1, a\mathbf{k}) = 0. \qquad (2\text{-}21)$$

This means that the state constructed through (2-18) is an eigenstate of H belonging to the eigenvalue E_{ak} (which is a pole of $G(z, \mathbf{k}, a)$.

Now, the simplest and most important information contained in the Greenian operator is the density of states. This last quantity is of fundamental interest in band theory and can be defined through the following staternent: "The density of state functions is such that $\rho(E) \, dE$ is the number of states, per volume Ω of the material (for each direction of the electron spin), with energies between E and E $+ dE$".

As is well known in band theory, once the band structure $\varepsilon_n(\mathbf{k})$ is known, the formula,

$$\rho(E) = \frac{\Omega}{(2\pi)^3} \int \frac{dS}{|\nabla_{\mathbf{k}} E|}, \qquad (2\text{-}22)$$

gives the density of states (the integral goes over the surface of constant energy $E = \varepsilon_n(\mathbf{k})$). Since

$$\text{Tr } G(z) = \sum_{a,\mathbf{k}} (\mathbf{ak} \,|\, G(z) \,|\, \mathbf{ak}) = \sum_{a,\mathbf{k}} (z - \varepsilon_{ak} - (\mathbf{ak} \,|\, \mathbf{H'} \,|\, ak \rangle)^{-1}, \qquad (2\text{-}23)$$

then, for a given band, defined by the quantum number **a**, we have

$$-\frac{1}{\pi} \text{ Im Tr } G(z = E + i0) = \sum_{\mathbf{k}} \delta(E - \varepsilon_{ak}). \qquad (2\text{-}24)$$

Using the usual prescription $\sum_{\mathbf{k}} \rightarrow \frac{R}{(2\pi)^3}$ and the fact that

$$d^3k = dS \frac{dE}{|\nabla_{\mathbf{k}} E|},$$

it follows that

$$-\frac{1}{\pi} \text{ Im Tr } G(z = E + i0) = \frac{\Omega}{(2\pi)^3} \iint dS \frac{dE}{|\nabla_{\mathbf{k}} E|} \delta(E - \varepsilon_{ak})$$

$$= \frac{\Omega}{(2\pi)^3} \int \frac{dS}{|\nabla_{\mathbf{k}} \varepsilon_{ak}|}, \qquad (2\text{-}25)$$

which is precisely $\rho(E)$ as given by Eq. (2-22).

3. Analytical Properties of the Resolvent and Self-Energy Operators. The Ensemble Average[10]

In Section 2, $G(z)$ has been defined. Here its analytical properties are determined in order that its spectral representation and that for the self-
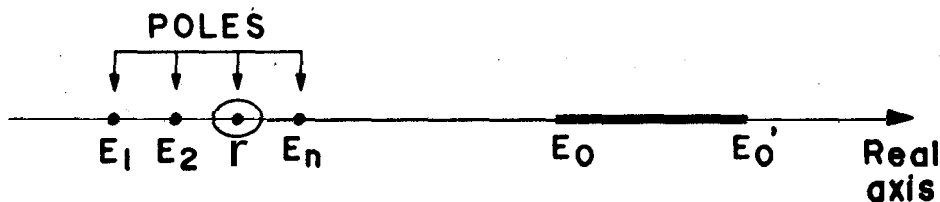

Fig. 1 — Singularities of $G(z)$ in the complex z-plane.

energy can be derived. The discussion is also important in the sense that one can observe what happens when a discrete spectrum is approximated by a continuous one.

