

MASTER

ATOMISTIC STUDIES OF GRAIN BOUNDARIES WITH SEGREGATED IMPURITIES

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Abstract

The necessary precursor for any atomistic studies is a description of interatomic forces. Since no satisfactory description of interatomic forces in binary alloys could be found, the first stage of the research was devoted to this problem. The energy of the lattice was written as a sum of pair interactions and of a density dependent term. For pure metals the parameters in both the pair potential and the density dependent term were determined so as to fit the cohesive energy and elastic constants, and satisfy the condition of equilibrium for the experimentally known lattice parameter. The potentials and density dependent terms for pure metals were then used in constructing the corresponding description of interatomic interactions in alloys, using a modified method of Machlin (4). The principle modifications are use of density dependent terms and fitting of the enthalpy of mixing. These procedures are described in detail in this report.

The grain boundary studies were started for the systems Cu-Ag, Cu-Bi and Au-Ag. However, since the density dependent part of the energy must now be taken into account explicitly a substantial modification of existing computer programs for grain boundary calculations is needed. This is at present in progress and thus only the directions of this work are reported.

A limited effort was also devoted to the development of a theory of intergranular fracture in embrittled materials. The main purpose is to establish a relationship between the cohesive energy and the plastic work which would enable us to use the recently developed technique of measuring the local stress of fracture for direct studies of intergranular cohesion. This is described in more detail in the enclosed preprint (ref. 3).

1. Introduction

The principal aim of this research project is to carry out atomistic studies of the influence of segregated impurities upon the structure and properties of grain boundaries. The essential precursor for such studies is a description of interatomic forces which has been done almost exclusively by using central force pair potentials. In the case of pure metals a large number of empirical and first principle potentials were developed in the last two decades. However, for alloys only a few attempts have been made, as already mentioned in the original proposal, and, therefore, the first stage of this research was mainly devoted to the construction of such central force potentials for binary alloys which can be used in the atomistic studies of lattice defects. This work has now been almost completed and it is described in more detail in this report.

The basic concept of the calculations of the structure of grain boundaries with impurities is similar to that applied in the previous studies of boundaries in pure metals (for a review see ref. 1, preprint enclosed). However, the calculations in pure metals were always carried out at constant total volume and, therefore, the volume dependent part of the energy of the assembly of atoms was not used implicitly. On the other hand the volume dependent part of the energy must be included directly into the present calculations because it is a function of the concentration of the alloying element and thus, will not be the same at the boundary and far away from it. This means that the relaxation procedures developed in the studies of grain boundaries in pure metals cannot be used directly, but substantial modifications have to be made first. This work is presently in progress.

A limited effort was also devoted to the development of the theory of intergranular fracture in which the bond breaking and dislocation emission at the microcrack tip are regarded as concomitant processes. In this theory the plastic work, γ_p , is calculated as a function of the ideal work to fracture, i.e., of the cohesive energy, γ . This research is part of a study of the micromechanisms of low temperature fracture carried out by the principal investigator. However, the above mentioned development has a direct bearing on this project. The reason is that recently a method for measuring the local stress needed for the initiation of the brittle fracture at a grain boundary as a function of the concentration of segregated impurity on that boundary has been developed (2) and if a relationship between γ_p and γ is established, a direct measurement of the grain boundary cohesion as a function of the impurity concentration and also of other grain boundary parameters may be possible. The state of this development is described in more detail in the enclosed preprint (ref. 3).

2. Interatomic Potentials

The construction of the pair potentials has been carried out semi-empirically since no first principle calculations are available at present for most of the materials of interest. Originally, it was suggested that the potentials describing interactions between the atoms of an alloy consisting of two elements A and B would be derived using a modified Machlin's procedure (4). In this method the A-A and B-B interactions (in the form of Lenard-Jones potentials) are first fitted to the cohesive energies and in equilibrium lead to the experimental lattice parameters. The A-B interaction is taken as an average of A-A and B-B interactions.

