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**DETERMINATION OF EFFECTIVE PAIR INTERACTIONS IN RANDOM ALLOYS  
BY CONFIGURATIONAL AVERAGING**

by

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**ABSTRACT**

A real-space method is presented for calculating effective pair interactions (EPI) in substitutionally disordered alloys, starting from electronic structure information for the constituting elements. The EPI are obtained by averaging over a small number of randomly generated configurations. The electronic structure is calculated by tridiagonalizing a tight-binding (TB) Hamiltonian using the recursion method. Convergence, both as a function of the number of configurations and the number of recursion levels, is rapid and the results compare very well with other calculations. The advantage of the present scheme is that deviations from lattice periodicity can be taken into account in a completely straightforward way. The EPI are essential ingredients in statistical methods for determining alloy phase diagrams.

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## I. Introduction.

The electronic structure is the driving force behind a large variety of physical and chemical properties of solids<sup>1</sup>. The phase formation and stability of substitutionally disordered solid solutions are examples of such properties and it is their determination which is the object of the present work<sup>2</sup>. The most successful statistical models depend on the availability of reliable approximate expressions for the configurational energy and entropy. These are most conveniently formulated in terms of effective pair (and, if necessary, larger cluster) interactions. Such interactions can in principle be measured experimentally through diffuse intensities in neutron and X-ray scattering<sup>3</sup>. Several phenomenological approaches have been proposed in the past as well<sup>4</sup>. However, in keeping with a general trend in recent years, the possibility of a first-principles calculation of EPI has received increasing attention by various groups. Several schemes have been developed and investigated. One possibility is to start from density-functional total-energy calculations for the perfectly ordered compounds<sup>5-6</sup>. Alternatively, one can perturb the completely disordered alloy in several ways : by imposing a concentration wave<sup>7</sup>, by means of the generalized perturbation method<sup>8</sup> or using embedded clusters<sup>9-10</sup>. All of these methods have closely related free energy expansions<sup>11</sup>. The electronic structure of the disordered compound is most frequently determined within the coherent potential approximation (CPA)<sup>12</sup>. The CPA is a mean-field theory for the completely random alloy and has been shown to be optimal within the single-site approximation. It has been applied very successfully to a wide variety of disordered metallic alloys. However, attempts to go beyond the single-site approximation suffer from severe analyticity problems. Thus the inclusion of short- or long-range order in the CPA framework is by no means straightforward.

In the CPA an effective medium is constructed through a self-consistency requirement on the scattering operators and the electronic properties are calculated, either by tight-binding or multiple scattering (KKR) techniques. More generally, any alloy electronic structure calculation involves these two steps : 'averaging' and band structure determination. In

the present work, it is proposed to interchange these steps. That is, one first determines the electronic structure for a randomly generated configuration (the only constraint being a fixed concentration) and the resulting physical quantities are averaged over a sufficiently large number of independent configurations. This procedure can be implemented very efficiently using the recursion method<sup>13</sup> applied to a tight-binding Hamiltonian as will be discussed below. Certainly the idea of configurational averaging is not new<sup>14</sup> and everything depends on the rate of convergence with respect to the number of configurations needed. Earlier work focused mostly on densities of states (DOS), for which it was concluded that it was necessary to perform an exact average over the first shell of neighbors in the fcc lattice<sup>15</sup>. Since this involved 144 inequivalent configurations, the method was very time consuming and has not been widely used, although the agreement with the CPA was satisfactory as well as the extension to partially ordered systems<sup>16</sup>. Moreover, for the bcc lattice the scheme could become intractable, since it is very likely that exact averages would need to be performed over the first and second shell, because the bcc structure does not contain any triangles entirely confined to nearest neighbors in the the first shell.

It will be shown in this work that it is not necessary to enumerate all possible occupancies of the first shell to obtain accurate EPI, but that a rather small number of configurations, say 10, is sufficient. The reason for this faster convergence, compared to DOS, is that the EPI are essentially integrated quantities, i.e. total energy differences of different pairs in the alloy, and therefore they are less sensitive to local perturbations that conserve the total number of electrons. An attractive feature of the recursion method is that it is not necessary to calculate individual cohesive energies for the different pairs, which would lead to a large subtractive cancellation of terms. Rather, it is possible to compute these quantities directly in the recursion formalism and in this way avoid numerical instabilities.

The feasibility of this new approach has already been illustrated in a previous short paper<sup>17</sup> for canonical tight-binding parameters and d-bands only. In the present work

the underlying formalism is worked out in more detail and the treatment is extended to include s- and p-orbitals. In a first group of calculations arbitrary, but realistic, tight-binding parameters were selected for an alloy  $A_cB_{1-c}$  in which the number of d-electrons  $N_A$  ( $N_B$ ) was equal to 3 (8). These values will henceforth be called 'canonical', a term which should not be confused with that used in the context of calculations involving d-bands only<sup>17</sup>. In a second group of calculations first-principles parameters appropriate for the binary system  $Rh_cTi_{1-c}$  were used. The remainder of this paper is organized as follows. Section II sets out the background and theoretical aspects of the present approach and discusses some numerical details. Section III is devoted to a discussion of the results for the canonical 3-8 system and the binary alloy  $Rh_cTi_{1-c}$ . EPI obtained by the present method are presented and the convergence as a function of the number of levels and the number of configurations is analyzed. As a first step towards a phase diagram calculation, heats of mixing for the different phases in  $Rh_cTi_{1-c}$  are computed. The paper concludes with a summary and some comments in Sec. IV.

## II. Formalism.

A given configuration  $\sigma$  of the binary system can be described by the following tight-binding Hamiltonian :

$$H(\sigma) = \sum_{n,\lambda} |n,\lambda\rangle \epsilon_n^\lambda \langle n,\lambda| + \sum_{n \neq m, \lambda, \mu} |n,\lambda\rangle \beta_{nm}^{\lambda\mu} \langle m,\mu|, \quad (2.1)$$

where  $n$  and  $m$  are lattice sites and  $\lambda$  and  $\mu$  label the orbitals ( $\lambda, \mu = 1, \dots, 9$  for s-, p- and d-orbitals). The on-site energies  $\epsilon_n^\lambda$  depend, strictly speaking, on the local environment in the disordered system, but one often makes the approximation to replace them by 'atomic' values  $\epsilon_n^A$  or  $\epsilon_n^B$  depending on whether site  $n$  is occupied by an A or a B atom (diagonal disorder). It will be seen, however, that such a simplification would lead to unphysical results in the present case. The hopping parameters  $\beta_{nm}^{\lambda\mu}$  are likewise restricted to three values  $\beta^{AA}$ ,  $\beta^{BB}$  or  $\beta^{AB}$ . In the Slater-Koster<sup>18</sup> parametrization scheme these are related to the three- and two-center integrals for the pure elements. Off-diagonal disorder is usually taken into account by



geometrically averaging the pure element hopping parameters<sup>19</sup> :

$$\beta^{AB} = \sqrt{\beta^{AA} \beta^{BB}}. \quad (2.2)$$

Several methods are available for obtaining tight-binding parameters for the pure elements. Canonical values (for d-bands only) have been used quite successfully to predict ordering tendencies and lead in some cases to remarkable agreement with experiment<sup>20,21</sup>. A semi-phenomenological set of parameters has been tabulated by Harrison<sup>22</sup>. Closer to a first-principles determination are the values obtained by Papaconstantopoulos<sup>23</sup> by a least squares fit to LAPW band structures. Potentially the most accurate first-principles results are those given directly by the TB-LMTO method of Andersen and co-workers<sup>24</sup>. In the first part of the present work, 'canonical' s-, p- and d-parameters appropriate for a 3-8 system are used, while in the second part the binary alloy  $\text{Rh}_c\text{Ti}_{1-c}$  was investigated with the parameters calculated by Papaconstantopoulos<sup>22</sup>. The latter system was studied previously using canonical d-band parameters<sup>21</sup>.

The recursion method<sup>13</sup> provides an algorithm for calculating diagonal matrix elements of the resolvent or Green's function, associated with the Hamiltonian (2.1) and defined as

$$G(z) = (z - H)^{-1}. \quad (2.3)$$

Given a starting state  $|u_0\rangle$  one generates a discrete chain of vectors  $|u_i\rangle$ , which can be constructed to be orthonormal, through the following set of operations :

$$b_0^2 = \langle u_0 | u_0 \rangle, \quad (2.4a)$$

$$a_i = \langle u_i | H | u_i \rangle, \quad (2.4b)$$

$$H | u_i \rangle = a_i | u_i \rangle + b_{i+1} | u_{i+1} \rangle + b_i | u_{i-1} \rangle. \quad (2.4c)$$

This prescription essentially transforms the Hamiltonian into (Hermitian) tridiagonal form and

thus leads directly to a continued fraction representation for the Green's function matrix element  $\langle u_o | G | u_o \rangle$ . If the algorithm is stopped after  $L$  steps,  $L$  exact levels of the continued fraction are obtained. This computational scheme is also closely related to the theory of orthogonal polynomials, a fact that can be exploited in the development of stable and efficient computer codes<sup>25</sup>. One of the attractive features of the recursion method is the fact that it allows for a direct physical interpretation, apart from its formal mathematical elegance. Indeed, it is clear from equations (2.4) that the matrix element after  $L$  levels contains the exact contributions from all closed paths of  $L$  steps starting and ending at the central orbital. Thus if one tries to model an infinitely extended system, the recursion algorithm after  $L$  steps contains contributions only from a central cluster consisting of  $O(L^3)$  atoms. For numerical purposes, this limits the number of atoms that can be modeled and also implies that one is always studying a finite system. In order to reduce the necessary amount of computer storage, it is possible to decouple the number of levels and the number of atoms in the cluster, a point that will be pursued in the next section. In either case, a terminating continued fraction is obtained, which yields a number of isolated bound states, appropriate for a finite cluster. For most purposes this is an unphysical approximation to the problem under investigation and some way needs to be found to eliminate finite size effects by embedding the cluster in an infinite medium. Mathematically, this means that a terminator must be appended to the continued fraction expansion, so as to obtain a Green's function with a branch cut, rather than a set of simple poles. The problem of finding a terminator that gives an optimal description of the surrounding medium has been studied in many papers (Ref. 26 and references therein) and several prescriptions are available. It has been established in our previous paper<sup>17</sup> that the EPI (for transition metal alloys) are not very sensitive to the exact nature of the terminator and therefore the simple quadratic terminator can be used with confidence. This amounts to putting all  $a_i, b_i$  with  $i > L$  equal to  $a_L, b_L$ , and approximates the density of states of the embedding medium with a semi-elliptical band.