As is well known, the spectrum of H has, in general, a discrete and a continuous part. The discrete points correspond to poles of $G(z)$ and the continuous part to a branch cut extending from E_0 to E_0', in the case of a bounded spectrum. Eventually, E_0' can go to infinity. In order to obtain this, let $E_,$, $E_,$, ... $E_,$, ... be the discrete eigenvalues of H, and E the continuous eigenvalues. Introducing the projector operators P_i and $P(E)$ such that

$$HP_i = E_i P_i, \quad HP(E) = EP(E), \tag{3-1}$$

and remembering that

$$\sum_i P_i + \int_{E_0}^{E_0'} dE \frac{dP(E)}{dE} = 1, \tag{3-2}$$

it follows that

$$G(z)P_i = \frac{P_i}{z - E_i}, \quad G(z)P(E) = \frac{P(E)}{z - E}. \tag{3-3}$$

Then

$$\sum_i G(z)P_i = \sum_i \frac{P_i}{z - E_i}, \quad \int_{E_0}^{E_0'} dE \frac{dP(E)}{dE} G(z) = \int_{E_0}^{E_0'} \frac{dE \frac{dP(E)}{dE}}{z - E}, \tag{3-4}$$

and, from Eq. (3-2), one obtains

$$G(z) = \sum_i \frac{P_i}{z - E_i} + \int_{E_0}^{E_0'} \frac{dE\, P'(E)}{z - E} \tag{3-5}$$

Thus, each discret eigenvalue $E_,$ of H is a simple pole of $G(z)$, whose residue is the projector P_i, i.e,

$$P_i' = \frac{1}{2\pi i} \oint_{\Gamma_i} G(z)dz, \tag{3-6}$$

where Γ_i is a closed contour in the complex plane including E_i and excluding all the other singularities of $G(z)$. Since H is an Hermitian operator and $G(z)$ is real for real z not on the cut, one has

$$\bar{G}(z) = G(\bar{z}). \tag{3-7}$$

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On the other hand, in order to unaerstand the meaning of the integral in Eq. (3-5), it is assumed that H has only a continuous spectrum. Using the fact that $G(z)$ satisfies Eq. *(3-7)*, one obtains

$$G(z) = \frac{1}{2\pi i} \int_C \frac{G(z')dz'}{z' - z},\qquad(3\text{-}8)$$

for z outside the real axis and using the countour of Fig.2. Eq. (A-5) allows us to write

$$G(z) = \frac{1}{\pi} \int_{E_0}^{E_0'} \frac{\text{Im } G(E' + i0)dE'}{E' - z}\qquad(3\text{-}9)$$

From the comparison between the integral part of Eq. (3-5)and Eq. *(3-9)*, it follows that

$$\frac{dP}{dE} = -\frac{1}{\pi} \text{ Im } G(E + i0).\qquad(3\text{-}10)$$

*Eq. (3-10)*shows that dP/dE is the boundary value of the imaginary part of the "Greenian function" $G(z)$ as z tends to the real axis from above.

The analytical properties of $\Sigma(z, k, a)$ are more involved. From Eq. (2-15), we can write

$$\overline{\Sigma}(z, \mathbf{k}, a) = \overline{\Sigma}(\overline{z}, \mathbf{k}, a),\qquad(3\text{-}11)$$

where Eq. (3-7) has been used. The analytical properties of Σ are then determined by the properties of $G_0(z)$. When a continuous'spectrum is used, we may write a dispersion relation for $\Sigma(z, k, a)$. It is only necessary to remember that, due to Eq. (2-15), there is always a real constant part in $\Sigma(z, k, a)$.

Once $G(z)$ is known, the density of states can be calculated using the formula

$$\rho(E) = -\frac{1}{\pi} \text{ Im Tr } G(z = E + i0).\qquad(3\text{-}12)$$

But, as

$$(ak|G(z)|ak) = (ak|(z - H_0 - H')^{-1}|ak) \equiv (ak|(z - H_0 - \Sigma(z))^{-1}|ak),\qquad(3\text{-}13)$$

an electron in a system having the diagonal Hamiltonian $H_0 + \Sigma(z)$ has the same density of states as one in the system whose Hamiltonian is is $H_0 + H'$. However, $\Sigma(z)$ is, in general, a complex function of z,

$$\Sigma(z, k, a) = \text{Re } \Sigma(z, k, a) + i \text{ Im } \Sigma(z, k, a)\qquad(3\text{-}14)$$