All three interactions are then modified by taking into account the charge transfer between the atoms A and B. However, the energy of the lattice is expressed in terms of central forces only and thus the elastic constants have to satisfy the Cauchy relations which are known not to be valid. Furthermore, the potentials constructed in this way do not reproduce correctly any of the elastic constants both in the pure materials and in the alloys. At the same time the elastic constants are quantities which should be reasonably reproduced when the potentials are to be used in defect studies. They have been measured for all pure metals and for a large number of alloys, and are thus suitable parameters which can be fitted when constructing the potentials. Moreover, it is not physically reasonable to assume that the cohesive energy can be expressed entirely in terms of pair interactions. On the contrary, the existing theories of cohesion in both simple (5) and noble and transition metals (6, 7) suggest that the cohesive energy is almost entirely determined by the purely density dependent term rather than by the structurally sensitive pair interactions. The construction of the potentials was, therefore, carried out using the basic ideas of the Machlin's approach (e.g., incorporation of the charge transfer) but taking into account the above mentioned facts and using elastic constants and the enthalpy of mixing as additional empirical parameters. The pair potentials were first constructed for pure elements. The energy per atom, i , was written as:

$$E_i = \frac{1}{2} \sum_{j \neq i} \phi(r_{ij}) + U_v(\bar{v}_a) \quad (1)$$

where ϕ is the pair potential and U_v is the part of the energy which is a

a function of the average volume per atom \bar{v}_a . Several functional forms for ϕ were tested and the most suitable was found to be

$$\phi(r) = a/r^4 + br^3 + cr^2 + fr + g \quad (2)$$

where a, b, c, f, g are constants. The volume dependent part of the the energy was written as the expansion

$$\begin{aligned} U_v(\bar{v}_a) &= U_v(\bar{v}_a^0) + U'_v(\bar{v}_a^0)(\bar{v}_a - \bar{v}_a^0) \\ &\quad + \frac{1}{2} U''_v(\bar{v}_a^0 - \bar{v}_a^0)^2 \end{aligned} \quad (3)$$

where \bar{v}_a^0 is the average volume per atom in the equilibrium. It was than assumed that in equilibrium the pair potential does not contribute to the cohesion and thus that the cohesive energy, E_c , is described entirely by the density dependent term, i.e., $E_c = U_v(\bar{v}_a^0)$.

The pair potentials were truncated at $r = r_t$ which usually lies in between third and fourth nearest neighbors; for $r_{ij} = r_t$ it was required that $\phi(r_t) = \phi'(r_t) = 0$. The coefficients a, b, c, f, g, U'_v , and U''_v were then determined so as to satisfy (i) the equilibrium condition for experimentally measured lattice parameter, (ii) truncation conditions, (iii) requirement of zero contribution of ϕ to the cohesive energy and (iv) fit experimental values of three independent elastic constants. Thus, all elastic constants were fitted in the case of cubic structures. For hexagonal metals only three of the five elastic constants were fitted but it was always found that the other constants were then well reproduced. In the case of elements such as Bi and Sb which crystalize in the trigonal structure the cubic components of the elastic constant terms were fitted after it was shown that to a first approximation the non-cubic components may be neglected.

When constructing the potentials for the alloy the energy per atom, i , is written as:

$$\begin{aligned}
 E_i = & C_A^2 \frac{1}{2} \sum_{j \neq i} \phi^{A-A}(r_{ij}) + C_B^2 \sum_{j \neq i} \phi^{B-B}(r_{ij}) \\
 & + 2C_A C_B \sum_{j \neq i} \phi^{A-B}(r_{ij}) + C_A U_A^A + C_B U_B^B
 \end{aligned} \tag{4}$$

where C_A and C_B are concentrations of the elements A and B, respectively.

The potentials ϕ^{A-A} , ϕ^{B-B} and ϕ^{A-B} have the same functional form as eq.(2) but ϕ^{A-A} and ϕ^{B-B} are not the same as in pure metals. They are based on the potentials in pure metals but modified in a way similar to that used by Machlin (4): First the concept of reference structure is introduced; i.e., both elements A and B are taken as possessing the crystal structure of the alloy (i.e., for example in the case of Cu-Zn alloy, Zn is taken as f.c.c.). Next the polar correction due to the charge transfer is taken into account. The parameters of the A-A and B-B potentials which describe repulsion are then modified so that the reference structure of the pure elements is in equilibrium for a polar corrected nearest neighbors separation; this polar corrected separation is as given by eq. (13) of the first paper of ref. (4).