Although most applications of the recursion method involve the determination of

the (local) density of states, any observable that can be related to the Green's function (2.3) can be calculated recursively<sup>27</sup>. In particular, the present work is aimed at the calculation of effective pair (and cluster) interactions in disordered alloys, quantities that are the main ingredients in statistical techniques such as the cluster variation and Monte Carlo method. In these treatments, averages are taken involving the density function  $\rho(\sigma)$ , which gives the probability of finding a specific configuration  $\sigma$  in an ensemble of systems. This function is given by :

$$\rho(\sigma) = Z^{-1} e^{-E(\sigma)/kT}, \quad (2.5)$$

where  $Z$  is the partition function :

$$Z = Tr^{(N)} e^{-E(\sigma)/kT}, \quad (2.6)$$

and the trace operator  $Tr^{(N)}$  denotes a sum over all configurations of a system with  $N$  sites. In the work of Sanchez *et al*<sup>28</sup> it has been shown that the state of order of an alloy can be expressed in terms of a complete set of orthogonal functions involving various clusters, used to approximate the configurational entropy. The function relative to cluster  $\alpha$  is defined as :

$$\Phi_{\alpha}(\sigma_{\alpha}) = \sigma_1 \sigma_2 \cdots \sigma_n, \quad (2.7)$$

where the  $\sigma_i$  are pseudo-spin variables (+ 1 if site  $i$  is occupied by an A atom, -1 otherwise). Any function of the alloy configurations can be expanded in terms of these functions; in particular the density function (2.5) can be written as :

$$\rho(\sigma) = 2^{-N} [1 + \sum_{\alpha} \Phi_{\alpha}(\sigma) \xi_{\alpha}] \quad (2.8)$$

where

$$\xi_{\alpha} = \langle \Phi_{\alpha}(\sigma) \rangle \quad (2.9)$$

is one of a hierarchy of linearly independent correlation functions. The internal energy of the

alloy system can be written as a functional of the density :

$$E[\rho] = Tr^{(N)}\rho(\sigma)E(\sigma), \quad (2.10)$$

or, after substitution of (2.8) :

$$E = \varepsilon_o + \sum_{\alpha} E_{\alpha} \xi_{\alpha}, \quad (2.11)$$

where

$$\varepsilon_o = 2^{-N} Tr^{(N)}E(\sigma) \quad (2.12)$$

is configuration independent, and

$$E_{\alpha} = 2^{-N} Tr^{(N)}\Phi_{\alpha}(\sigma)E(\sigma), \quad (2.13)$$

are the effective cluster interactions. For a pair of atoms, one at site  $p$  and one at site  $q$ , the trace in (2.13) can be broken up into two parts, one over the points  $p$  and  $q$ , and one over the remainder of the configuration, which leads to the final expression :

$$E_{pq} = \frac{1}{4}(V_{AA} - V_{AB} - V_{BA} + V_{BB}), \quad (2.14)$$

where  $V_{IJ}$  is the total energy of a pair  $I$  (at site  $p$ ),  $J$  (at site  $q$ ) embedded in the average medium at a given concentration, or explicitly :

$$V_{IJ} = 2^{2-N} Tr^{(N-2)}E(IJ;\sigma'), \quad (2.15)$$

where  $E(IJ;\sigma')$  is the energy of a configuration  $\sigma$  consisting of atom  $I$  ( $J$ ) at site  $p$  ( $q$ ), with the remaining sites denoted by  $\sigma'$ . It is known that the  $V_{IJ}$  are generally long-ranged and cannot be expressed in terms of pair potentials. In a similar fashion one can define triplet and higher order interactions, for example :

$$E_{pqr} = \frac{1}{8}(V_{AAA} - 3V_{AAB} + 3V_{ABB} - V_{BBB}), \quad (2.16)$$

in an obvious notation and assuming that all sites are equivalent. Typically these ordering energies converge quickly as a function of cluster size and interatomic distance, but the expressions (2.14) and (2.16) are not very useful for computer calculations, since one needs the difference of nearly equal large numbers. However, it turns out that the ‘orbital peeling trick’ developed by Burke<sup>29</sup>, following the work of Einstein and Schrieffer<sup>30</sup>, permits a direct calculation of the EPI, as will now be shown.

The total energy of a solid consists of two terms, a one-electron band structure contribution  $V_{bs}$  and an electrostatic term  $V_{es}$ , which includes the double counting correction and the ionic repulsion. It is usually assumed that upon taking differences like in (2.14) the electrostatic contributions cancel out and one is left with solely the one-electron band structure term<sup>31</sup>. Thus, what is needed to calculate the EPI is an average over all configurations  $\sigma$ , with fixed occupancy of sites  $p$  and  $q$ , of the one electron band structure term :

$$V(\sigma) = \int_{-\infty}^{E_F} E n(E, \sigma) dE, \quad (2.17)$$

where  $n(E, \sigma)$  is the electronic DOS and  $E_F$  is the Fermi-level, assumed to be independent of the configuration  $\sigma$ , a point that will be addressed further in this section.

At this point it is important to specify the choice of the basis set. Often in substitutional impurity problems one assumes a unique set of orbitals at each site and thus the impurity is described using the same orbitals as the atom that was removed (Ref. 32 and references therein). This may be a bad approximation, in particular if the two atomic species that are involved are very dissimilar. However, the adspace-subspace description developed by Williams *et al*<sup>33</sup> and extended by Riedinger<sup>34</sup> avoids this shortcoming and provides a more general setting for this type of studies. In an EPI calculation two atoms need to be embedded and therefore a basis set  $\Omega$  is defined as follows:

$$\Omega = \omega \cup A_p \cup A_q \cup B_p \cup B_q, \quad (2.18)$$

where  $\omega$  is the set of atomic orbitals describing the host (the recursion cluster except for the sites  $p$  and  $q$ ),  $A_p, A_q, (B_p, B_q)$  are sets of atomic orbitals for an  $A$  ( $B$ ) atom at site  $p$  resp.  $q$ . In this formalism the Hamiltonian for an  $A$  atom at site  $p$  and a  $B$  atom at site  $q$ , for example, would be written in block form as:

$$\mathbf{H}_{AB} = \begin{bmatrix} H_A^p & 0 & 0 & H_{AB} & H_{AO} \\ 0 & H_A^\infty & 0 & 0 & 0 \\ 0 & 0 & H_B^\infty & 0 & 0 \\ H_{BA} & 0 & 0 & H_B^q & H_{BO} \\ H_{OA} & 0 & 0 & H_{OB} & H_O \end{bmatrix} \quad (2.19)$$

where  $H_A^\infty$  and  $H_B^\infty$  are the Hamiltonians for the isolated atoms,  $H_A^p$  ( $H_B^q$ ) are the Hamiltonians describing the  $A$  ( $B$ ) atom at site  $p$  ( $q$ ),  $H_O$  is the Hamiltonian for the host and the other matrices couple the different subsystems. This representation is overcomplete, but this introduces no errors, since only one set of orbitals for each site is coupled to the host in each of the four cases needed in (2.14). The adspace-subspace description also eliminates the potential problems due to particle non-conservation: two atoms, namely those that are not coupled to the rest of the system, can be thought of as located at infinity. The physical system then consists of these two isolated atoms and the full recursion cluster. Thus the total number of atoms of each species is the same in all four cases in (2.14).

The process involved in an EPI calculation is the interchange of two atoms. Provided that the Hamiltonian is self-consistent, this will produce a perturbation of the order  $1/N$  on the Fermi-level, which is negligible for all practical purposes. The self-consistency procedure, which takes into account the charge transfer due to the perturbation, consists of a uniform shift of the diagonal elements of the Hamiltonian<sup>35</sup>:

$$\epsilon_n^\lambda = \epsilon_n^{\lambda,0} + \alpha_n^\lambda + \sum_\mu U_n^\mu N_n^\mu + \sum_m V_{nm}^\lambda N_m^\lambda, \quad (2.20)$$

where  $\epsilon_n^{\lambda,0}$  is the atomic energy level,  $\alpha_n^\lambda$  is the shift integral,  $N_n^\lambda$  is the total charge corresponding to orbital  $\lambda$  at site  $n$  and  $U_n^\lambda, V_{nm}^\lambda$  are the intra- and interatomic Coulomb

integrals. In the case of a disordered alloy studied here, one would *a priori* need to determine  $\epsilon_n^\lambda$  for each atom. This is clearly an impossible task. The crudest approximation is to consider only two different atomic levels  $\epsilon^A$  and  $\epsilon^B$ , independent of the atomic environment. As a first improvement on this scheme, one can allow for changes in the potential ( $\epsilon_n^\lambda$ ) only for the atoms at the sites  $p$  and  $q$ . In these two cases  $H_0$  does not depend on the nature of the atoms at positions  $p$  and  $q$ . A further refinement of this approach would be to include some potential perturbations on the atomic sites surrounding the atoms at  $p$  and  $q$ . In fact, as will be seen in the next section, it turns out that taking  $\epsilon_n^\lambda$  independent of the position  $n$  yields good results for the EPI, but is insufficient for the mixing energies. In the following, it will be assumed that the host Hamiltonian  $H_0$  is independent of the nature of the atoms at sites  $p$  and  $q$ .