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and, for a band a, Eq. (3-12) can be written as

$$\rho(E,a) = -\frac{1}{\pi}\sum_{\mathbf{k}}\frac{\operatorname{Im} C\,(E,\mathbf{k},a)}{[E-\varepsilon_{a\mathbf{k}}-\operatorname{Re}\Sigma(E,\mathbf{k},a)]^2 + \left[\operatorname{Im}\Sigma(z,\mathbf{k},a)\right]^2}, \quad (3\text{-}15)$$

which seems to imply that $\rho = 0$ when Im C $= 0$, but this is not true. Indeed, as in this case

$$\Sigma(z,\mathbf{k},a) = \operatorname{Re}\Sigma\,(z,\mathbf{k},a), \qquad (3\text{-}16)$$

Eq. (3-12) gives

$$\rho(E) = \int \frac{dS}{|\nabla_{\mathbf{k}}E|}, \qquad (3\text{-}17)$$

where the integral is performed on the surface of constant energy

$$E = \varepsilon_{a\mathbf{k}} + \operatorname{Re} C(z,\mathbf{k},a). \qquad (3\text{-}18)$$

We come now to a very important point. The alloy has been considered as a periodic lattice containing N equivalent sites occupied in a random way by two kinds of constituents, A and B, with concentrations m~ and m ~ These conditions define a whole ensemble of possible arrays. Without knowing the configuration resulting from the process of alloy formation, we transfer our attention to the physical characteristics of the alloy averaged over the ensemble of all possible configurations. The averaged quantities are denoted by a bracket. Then, $\langle G(z)\rangle$ means the ensemble average of the resolvent operator.

$\langle G(z)\rangle$, Ref. 11, determines all interesting macroscopic quantities. It obviously has the full symmetry of the empty lattice, while G has not. An effective Hamiltonian characterizing'the average crystal can then be defined as

$$\langle G(z)\rangle = (z - \tilde{H})^{-1}, \qquad (3\text{-}19)$$

where $\tilde{H}$, like $\langle G(z)\rangle$, has the full symmetry of the empty lattice and is non-Hermitian and energy dependent. Obviously, $\tilde{H}$ is diagonal in the Bloch representation.

An equation for $\tilde{H}$ (z) can be easily derived taking the ensemble average of Eq. (2-16) and remembering that

$$\Sigma(z,\mathbf{k},a) = (a\mathbf{k}\,|H'|a\mathbf{k}) + \sum_{\substack{\mathbf{k}'\neq\mathbf{k}\\a'=a}}(a\mathbf{k}\,|\mathrm{H}|a'\mathbf{k}')G_0(z,\mathbf{k},a)\langle a'\mathbf{k}'|\mathrm{H}|a\mathbf{k}\rangle + \dots,$$

it follows that

$$\langle a'\mathbf{k}'| \tilde{H} |a\mathbf{k}\rangle = \delta_{aa'}\delta_{\mathbf{kk}'} \ \tilde{H}(z, \mathrm{k}, \mathrm{a}), \tag{3-20}$$

where

$$\tilde{H}(z, \mathrm{k}, \mathrm{a}) = \langle\!\langle a\mathbf{k} | H_0 | a\mathbf{k} \rangle\!\rangle + \langle\!\langle a\mathbf{k} | \mathrm{H'}] a\mathbf{k} \rangle\!\rangle$$

$$+ \sum_{\substack{\mathbf{k}' \neq \mathbf{k} \\ a' \neq a}} \langle\!\langle a\mathbf{k} | \mathrm{H'} | \mathrm{a'k'}) \ (\mathrm{a'k'} \ | \mathrm{H'} | a\mathbf{k} \rangle\!\rangle \ \frac{1}{z - \varepsilon_{a'\mathbf{k}'}} + \dots \tag{3-21}$$

or, equivalently,

$$\tilde{H}(z, \mathrm{k}, a) = \varepsilon_{a\mathbf{k}} + \tilde{\Sigma} \ (z, \mathbf{k}, a), \tag{3-22}$$

with

$$\tilde{\Sigma}(z, \mathrm{k}, \mathrm{a}) \equiv \langle \Sigma(z, \mathbf{k}, \mathrm{a}) \rangle. \tag{3-23}$$

The explicit calculation of the ensemble average depends on the model used. All that can be said, at this point, is that normally it is a very difficult task. In the next Section, it is shown how the ensemble averaging procedure can be avoided by imposing self-consistent requirements in the theory.

4. Choice of the Hamiltonian and the Coherent Potential Approximation[12]

Up to this goint, H_0 and H' have been left unspecified in the calculations. Let us now study what conditions H_0 and H' must satisfy in order to have a reasonable theory for a disordered alloy.

In view of the results of Section 2 [Eq. (3-13)], the density of states can be written as

$$\rho(E) = \sum_{a, \mathbf{k}} \delta(E - \varepsilon_{a\mathbf{k}} - \langle a\mathbf{k} | H' | a\mathbf{k} \rangle), \tag{4-1}$$

for a given configuration of the alloy, which shows explicitly the fundamental role played the diagonal matrix elements of the operator H'. If, for example,

$$(\mathrm{ak} \ | \mathrm{H'} | \mathrm{ak}) = 0, \tag{4-2}$$

then the density of states vanishes outside the band defined by H_0. Clearly, perturbation theory tells that there is a shift in the energy bands of H_0, but this does nothing to $\rho(E)$. Thus, if Eq. (4-2) holds, one has a

theory like the rigid band model of Jones and Mott (remember that, by construction, all properties due to alloying are contained in H').

Now it is shown that, if H_0 is chosen as the Virtual Crystal Hamiltonian, then condition *(4-2)* is satisfied. Indeed, if

$$H_0 = \frac{\mathbf{p}^2}{2m} + V,,$$

(4-3)

with

$$V_c = m_A V_A(\mathbf{r}) + m_B V_B(\mathbf{r}),$$

(4-4)

is the virtual or average potential, then

$$H' = \sum_\alpha \{V^\alpha(\mathbf{r} - \mathbf{R}_\alpha) - m_A V_A^{(a)}(\mathbf{r} - \mathbf{R}_\alpha) - m_B V_B^{(a)}(\mathbf{r} - \mathbf{R}_\alpha)\},$$

(4-5)

where $V^a(r - R,)$ is the real potential centered in the lattice point defined by $R,$ and can be $V_A^{(a)}$ or $V_B^{(a)}$, depending on the type of atom existing in $R,$. With this choice for H_0, then $\{|ak))\} = \{|nk))\}$, where $|nk)$ is an eigenstate of H_0 with energy ε_{nk}, i.e.

$$H_0 |n\mathbf{k}\rangle = \varepsilon_{nk} |n\mathbf{k}\rangle,$$

(4-6)

n being the band index and k a vector in the first Brillouin zone. The state $|nk)$ satisfies the Bloch condition and the corresponding wave function can be written as

$$\langle \mathbf{r} | n\mathbf{k}\rangle = \frac{1}{\sqrt{N}} u_{nk}(\mathbf{r}) e^{ik \cdot \mathbf{r}},$$

(4-7)

where $u_{nk}(\mathbf{r})$ has the periodicity of the lattice. The matrix elements of $(nk|H'|n'k')$ can now be determined. We have

$$(n\mathbf{k}|H'|n'\mathbf{k}'\rangle = \frac{1}{N}\int_\Omega u_{nk}^*(\mathbf{r}) e^{-ik \cdot \mathbf{r}} \sum_a \{V^\alpha(\mathbf{r} - R,) - [m_A V_A^{(a)}(\mathbf{r} - R,)$$

$$+ m_B V_B^{(a)}(\mathbf{r} - R,)]) u_{n'k'}(\mathbf{r}) e^{ik' \cdot \mathbf{r}'} \, d\mathbf{r}$$