The electronic DOS is related to the Green's function through the equality

$$n_{IJ}(E) = -\frac{1}{\pi} \text{Im Tr } G_{IJ} \equiv -\frac{1}{\pi} \text{Im Tr } (E - \mathbf{H}_{IJ})^{-1} \quad (2.21)$$

where  $\mathbf{H}_{IJ}$  is the Hamiltonian for the full system, of the form (2.19). It is well known that this can be written as

$$n_{IJ}(E) = \frac{1}{\pi} \text{Im } \frac{\partial}{\partial E} \ln \det (E - \mathbf{H}_{IJ}), \quad (2.22)$$

which will be the starting point for the numerical calculations. It is now obvious that the EPI can be written as :

$$E_{pq} = \frac{1}{4} \int_{-\infty}^{E_F} dz z \text{Im } \frac{d}{dz} \eta(z) \quad (2.23)$$

where  $\eta(z)$  is the generalized phase shift given by :

$$\eta(z) = \ln \frac{\det G_{AA} \det G_{BB}}{\det G_{AB} \det G_{BA}} \quad (2.24)$$

The Friedel sum rule, which expresses the conservation of the total number of electrons, can be written quite generally as :

$$\int_{-\infty}^{E_F} dz \operatorname{Im} \frac{d}{dz} \eta(z) = 0. \quad (2.25)$$

Now integrating by parts in (2.23) and using the Friedel rule one finally finds for the EPI :

$$E_{pq} = -\frac{1}{4\pi} \operatorname{Im} \int_{-\infty}^{E_F} \eta(z) dz. \quad (2.26)$$

It is obviously out of the question to calculate the full determinants in equation (2.22), since they are of the order  $N \times v$ , where  $N$  is the number of atoms in the cluster and  $v$  the number of orbitals per site. Since in the exchange of the atoms on sites  $p$  and  $q$  the perturbation is of finite range, the phase shift  $\eta(z)$  has a finite size, as can also be seen as follows. From the properties of a partitioned matrix it follows that<sup>29</sup> :

$$\det(E - \mathbf{H}_{IJ}) = \det G_{IJ}^{-1} \det(E - H_O), \quad (2.27)$$

where  $G_{IJ}$  is the  $4v \times 4v$  top left block of the matrix  $(E - \mathbf{H}_{IJ})^{-1}$ . Upon substitution of (2.27) in (2.24) one finds :

$$\eta(z) = \ln \frac{\det G_{AA} \det G_{BB}}{\det G_{AB} \det G_{BA}} \quad (2.28)$$

Thus it is not necessary to calculate the determinant of order  $(N - 4)v \det(E - H_O)$ , which otherwise would lead to an unacceptable increase in computer time.

All that remains is the calculation of the generalized phase shift (2.24) and this can be done very efficiently by means of the 'orbital peeling' scheme as will now be discussed. For short, denote by  $A$  any one of the four matrices  $(E - \mathbf{H}_{IJ})$ :



$$\mathbf{A} = \begin{bmatrix} a_{11} & a_{12} & \cdots & a_{1,M-1} & a_{1M} \\ a_{21} & a_{22} & & & \\ \vdots & \vdots & & & \\ a_{M-1,1} & a_{M-1,2} & & a_{M-1,M-1} & a_{M-1,M} \\ a_{M1} & a_{M2} & & a_{M,M-1} & a_{MM} \end{bmatrix} \begin{matrix} A_1 \\ A_2 \\ \vdots \\ A_{M-1} \\ A_M \end{matrix} \quad (2.29)$$

with  $M = Nv$  and 'principal' submatrices  $A_1, \dots, A_M$  have been indicated. For any  $1 \leq k \leq M$  one has, with  $D_k = \det A_k$ :

$$\frac{D_{k+1}}{D_k} = \bar{g}_k \quad (2.30)$$

where  $\bar{g}_k$  is the top left element of the inverse of  $A_k$ . From this it follows that :

$$\prod_{k=1}^M \bar{g}_k = \frac{1}{\det \mathbf{A}}. \quad (2.31)$$

Using these representations in (2.28) and keeping in mind that common factors cancel, one finds :

$$\eta(z) = \sum_{k=1}^{4v} \ln \frac{\bar{g}_k^{AA} \bar{g}_k^{BB}}{\bar{g}_k^{AB} \bar{g}_k^{BA}}. \quad (2.32)$$

Each  $\bar{g}_k^{IJ}$  is the top left element of a partial Green's matrix, with the designated atom at sites  $p$  and  $q$ . It can be seen that only diagonal elements of the Green's function are needed, but that each  $\bar{g}_k^{IJ}$  must be calculated separately for each of the  $4v$  cases : the  $4v$  orbitals are 'peeled off' one by one<sup>29</sup> and this can be readily included in the recursion framework<sup>25</sup>. In this method matrix elements  $\bar{g}_k$  are obtained, with every row and column of the Hamiltonian with an index  $i < k$  equal to zero.

It is important to note that only 4 atoms need to be 'peeled'. Obviously a cancellation of terms occurs from the matrices  $H_A^\infty$  and  $H_B^\infty$  since these are diagonal and not coupled to the system. Thus for each pair  $(I, J)$ , one has two atoms to peel, but it is possible to show that because of the symmetry in the definition of the EPI, for each pair  $(I, J)$  only one atom

needs to be 'peeled'. To this end one defines  $G(X-Y/i)$  as the term obtained by 'peeling' for a pair  $X-Y$  the orbitals for the  $X$  atom on site  $i$  where  $X$  and  $Y$  are  $A, B$  or a vacancy, denoted by  $V$  and  $i = 1, 2$  referring to site  $p$  and  $q$  respectively. The term  $\frac{\det G_{AA} \det G_{BB}}{\det G_{AB} \det G_{BA}}$

in the phase shift can then be written symbolically as :

$$\begin{aligned} & G(A-A/1) + G(V-A/2) + G(B-B/1) + G(V-B/2) \\ & - G(A-B/1) - G(V-B/2) - G(B-A/1) - G(V-A/2) \quad (2.33) \\ & = G(A-A/1) + G(B-B/1) - G(B-A/1) - G(A-B/1) \end{aligned}$$

Thus this quantity is computed by 'peeling' only on the atom at position 1 for each of the four possible configurations.

The choice of the Fermi level and the description of the Hamiltonian used pose delicate questions in the case of a disordered alloy. One cannot simply assume that the on-site energies depend only on the nature of the atoms in the disordered alloy and use the tight-binding parameters for the pure elements ( $\epsilon_A^s, \epsilon_A^p, \epsilon_A^{i2s}$  and  $\epsilon_A^e$ , and likewise for the  $B$  atoms), since coupling  $A$  and  $B$  will introduce changes in these energies. In the present work a rigid shift  $\delta$  of the pure compound values for one species, say  $B$ , will be assumed. That is, the values of the on-site energies for the  $A$ -atoms will be left unchanged from those of the pure element, while the  $B$ -values are taken to be  $\epsilon_B^s + \delta, \epsilon_B^p + \delta, \epsilon_B^{i2s} + \delta, \epsilon_B^e + \delta$ . Thus for a given concentration one has to determine this parameter  $\delta$  as well as the Fermi level  $E_F$ . Since a fully self-consistent calculation is not feasible for the disordered case, as discussed previously, these values have been calculated for the pure elements as well as the ordered structures ( $AB, A_3B$  and  $AB_3$ ) under the assumption of local charge neutrality. If, for a given structure, two or more atoms of a given type are present (like the two inequivalent  $B$  sites in the  $DO_3$  structure with composition  $AB_3$ ), an average is made. For other concentrations (in the disordered state)  $\delta$  and  $E_F$  are found by interpolating between the values for the pure compounds. In general, a linear variation of  $E_F$  and  $\delta$  with concentration is obtained, compa-

tible with a Taylor's expansion truncated after the second term.

For the calculation of EPI this scheme gives satisfactory results. Mixing energies, however, are differences of integrated quantities and it turns out that this approach needs to be refined. The mixing energy for the completely disordered state, for example, is given by :

$$\Delta E_m^{dis}(c) = c \left\langle \int_{-\infty}^{E_F} E n^A(E) dE \right\rangle + (1 - c) \left\langle \int_{-\infty}^{E_F} E n^B(E) dE \right\rangle - (1 - c)E_A - cE_B, \quad (2.34)$$

where  $E_A$  and  $E_B$  are the cohesive energies of the pure elements. The first two terms in this expression are computed by means of configurational averaging in a manner completely similar to the EPI. That is, the one-electron band structure term is calculated, with a given site first occupied by an  $A$  atom and then by a  $B$  atom. It turns out that a simple rigid shift of the on-site energies gives insufficient accuracy as far as mixing energies are concerned. A first improvement is to allow for a shift of the Fermi level on the central atom, so as to satisfy some property, for example, since charge transfer is small in metallic systems, one can impose local neutrality. This approach can be understood by the following argument : the small shift of the Fermi level arises because of the replacement of an atom<sup>30</sup>. In such a case no perturbing potential exists to screen the electronic charge displaced because of the exchange of atoms. The shift in the Fermi level is small and can be considered within a perturbation framework. To first order it is equivalent to having an unknown perturbing potential on the site under consideration. Rather than introducing such an adjustable parameter, the Fermi level shift is calculated self-consistently in the present scheme. Finally, it must be pointed out that further improvements can be made by applying the perturbation method developed by Foulkes and Haydock<sup>27</sup>, but this is outside the scope of the present work.

### III. Results.

The formalism described in the previous section has been applied to calculate nearest neighbor and next nearest neighbor EPI's in the fcc and bcc lattice for two types of

transition metal alloy systems. In the first group of calculations, in which the configurational averaging method was tested for convergence and other general properties, 'canonical' s-, p- and d-orbitals were considered for a fictitious 3-8 system. To this end arbitrary, but realistic, tight binding parameters were taken to represent a disordered  $A_c B_{1-c}$  alloy in which the number of d-electrons  $N_A$  ( $N_B$ ) was equal to 3 (8). As a consequence all results are expressed in canonical units (c. u.). Subsequently, the binary alloy  $Rh_c Ti_{1-c}$ , which is one example of such a system, was investigated using the tight-binding values tabulated by Papaconstantopoulos<sup>23</sup>. Off-diagonal disorder was treated by means of Shiba's prescription (2.2). Note, however, that this is an approximation that need not be made in a real-space method, provided that hopping parameters for the ordered compound AB are known. The configurational average  $\langle \dots \rangle_{IJ}$  was calculated by generating random configurations (at fixed concentration) and averaging the resulting EPI, a procedure that has been shown to converge quickly<sup>17</sup>.

In the remainder of this paper, EPI obtained by configurational averaging will be presented and their general properties discussed. A unique  $\delta$  and  $E_F$ , function of the concentration  $c$ , will be considered for the canonical 3-8 alloy. However, for the purpose of illustration the EPI will be plotted as a function of the position of the Fermi level. Strictly speaking, since a constant value of  $\delta$  has been used, the results are only valid at the exact Fermi level for the 3-8 alloy. It seems reasonable though to assume that the general trends in the EPI will be found in this way and this approach also provides a general check on the method.

As noted before, the computing time grows very quickly as a function of the number of levels in the continued fraction. To illustrate this point, Fig. 1 shows results for the nearest neighbor EPI in the fcc structure with canonical 3-8 values and  $c_A = 0.25$ . It can be seen that the necessary cpu time (plotted in arbitrary units) grows exponentially with increasing number of levels. This rapid growth puts a serious limit on the number of levels for which the recursion scheme is computationally tractable. Next, Fig. 2 shows the same

nearest neighbor EPI as a function of the number of configurations (N) and the number of levels (L). It can be seen that the convergence as a function of N is very fast : the results for N = 10 and N = 20 are virtually identical. As a function of L, the asymptotic value seems to be approached quite closely for L = 7 or 8. These results are similar to those found before<sup>17</sup> and exhibit the same trends. The uncertainty in the EPI after averaging over 10 configurations is approximately 1 % and improved accuracy can be obtained by increasing the number of levels, rather than the number of configurations. It is interesting to note that the self-consistency parameters, i.e. the Fermi-level  $E_F$  and the on-site energy shift  $\alpha_n^\lambda$  (which are functions of the number of levels), have a considerable influence on the EPI's. The solid curve is obtained by using seven recursion levels, but with the self-consistency parameters corresponding to eight. The resulting EPI (obtained by averaging over identical random configurations in all cases) deviates strongly from that obtained for 7 and 8 levels, with the appropriate  $E_F$  and  $\alpha_n^\lambda$ . Similar calculations were made for a bcc alloy, taking into account interactions up to third neighbors. The results show that for an fcc alloy with first and second neighbor interactions, 7 levels of the continued fraction are necessary, while for the bcc alloy only 6 levels are needed. In general the error is of the order of 0.01 eV and depends only weakly on the actual values of the EPI. Thus it appears that the uncertainty in the EPI obtained by configurational averaging is an absolute one. Finally it also needs to be pointed out that the convergence as a function of the number of levels is faster for a disordered system than for an ordered one (see also Fig. 3).

From the foregoing it can be concluded that increasing the number of levels in the continued fraction expansion leads to improved accuracy, but that this is accompanied by a prohibitive increase in computer time. Therefore it is logical to decouple the number of levels and the number of atoms in the cluster and it will now be shown how this can be done. To determine the set of coefficients in the continued fraction, one can use the 'zebra' developed by Dreyssé and Riedinger<sup>37</sup>. This procedure builds a cluster organized into shells in such a way as to guarantee that the resulting structure has the minimal size compatible with the

number of levels used. In this way no additional sources of error are introduced. It has been conjectured<sup>37</sup> that the size of the cluster grows as  $L^d$  where  $d$  is the spatial dimension. In particular, for  $d = 3$  this term is equal to  $\frac{\tau}{6}L^3$ , where  $\tau$  is given by :

$$\Delta^2(s_n) = \tau, \quad (3.1)$$

$s_n$  is the number of sites in the shell  $n$  and  $\Delta^2$  is the second order finite difference operator. For an fcc lattice with hopping parameters up to first or second neighbors,  $\tau$  takes the values 20 and 36, respectively. For the bcc lattice with hopping parameters up to first, second or third neighbors, the corresponding values are 12, 24 and 80, respectively. In order to use tight-binding parameters determined from *ab initio* calculations, it is necessary to include second neighbor interactions in the fcc lattice and third neighbors in the bcc. This leads to a considerable increase in the size of the clusters used. An exact cluster, for the fcc lattice for example, with a unique point as seed for  $L$  levels, taking into account first and second neighbor interactions, would give  $2 \times L$  exact levels if only first neighbors were considered. Figure 3 reports results for the EPI of the ordered  $AB$  compound (with canonical 3-8 parameters) on the fcc lattice with first and second neighbors, as a function of the number of levels and the size of the cluster used (with  $E_F$  and  $\delta$  fixed at their values for 8 levels). The cluster size was determined by considering  $L_c$  exact levels for nearest neighbor hopping only. It can be seen that the results obtained with clusters exact for 4 to 8 levels are almost indistinguishable. This is confirmed in table I, which contains results for the bcc lattice with third neighbor interactions. From this it can be concluded that the cluster size must be such as to guarantee  $L$  exact levels for first neighbors only, in the range of levels considered here (6-10). Using such a 'truncated' cluster leads to an important gain in time : up to a factor of 4. Typically the number of atoms in the cluster is around 600 (instead of 4000-8000).

Next, Fig. 4 shows the nearest neighbor EPI for the canonical 3-8 case in the fcc structure at three different concentrations as a function of bandfilling. These results were

obtained by averaging over 10 configurations, using 8 levels in the continued fraction expansion. The number of nodes is in agreement with the values given by general theorems<sup>36</sup> and the curves have a similar overall shape, with a 'phase-separating' region at the band edges and an 'ordering' region near the center of the band (see also Ref. 17). It was also found that the local density of d-states on a Rh and Ti site has a bandwidth between 0. and 1. Changing the concentration did not affect the d bandwidth very much, so that it can be concluded that the EPI are mainly related to the d-orbitals. (This does not imply that the s- and p-orbitals are unimportant; for example they certainly affect the shape of the EPI.) Also note that only the position of the first node is affected by changing the concentration. Pair interactions involving more distant atoms are plotted in Fig. 5. As expected, the number of nodes increases, while the magnitude of the EPI decreases, with increasing separation of the atoms involved (note the change in scale, compared to Fig. 4). To sum up, at this stage, it was found in agreement with previous results<sup>17</sup> for d-orbitals only, that configurational averaging converges quickly and that 10 configurations are sufficient to obtain convergence. The number of levels is a crucial factor as far as computer time is concerned. Typically, a maximum of 8 levels is necessary and an important speed-up can be obtained by using 'truncated' clusters.

In order to study the influence of the environment on the EPI, three sets of configurations were generated. In the first one, the only constraint was the overall concentration of the recursion cluster, while in the second group the first coordination shell of the pair was also held at the fixed overall concentration and in the third group this constraint was imposed in every concentric shell around the central pair. In all cases adjustments were made by appropriate rounding of the shell occupancies to ensure that the total number of atoms was conserved. The resulting EPI are drawn as a function of the number of configurations (at a fixed concentration  $c_A = 0.25$ ) in Fig. 6(a) and as a function of bandfilling (averaged over 12 configurations, for 8 exact levels of the continued fraction) in Fig. 6(b). Although the influence of the ordering constraints is clearly visible in Fig. 6(a), the differences are

relatively small : a few percent between the first two cases, and approximately 20 % in the case of concentric shells with constant compositions. It can be seen in Fig. 6(b) that the positions of the nodes are the same and only the extreme values are affected. Note also that the bandfilling selected corresponds to a Fermi level near the maximum in Fig. 6(b) so that deviations will be rather larger than on the average.