$$= (m_B/N)\sum_a \exp[-i(k - k')\mathbf{R}_a]V_{kk'}^{nn'} -$$

$$- (m_A/N)\sum_b \exp[-i(k - k').R,]V_{kk'}^{nn'},$$

(4-8)

where

$$V_{kk'}^{nn'} = \int_\Omega e^{-i(k-k') \cdot \mathbf{r}} u_{nk}^*(\mathbf{r})[V_A^{(a)}(\mathbf{r}) - V_B^{(a)}(\mathbf{r})] u_{n'k'}(\mathbf{r}) \, d\mathbf{r}.$$

(4-9)

Remembering that

$$\sum_a \exp\left[-i(\mathbf{k}-\mathbf{k}').\mathbf{R}_a\right] + \sum_b \exp\left[i(\mathbf{k}-\mathbf{k}').\mathbf{R}_b\right] = \delta_{\mathbf{k}-\mathbf{k}',0}, \qquad (4\text{-}10)$$

then $(nk \mid H' \mid n'k')$ is zero for $|n\mathbf{k}\rangle = |n'k')$ and equals

$$NV^{nn'}_{\mathbf{k}\mathbf{k}'} \sum_a \exp\left[-i(\mathbf{k}-\mathbf{k}').\mathbf{R}_a\right] = -NV^{nn'}_{\mathbf{k}\mathbf{k}'} \sum_b \exp\left[-i(\mathbf{k}-\mathbf{k}').\mathbf{R}_b\right]. \quad (4\text{-}11)$$

This last equation shows that if H, is chosen as the Virtual Crystal Hamiltonian, then $\rho(E)$ vanishes outside the band defined by H,. But this is valid for any alloy configuration; thus, it must be true for $\langle\rho(E)\rangle$, the ensemble average of $\rho(E)$, a result which has some non trivial consequences. For example, in general if $(ak \mid H' \mid ak) = 0$, then

$$\text{Im } \Sigma(z, k, a) = 0. \qquad (4\text{-}12)$$

This can be easily obtained if we consider the series expansion of $\Sigma(z, k, a)$ (Eq. (2-15)).

Due to Eqs. (4-1) and (3-18), the following equality must hold:

$$\sum_{a,\mathbf{k}} \delta(E - \varepsilon_{ak}) = \sum_{a,\mathbf{k}} \delta(E - \varepsilon_{ak} - \text{Re } \Sigma(E, \mathbf{k}, a)), \qquad (4\text{-}13)$$

or, equivalently,

$$\sum_a \int \frac{dS}{|\nabla_{\mathbf{k}}E|} = \sum_a \int \frac{dS}{|\nabla_{\mathbf{k}}[E - \text{Re } \Sigma(E, \mathbf{k}, a)]|}, \qquad (4\text{-}14)$$

which means that

$$\nabla_{\mathbf{k}} \text{ Re } \Sigma(E, \mathbf{k}, a) = 0 \qquad (4\text{-}15)$$

and the self-energy operator is k — independent.

The above results, obtained by choosing H_0 as the Virtual 'Crystal Hamiltonian, are very important for the following reasons: (i) Since $\rho(E)$ vanishes outside the band'defined by H_0, it is not correct to use, for $\langle\rho(E)\rangle$, the formula

with
$$\langle\rho(E, n)\rangle = (4\pi^3 V)^{-1} \int \frac{dS}{|\nabla_{\mathbf{k}}E|},$$

$$E = \varepsilon_{nk} + \sum_{n'k'} \frac{\langle |(nk \mid H' \mid n'k') |^2\rangle}{\varepsilon_{nk} - \varepsilon_{n'k'}}, \qquad (4\text{-}16)$$

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as done in Stern's paper[13]. (ii) The main reason for using the self-energy operator (Dyson equation) is that it produces reasonable approximations when finite order perturbation theory is inadequate and this is precisely the case we are studying. The resolvent method has put us on the right direction.