Next a group of calculations was performed for the binary alloy  $\text{Rh}_c\text{Ti}_{1-c}$  with the orthogonal two-center tight binding parameters tabulated by Papaconstantopoulos<sup>23</sup>. Fig. 7 shows nearest neighbor fcc and nearest and next nearest neighbor bcc EPI as a function of concentration for this system. From these EPI one can determine the energy of mixing for the two structures as follows<sup>20</sup> :

$$\Delta E_m^I(c) = E_{dis}^I(c) - E_{lin}^I(c) + \Delta E_{ord}^I(c), \quad (3.2)$$

in which elastic and vibrational contributions, as well as volume changes, have been neglected. The different energy contributions involved are :

$$E_{lin}^I(c) = (1 - c)E_A^I + cE_B^I, \quad (3.3)$$

i. e. a linear interpolation between the cohesive energies of the pure elements in the crystal structure  $I$ ,  $E_{dis}^I$  is the cohesive energy of the completely disordered state given in (2.34), obtained by configurational averaging of the band structure term (2.17) and  $\Delta E_{ord}^I$  is the configurational part of the mixing energy, related to the EPI by :

$$\Delta E_{ord}^I = \sum_h q_h V_h \quad (3.4)$$

where  $V_h$  is the EPI between an atom and its  $h$ th neighbor and

$$q_h = \frac{1}{2}(cn_h^{BB} - c^2n_h) \quad (3.5)$$

where  $n_h$  is the coordination number and  $n_h^{BB}$  the number of BB pairs both corresponding to



the  $h$ th neighboring site. The energy of mixing corresponding to the EPI in Fig. 7 are shown in Fig. 8, for the bcc (upper curve) and fcc (lower curve) structure respectively. As noted before, the calculation of the term  $E_{dis}^I(c)$  must be performed very carefully. In (3.2)  $E_{dis}^I$  and  $E_{in}^I$  are large numbers and their difference is very sensitive to the position of the Fermi level. In order to ensure sufficient accuracy one can adopt the method discussed before involving a small shift of the Fermi energy. The correction introduced by this small variation leads to a negligible change to the EPI (less than 0.01 eV). A phase diagram calculation using these results is in progress and will be reported upon elsewhere.

#### IV. Summary and conclusions.

This paper has addressed the calculation of effective pair interactions in binary alloys, quantities that are essential to understand the statistical thermodynamics of these systems on a first principles basis. It has been shown that these EPI can be calculated accurately and reliably by means of direct averaging over random configurations. To this end the formalism set out previously<sup>17</sup> has been extended in order to include s- and p-orbitals in a recursion method approach to a realistic tight-binding Hamiltonian. The feasibility of this scheme depends crucially on the use of the orbital peeling trick to calculate cohesive energy differences directly. Since no reciprocal space transformation is made, the present method is ideally suited to treat problems with broken symmetry, such as partially ordered structures, or low-symmetric configurations, in particular surfaces and interfaces. For completely disordered systems, the results compare very well to those obtained within the coherent potential approximation<sup>17</sup>, although the present method is more time consuming since in the CPA only one recursive cycle needs to be performed once the effective medium is set up. On the other hand, since the configurational averaging method repeats the same set of instructions for each random configuration, it is very well suited for parallel implementation on computers with an SIMD architecture. It is also important to note that the present method takes ensemble averages (in an approximate way) of the appropriate physical quantities, rather than calculating

these quantities for an 'averaged' configuration. The former approach is of course the correct one in classical statistical mechanics.

The main difficulties in the present description of a disordered system arise because of charge transfer. They involve a shift in the on-site energies and the determination of the Fermi level. Simple procedures to take these effects into account have been presented here, but further extensions are straightforward, if necessary. A considerable saving in computer time can be obtained by decoupling the number of levels from the number of atoms in the recursion cluster. Numerical simulations indicate that it is sufficient to take the number of atoms in the cluster appropriate for nearest neighbor hopping parameters only, even if further neighbor interactions are present. A further conclusion of this work is that 10 configurations and a maximum of 8 levels are sufficient to guarantee an uncertainty of a few percent in the magnitude of the EPI. The main emphasis of the present paper has been on the formalism and general checks of convergence and other properties, and to this end 'canonical' tight-binding parameters have been used. However, some preliminary results are included for the system  $Rh_cTi_{1-c}$ , using the first-principles values obtained by a fit to an LAPW band structure. A further discussion of these EPI and the resulting phase diagram will be given in a forthcoming paper.

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### Figure Captions.

**Fig. 1** Cpu-time (in arbitrary units) for a full EPI calculation as a function of the number of levels ( $L$ ) in the continued fraction.

**Fig. 2** Nearest neighbor EPI (in canonical units) in the fcc structure for canonical 3-8 values with  $c_A = 0.25$ , as a function of the number of configurations ( $N$ ) and the number of levels ( $L$ ). Solid curve :  $L = 7$ , but with self-consistency parameters for  $L = 8$ . In all cases the same set of random configurations was used.

**Fig. 3** Nearest neighbor EPI (in c.u.) in the fcc structure for canonical 3-8 values with  $c_A = 0.25$ , as a function of the number of levels ( $L$ ) with fixed cluster size. The cluster size is chosen so as to be exact for nearest neighbor hopping only at a given number of levels  $L_c$ . The results for  $L_c = 4-8$  are indistinguishable.

**Fig. 4** Nearest neighbor EPI (in c.u.) in the fcc structure for canonical 3-8 values as a function of bandfilling, at concentration  $c_A = 0.25$  (short dashed line), 0.50 (solid line) and 0.75 (long dashed line).

**Fig. 5** Further neighbor EPI (in c.u.) in the fcc structure for canonical 3-8 values with  $c_A = 0.25$  as a function of bandfilling : solid line : second neighbor, long dashed line : third neighbor and short dashed line : fourth neighbor. Note the change in scale compared to Fig. 4.

**Fig. 6** Nearest neighbor EPI (in c.u.) in the fcc structure for canonical 3-8 tight-binding parameters with  $c_A = 0.25$  for various prescriptions to generate the configurations (see text) :

- (a) as a function of the number of configurations ( $N$ ).
- (b) as a function of bandfilling.

Full line : fixed concentration in every shell; short dashed line : fixed concentration in

first shell and long dashed line : fixed overall concentration.

**Fig. 7** EPI for  $Rh_cTi_{1-c}$  as a function of the  $Rh$  concentration. Filled squares : nearest neighbor EPI in the fcc structure, open squares : nearest neighbor EPI in the bcc structure, and filled circles : next nearest neighbor EPI in the bcc structure. The curves are drawn to guide the eye.

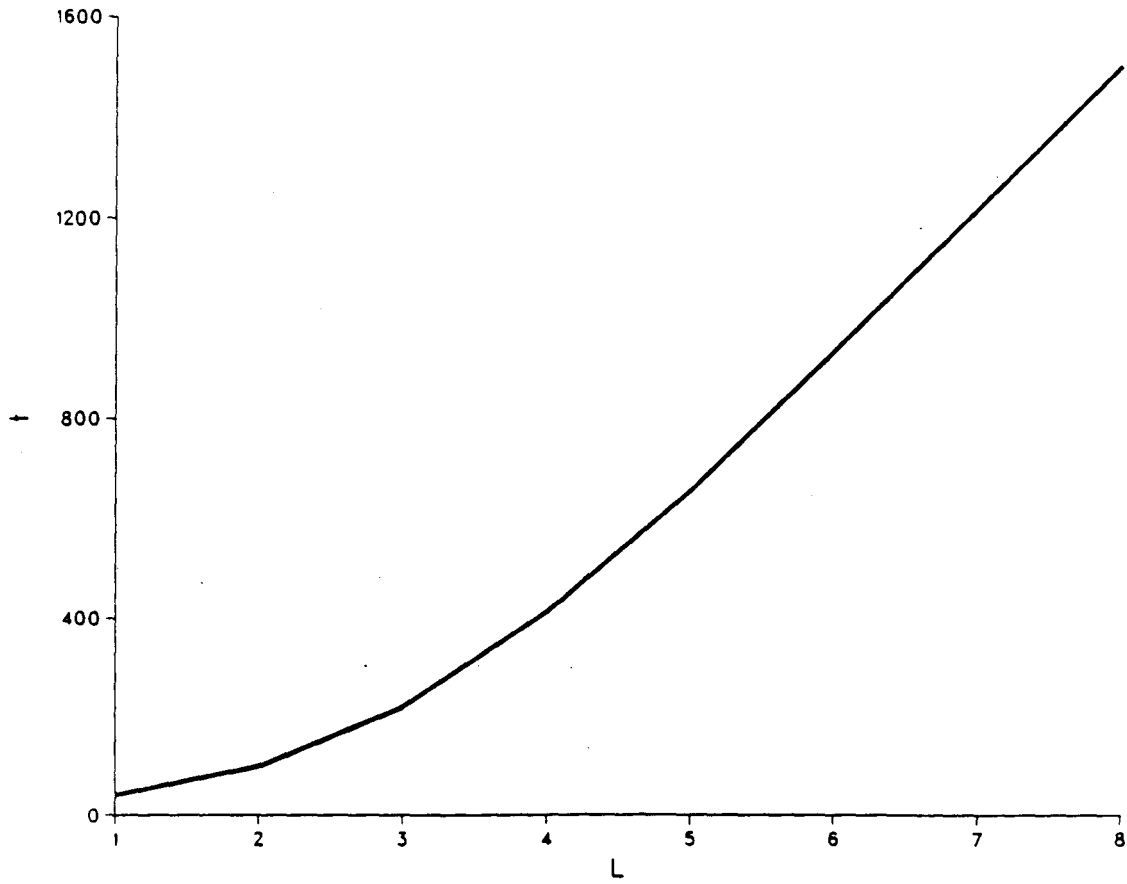
**Fig. 8** Energy of mixing of  $Rh_cTi_{1-c}$  in the bcc (upper curve) and fcc (lower curve) structure as a function of concentration.

**Table I.**

Position of the Fermi level for different 'truncated' cluster sizes in the bcc lattice with third neighbor interactions. The Fermi level  $E_F$  is computed for 8 exact levels of the continued fraction, with a cluster exact for  $L_c$  levels. Also given are the number of sites in each cluster and the computation time (in arbitrary units).

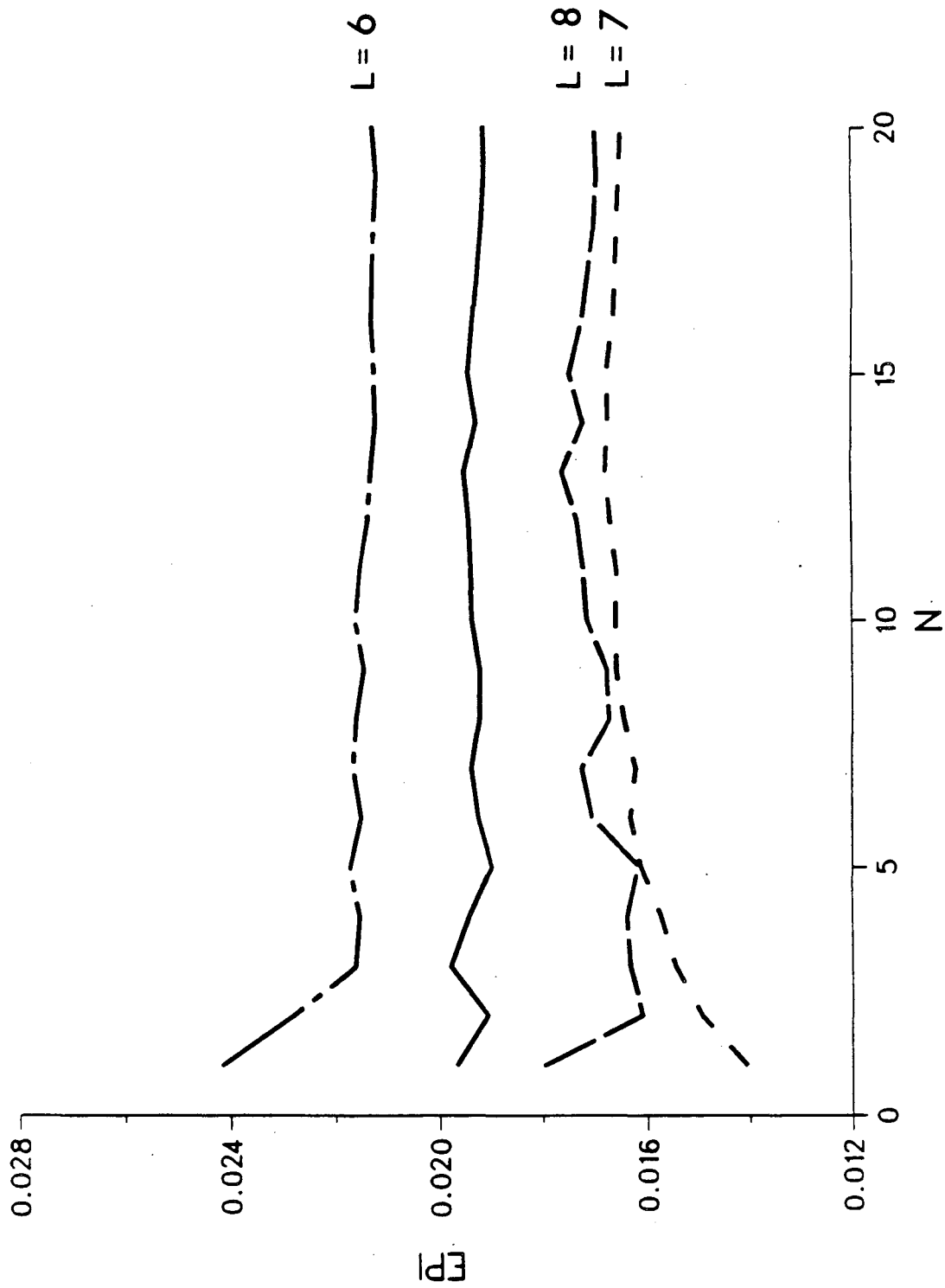
$L_c$	$E_F$	sites	time
2	0.68212	192	255
3	0.68369	538	417
4	0.68444	1158	754
5	0.68465	2132	1138
8	0.68468	7978	1940