We have shown that the density of states, obtained with H_0 as the Virtual Crystal Hamiltonian, is the same as the density of states obtained with H, $+ H'$. This is a surprising result, because all effects of alloying are contained in H', the nonperiodic part of the Hamiltonian. So, if non trivial results for the average density of states are to be obtained, then H_0 has to be different from the Virtual Crystal Hamiltonian.

In the work of Yonezawa and Matsubara[14], H_0 is chosen as

$$H_0 = \frac{p^2}{2m} + \sum_n V_A^{(a)} (r - R_n),\qquad(4\text{-}17)$$

where the sum is taken over all lattice sites. On the other hand, the perturbation caused by the potential $V_B^{(a)} (r - R_n)$, of the B constituents of the alloy, is

$$H' = \sum_{\{l\}} \left[V_B^{(a)} (r - R_l) - V_A^{(a)} (k - R,) \right] \equiv \sum_{\{l\}} V(r - R_l),\qquad(4\text{-}18)$$

where the notation $\{l\}$ means that the sum goes only over the lattice sites occupied 'by the B constituents.

In this case $(nk \,|\, H' \,|\, nk) \neq 0$ and non trivial results are obtained. Using the methods outlined in Section 2, the ensemble average of the Greenian operator is written as

$$\langle\!\langle nk \,|\, G(z) \,|\, n'k'\rangle\!\rangle = G_0^n (z, k)\, \delta_{nn'} \delta_{kk'} + G_0^n(z,k) M_1(k - k') V_{kk'}^{nn'} G_0^{n'}(z,k') +$$

$$+ G_0^n(z,k) \sum_{n'',k''} M_2(k - k'', k - k'' - k')\, V_{kk''}^{nn''} G_0^{n'}(z,k'')\, V_{k''k'}^{n''n'} G_0^{n'}(z,k) + \ldots,$$

$$(4\text{-}19)$$

where

$$V_{kk'}^{nn'} = \int_R u_{nk}^*(r) V(r)\, u_{n'k'}(r)\, \exp\left(- i(k - k'). r\right)\, dr,\qquad(4\text{-}20)$$

and the moments M_i are defined as

$$M_s(p_1 \ldots p_s) = \left\langle \sum_{\{l_1\}} \ldots \sum_{\{l_s\}} \exp\left(- i \sum_j p_j . R_{l_j}\right) \right\rangle.\qquad(4\text{-}21)$$

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They are calculated replacing the sum over impurity sites by one over all lattices points, multiplied by the concentration of the impurity atoms, i.e.,

$$\sum_{\{l\}} \rightarrow m_B \sum_n .$$

This is equivalent to assume a random distribution of impurities. The authors solved Eq. (4-19) introducing the cumulant average procedure of **Kubo**[15]. Then they developed a perturbative treatment for the self-energy operator by summing selected classes of **Feynman**-like diagrams.

It is, however, interesting to avoid the ensemble average procedure. This can be done as follows. The Virtual Crystal Hamiltonian H_0 is replaced by $H_0 + W$, where W should be self-consistently determined and the starting approximation, for the configurationally averaged alloy Greenian operator, should be chosen in such a way that, to a desired order in the approximation, the perturbative corrections vanish, i.e., the pertubation is referred to the self-determined effective alloy medium. Let us show how W can be chosen through a t-matrix formulation[16].

Let $\bar{G}_0$ be the Green function for a lattice of potentials $V_0 = V_{virtual} + W$. In this case,

$$\bar{G}_0 = G_0 + G_0 \left[\sum_\alpha V_0 (\mathbf{r} - \mathbf{R}_\alpha)\right] G_0, \qquad (4\text{-}22)$$

where G_0 is the free particle propagator. $\bar{G}_0$ determines the propagation through the not yet determined medium. Relative to it, the actual system consists of perturbing potentials $V_A - V_0$ and $V_B - V_0$; V denotes either V_A or V_B. The t-matrix describing the scattering of an electron propagating according to $\bar{G}_0$, when it reaches the perturbing potential $V_i - V_0$, is given by

$$t_i = (V_i - V_0) + (V_i - V_0) \bar{G}_0 t_i. \qquad (4\text{-}23)$$

For the alloy's Green function G, one can write

$$G = \bar{G}_0 + \sum_\alpha \bar{G}_0 t_\alpha \bar{G}_0 + \sum_\alpha \sum_{\beta \neq \alpha} \bar{G}_0 t_\alpha t_\beta \bar{G}_0 + \dots . \qquad (4\text{-}24)$$