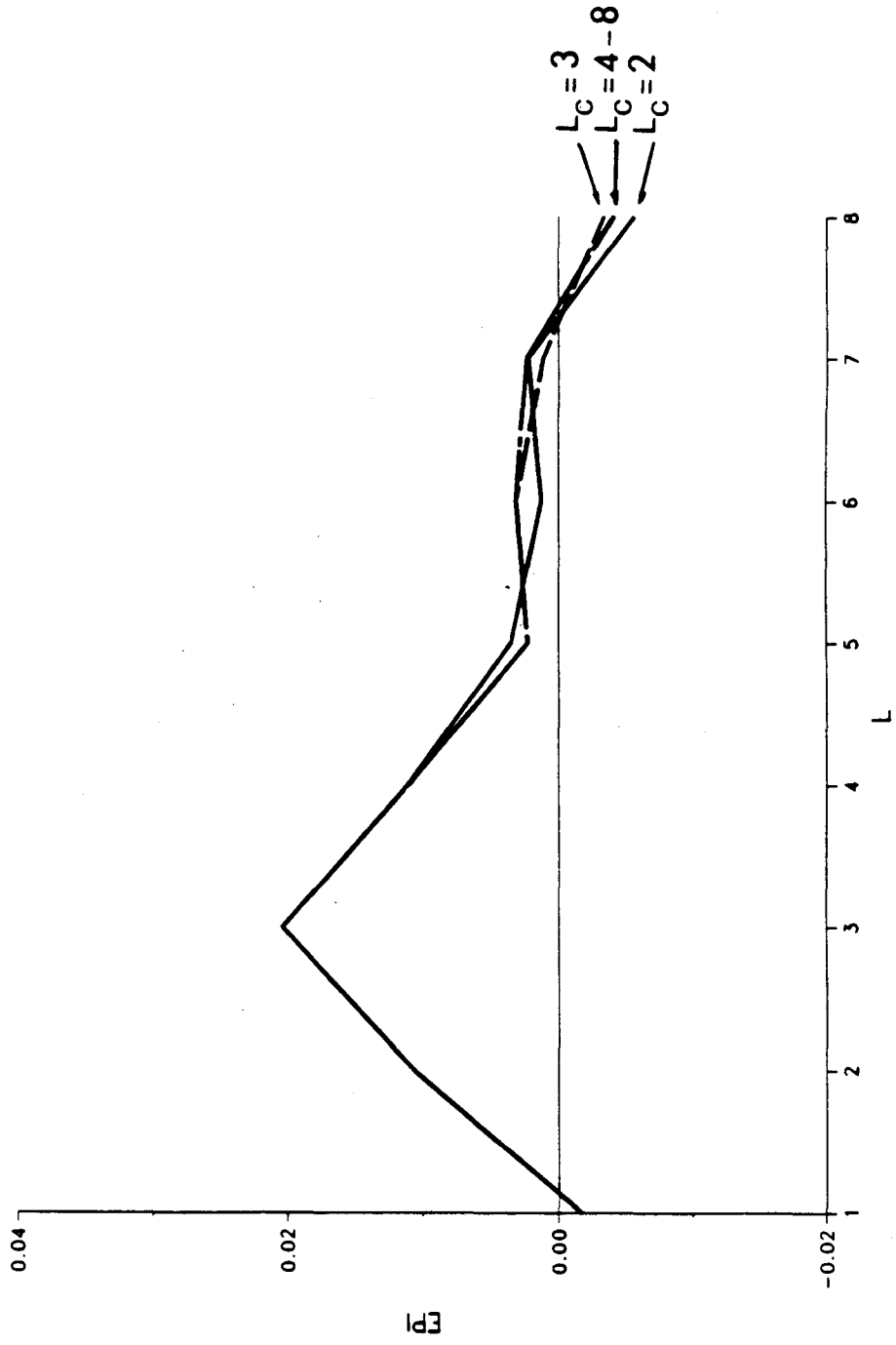
XBL 885-1885

Fig. 1



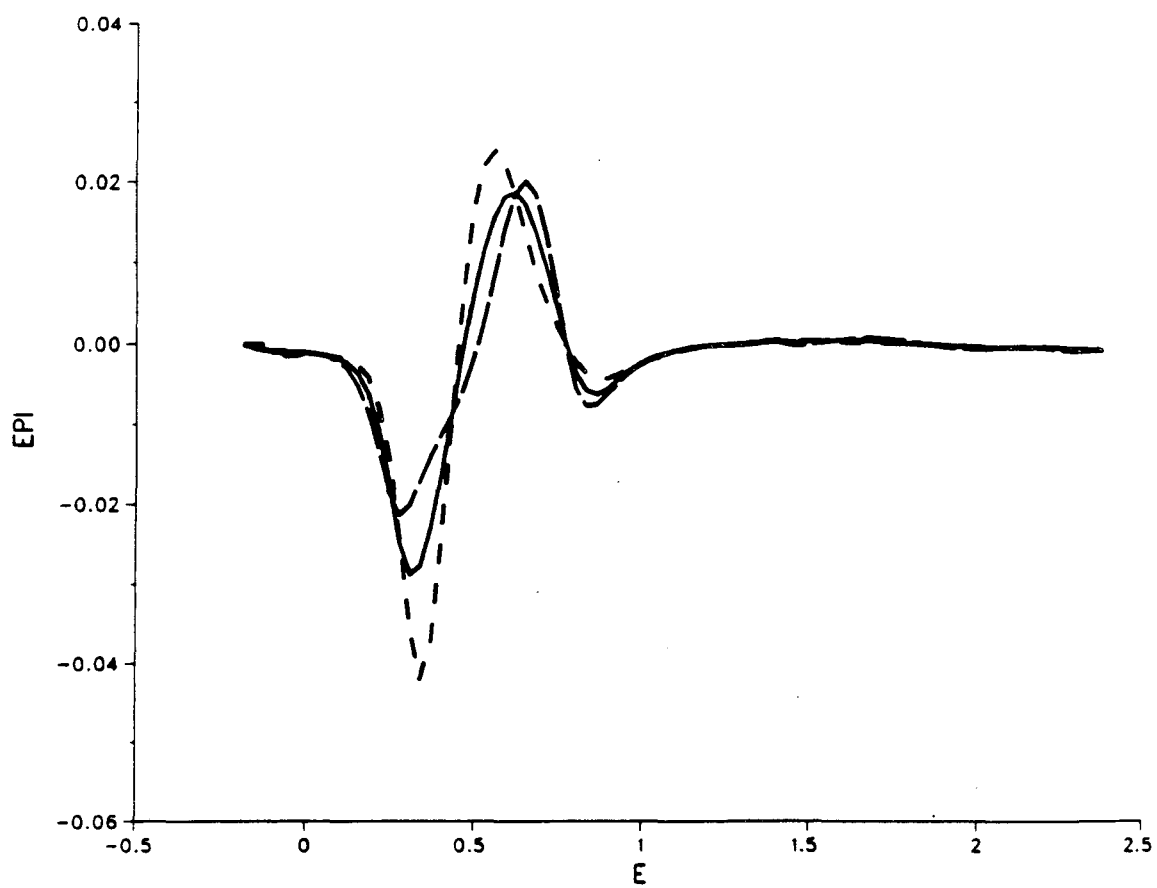
XBL 885-1886

Fig. 2



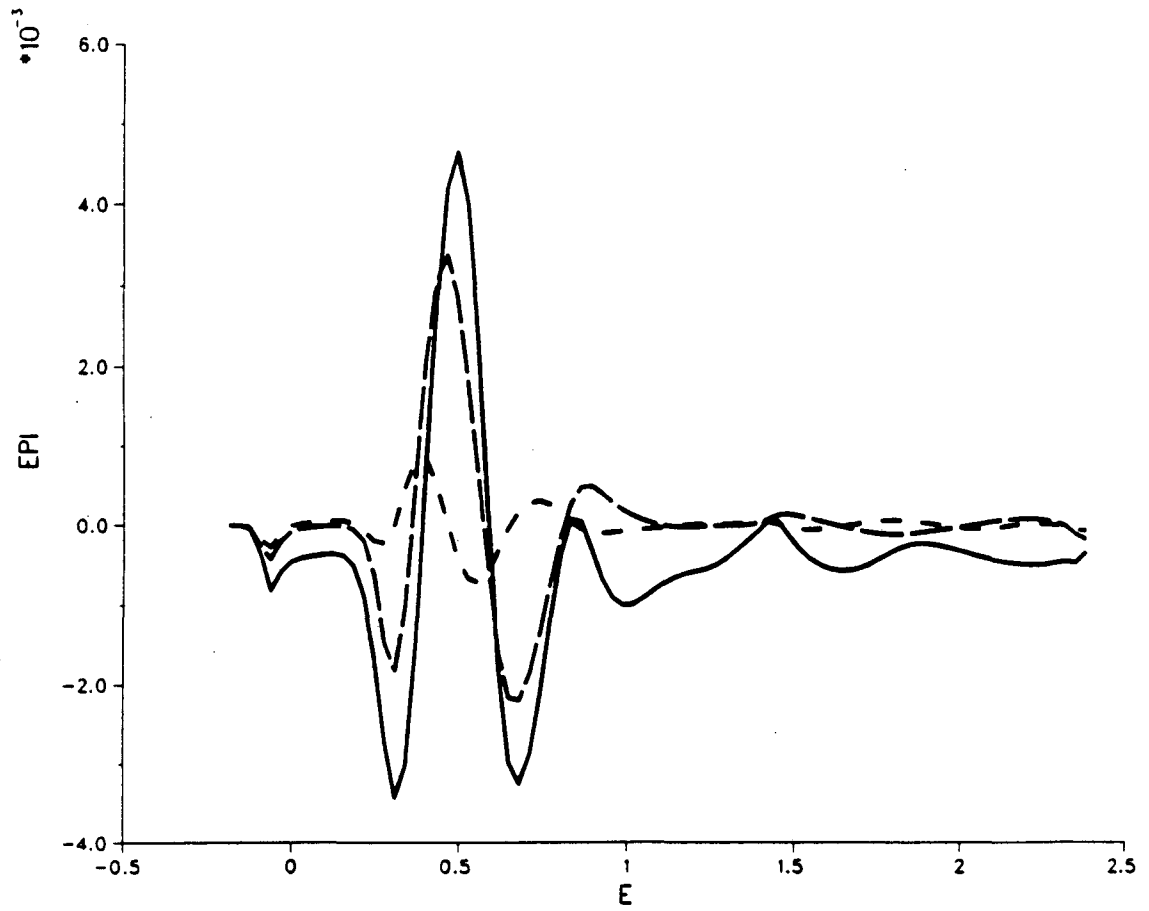
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Fig. 3



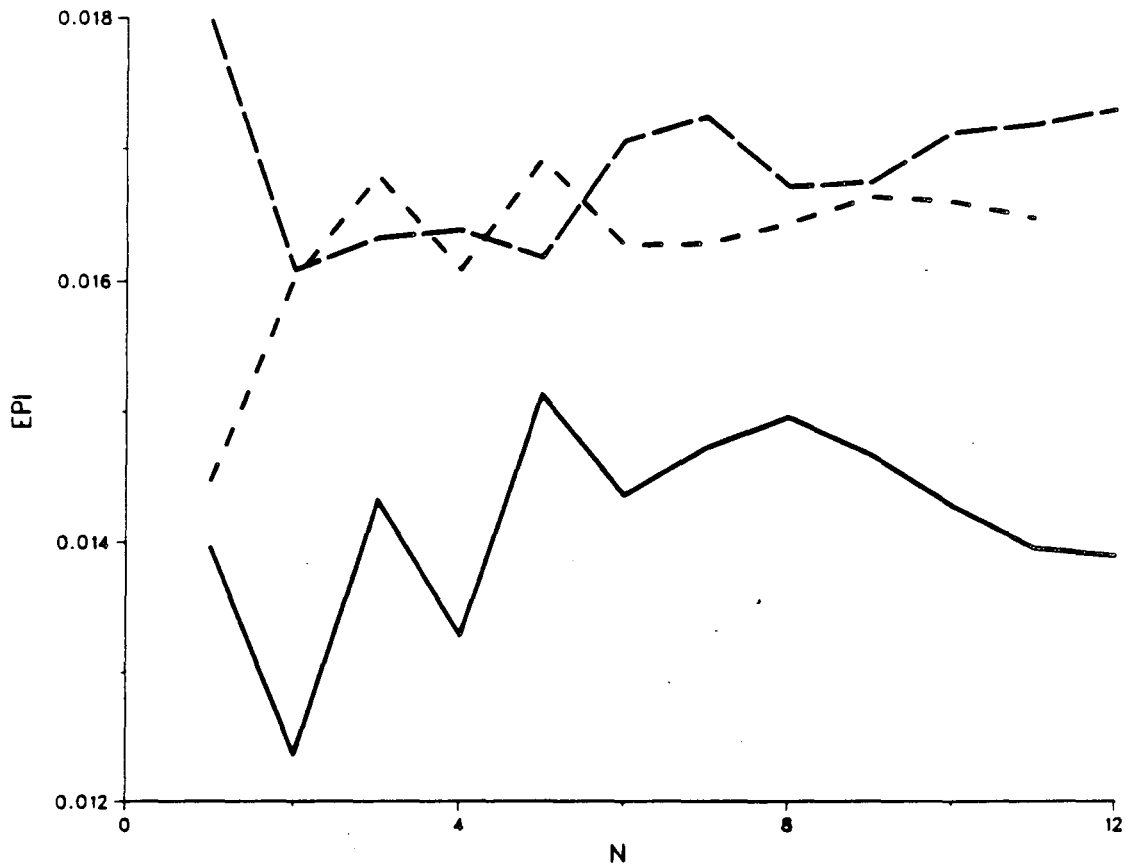
XBL 885-1888

Fig. 4



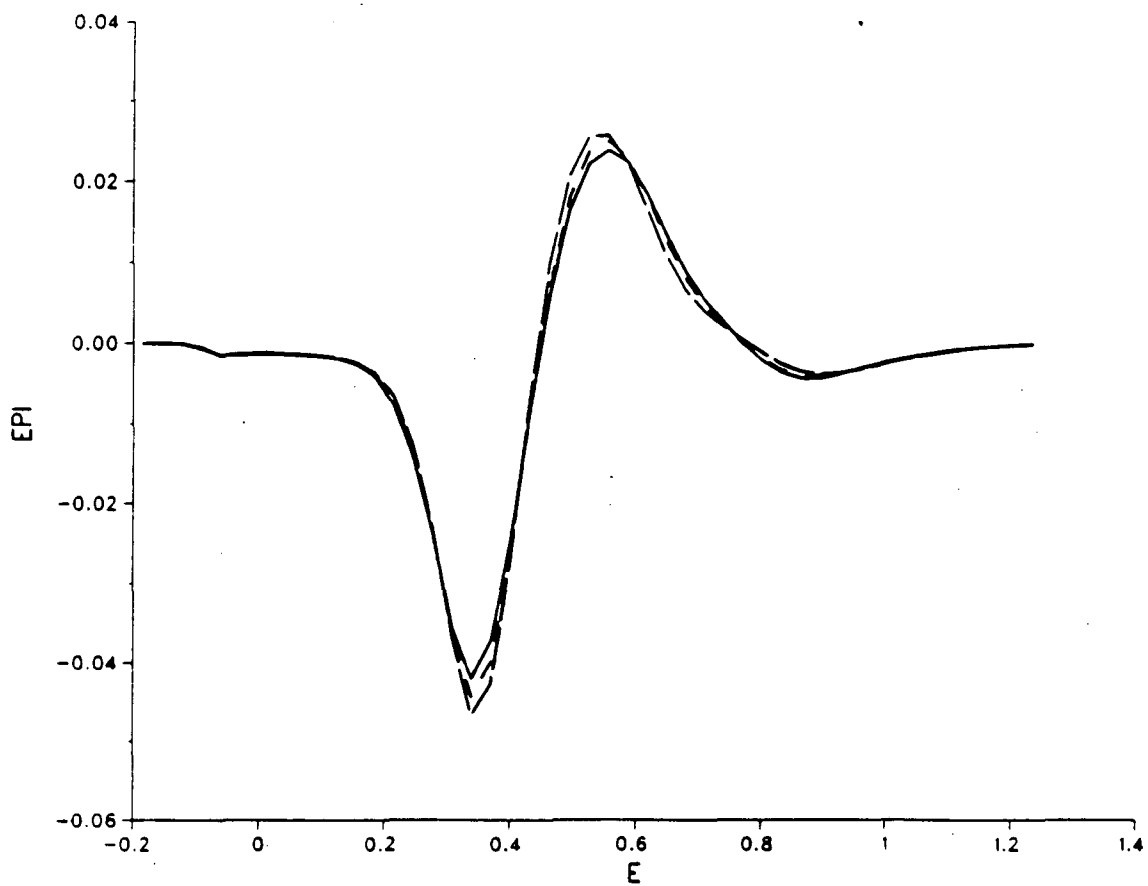
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Fig. 5



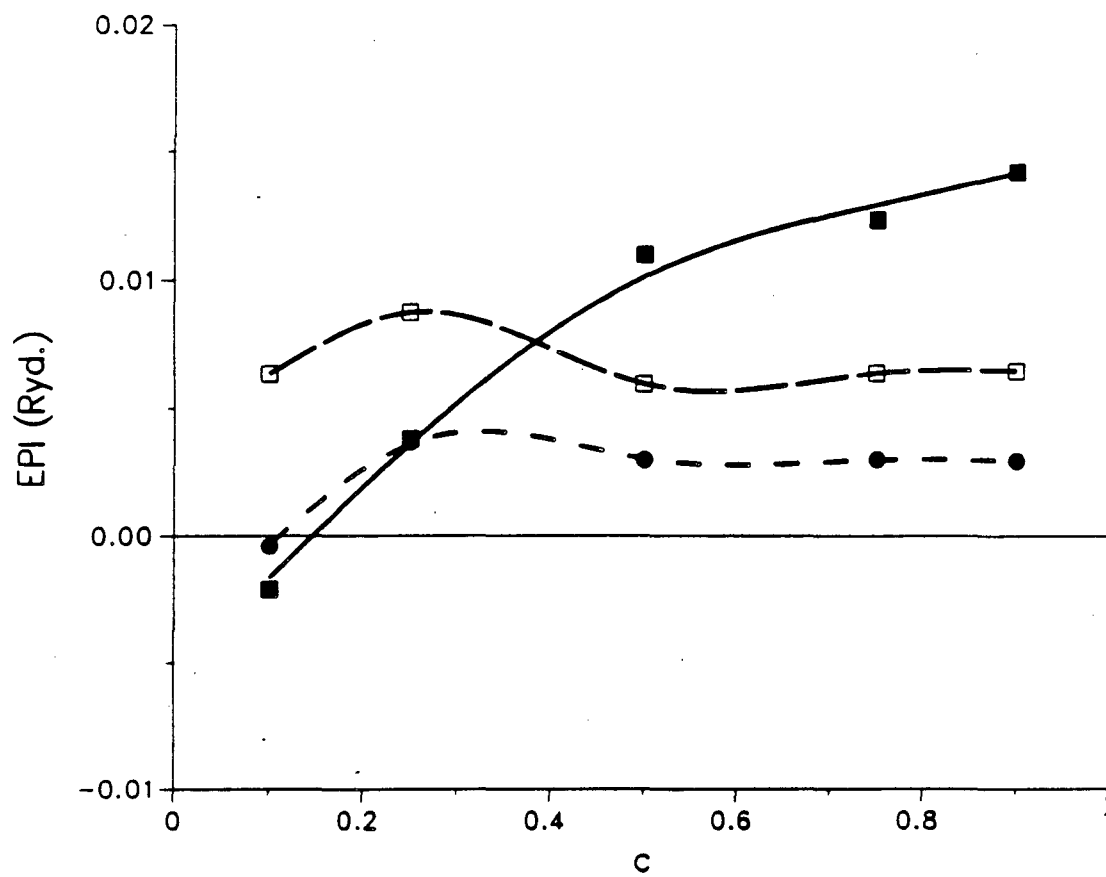
XBL 885-1890

Fig. 6a



XBL 885-1891

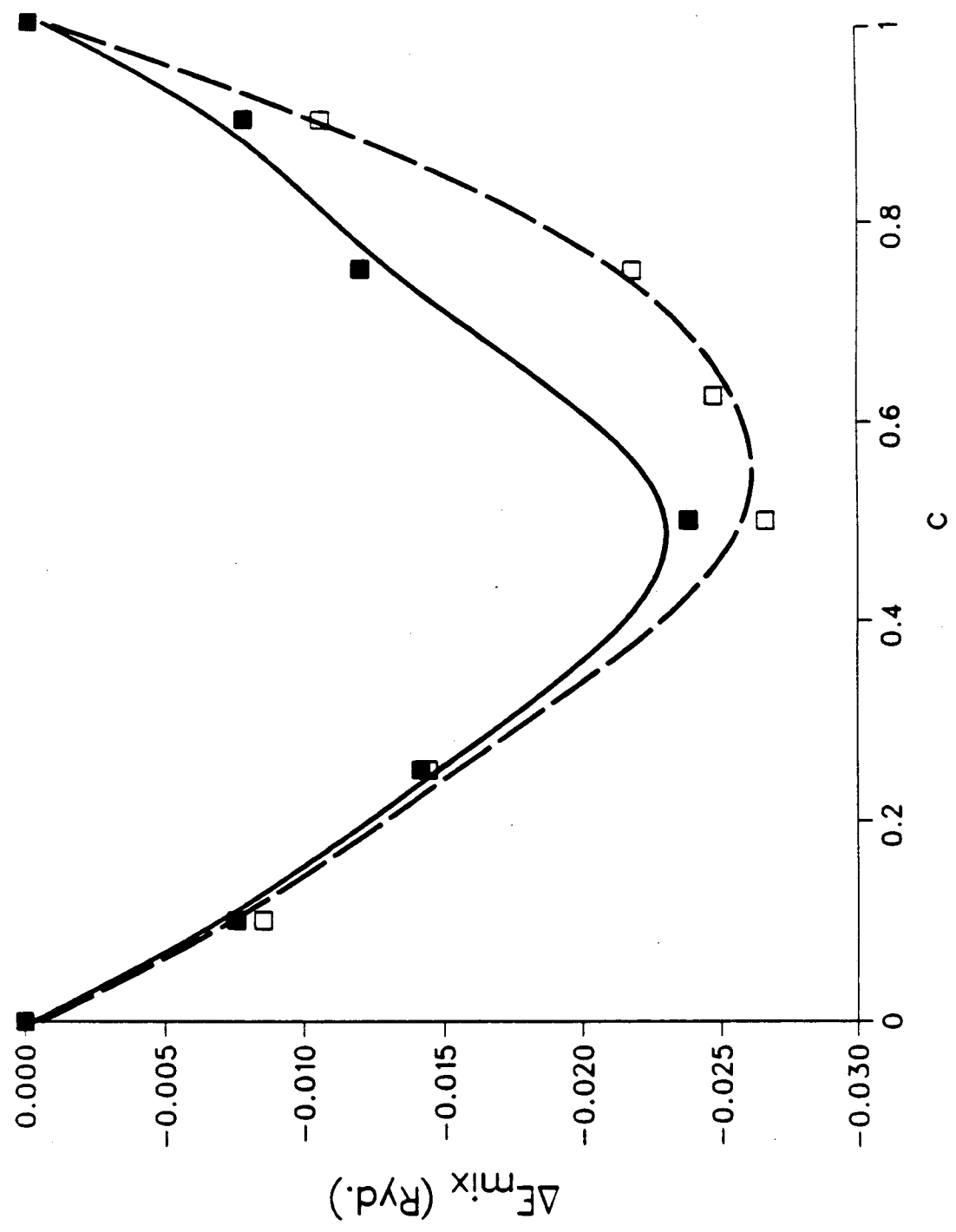
Fig. 6b



XBL 885-1892

Fig. 7





XBL 885-1893

Fig. 8

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