Now, if V_0 is defined requiring that on the average there is no further scattering from the perturbing potentials, i.e.

$$m_A t_A + m_B t_B = 0, \qquad (4\text{-}25)$$

then, the average of bq. (4-24) is given by

$$\langle G \rangle = \bar{G}_0 + \sum_\alpha \sum_{\beta \neq \alpha} \sum_{\gamma \neq \beta} \sum_{\sigma \neq \gamma} \langle \bar{G}_0 \, t_\alpha \, \bar{G}_0 \, t_\beta \, \bar{G}_0 \, t_\gamma \, \bar{G}_0 \, t_\sigma \, \bar{G}_0 \rangle, \qquad (4\text{-}26)$$

which shows that the first correction to $\bar{G}_0$ is consequently of the fourth order in the t-matrix. The corresponding. equation for V_0 is obtained inserting Eq. (4-25) into Eq. (4-23):

$$V_0 = V_{virtual} - (V_A - V_0) \, \bar{G}_0 \, (V_B - V_0). \qquad (4\text{-}27)$$

Finally, as the corrections to $\bar{G}_0$ are of fourth order in the t-matrix, one concludes that

$$\langle G \rangle \sim \bar{G}_0 \qquad (4\text{-}28)$$

which' is the Coherent Potential Approximation (C.P. A.).

S. Clusters and Localized States

In the preceeding section, we have seen how the various approximations differ in the way the ensemble average procedure is introduced into the theory.

Concerning now the problem of localized states, we know that they exist when a impurity is introduced in a perfect crystal. In disordered systems, we may expect localized states associated with the fluctuations of the potential from site to site. Their existence can be inferred from the arguments of Lifshitz, Kaue, Halperin and Lax, Zittartz and Longer, and particularly of Ziman in the context of classical percolation theory[17].

The methods presented in the preceeding sections, however, cannot take localized states into account. This is due to the fact[18] that the ensemble averaging procedure destroys all information about localized states, although such a state exists in every member of the ensemble. As $\langle G(z) \rangle$ has the full symmetry of the empty lattice then, in the averaged system, all points are equivalent and localized states cannot occur. In order to obtain them, in the translationally invariant averaged system, the symmetry must be broken. This can be done, for example, with the introduction of phenomenological short range order parameters, as done in the work of Pant and Joshi[19]. Another possibility is the introduction of an a *priori* fixed cluster in the system and considering the average only for the rest of the system.

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In the C. P. A., for example, the average is carried out in such a way that the effective potential experimented by an electron is the same on each site, i.e., the C. P. A. considers the response of an electron to the potential at a single site. A simple improvement in the method would be to consider the response of the electron to the potential of two sites. This, in turn, suggests the possibility of considering the response of the electron to a cluster of n constituents of fixed com' position and/or position, treating the rest of the material in an average way. This idea is the CPn approximation of Freed and Cohen[20]. This method defines a hierarchy of approximations containing the usual C. P. A. as its lowest order. We do not go into the details here but refer the reader to the bibliography. All we can say is that this and other methods[2'], developed to get beyond the C. P. A., suffer from enormous difficulties when practical calculations are performed.

Appendix: Dispersion Relations

Consider a function $h(z)$ which is analytic in the entire complex plane except for a cut along the real axis (from x_0 to x_1). It is assumed that $h(z)$ is real on the remaining part of the real axis and that $|h(z)|$ goes to zero faster than $1/z$ as $|z|$ goes to ∞.

For a point outside the real axis, one has

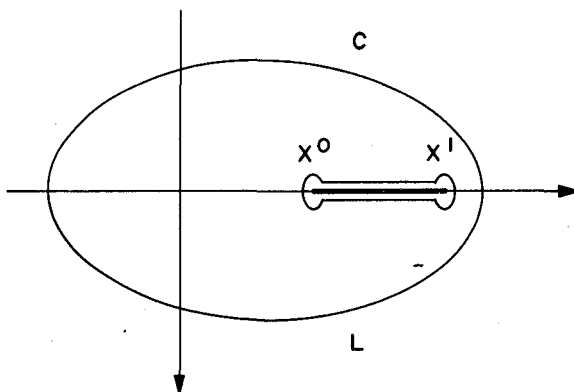$$h(z) = \frac{1}{2\pi i} \int_C \frac{h(z')}{z' - z} \, dz', \qquad (A\text{-}1)$$

Fig. 2 - Contour used to derive the dispersion relation.

where C is the contour shown in Fig. *2*. The contribution to Eq. *(A-1)*, from the large circle Γ, tends to zero as its radius tends to infinity. Then,

$$h(z) = \frac{1}{2\pi i} \left\{ \int_{x_0 + i\varepsilon}^{x_1 + i\varepsilon} \frac{h(z')}{z' - z} - \int_{x_0 - i\varepsilon}^{x_1 - i\varepsilon} \frac{h(z')}{z' - z} \right\}$$

$$= \frac{1}{2\pi i} \left\{ \int_{x_0}^{x_1} \frac{h(x' + i\varepsilon)}{x' - z + i\varepsilon} dx' - \int_{x_1}^{x_0} \frac{h(x' - is)}{x' - z - i\varepsilon} dx' \right\} \qquad (A\text{-}2)$$

as $\varepsilon \to 0$. The quantity $(\pm \, is)$ can be neglected in the denominators of Eq. *(A-2)* and, for z not on the real axis,

$$h(z) = \frac{1}{2\pi i} \int_{x_0}^{x_1} \lim_{\varepsilon \to 0_+} \frac{h(x' + i\varepsilon) - h(x' - i\varepsilon)}{x' - z} dx' \cdot \qquad (A\text{-}3)$$

The numerator of the integrand in Eq. *(A-3)* is the discontinuity of $h(z)$ across the cut and can be evaluated observing that $h(z)$ satisfies:

$$\bar{h}(z) = h(\bar{z}). \qquad (A\text{-}4)$$

Eq. *(A-4)* is a consequence of Schwarz reflection principle. Hence,

$$\lim_{\varepsilon \to 0_+} [h(x + i\varepsilon) - h(x - i\varepsilon)] = \lim_{\& - '0_+} [h(x + i\varepsilon) - \bar{h}(x + is)]$$

$$= \lim_{\varepsilon \to 0_+} 2i \ \text{Im} \ h(x + ie) = 2i \ \text{Im} \ h(x + i0) \qquad (A\text{-}5)$$

Inserting Eq. *(A-5)* into Eq. *(A-3)*, one obtains, in the limit when $\varepsilon \to 0_+$,

$$h(z) = \frac{1}{\pi} \int_{x_0}^{x_1} \frac{\text{Im} \ h(x' + i0)}{x' - z} dx'$$

$$= \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\text{Im} \ h(x' + i0)}{x' - z} dx' \qquad (A\text{-}6)$$

which is the dispersion relation satisfied by $h(z)$. Suppose now that there are two functions $h(z)$ and $f(z)$ satisfying

$$f(z) = c + h(z) \qquad (A\text{-}7)$$

where c is a real constant. Then, the dispersion relation for $f(z)$ becomes

$$f(z) = c + \frac{1}{\pi} \int_{-\infty}^{+\infty} \frac{\text{Im} f(x' + i0)}{x' - z} dx'. \qquad (A\text{-}8)$$

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