The parameters of the potential ϕ^{A-B} are then determined from the following conditions: (i) The alloy is in equilibrium with the nearest neighbors distance equal to the average nearest neighbors distance of reference structures A and B. (ii) The potential is truncated at a distance equal to the average of the truncation radii of the potentials ϕ^A and ϕ^B . (iii) The minimum of A-B interaction is the average of the minimum of A-A and B-B interactions. (iv) The experimentally determined enthalpy of mixing $\Delta H = E - (C_A E_C^A + C_B E_C^B)$, where E_C^A and E_C^B are the cohesive energies of elements A and B, respectively, is reproduced. The last condition has not been

used by Machlin (4). However, its use enables us to reproduce correctly the enthalpy of mixing which may be the parameter which plays an important role in the control of segregation. Furthermore, the original procedure used in ref. (4) would not reproduce the situation when $\Delta H > 0$.

The potentials constructed for the systems of Cu-Ag, Au-Ag and Cu-Bi are shown in Figs. 1a, 2a and 3a, respectively. The corresponding concentration dependence of the nearest neighbor's distance D , of the elastic constants C_{11} , C_{12} , and C_{44} and of the enthalpy of mixing ΔH (which has been fitted) are shown in Figs. 1b, 2b and 3b, respectively. It is seen that in the case of Au-Ag alloy (Fig. 2b) the calculated concentration dependences of the elastic constants and of D are in good agreement with the measured values (marked by +). Unfortunately, no experimental data are available for Cu-Ag and Cu-Bi.

3. Grain Boundary Studies

The calculation of the structure of grain boundaries with impurities have been started for the systems Cu with Ag and Bi as impurities, Au with Ag as an impurity and Ag with Au as an impurity. The scheme for the construction of the potentials can, of course, be used for any metallic binary alloys but these three systems were chosen for the beginning for the following reasons: (i) The Cu and Bi atoms have very different sizes and segregation of Bi in Cu and associated embrittlement are well established (8 - 13). On the other hand Au and Ag have very similar sizes and it is possible that segregation will have little influence on the grain boundary structure. The system Cu-Ag may be in between the two extremes. Hence, using these three alloy systems we are able to investigate a

range of different behaviors each of which may be characteristic for a class of alloys.

(ii) A number of experimental studies of the segregation of Bi in Cu have been made (8 - 13) and recently also electron microscopic studies of the grain boundaries in this alloy have been performed (14, 15). This gives an opportunity for comparing the calculations with experiments. Similarly, the effect of segregation on the grain boundary energy in Ag-Au alloys have been studied (16) and at present the effect of segregation on the grain boundary structure in Au-Ag alloys is being investigated using X-ray topography and electron microscopy by Prof. S. Sass at Cornell University.

As mentioned in the Introduction, the computer programs which have been used in the studies of grain boundaries in pure metals require substantial modifications before they can be used in the present work. The main reason is that it is necessary to consider explicitly the density dependent part of the energy which has not been appreciated before this investigation was started. In the previous case the relaxation was carried out with respect to the local atomic positions and the relative displacements of the two grains. As explained in ref. (1) this calculation could be carried out keeping the total volume of the relaxed block constant. In the present study, however, the relaxation must be carried out not only with respect to the local atomic positions and grain displacements but also with respect to local average atomic volume which will vary with separation from the boundary. In this case expansion or contraction of the relaxed block must be allowed. At the same time dependence of both the pair potentials and the volume dependent part of the energy on the local concentration of the alloying element

has to be taken into account. This means that ϕ and U_v will again vary with separation from the grain boundary. The incorporation of these features into the relaxation program is carried out at present. We expect that this development will be completed in the near future and preliminary studies using the above mentioned potentials will be made within the next four months.

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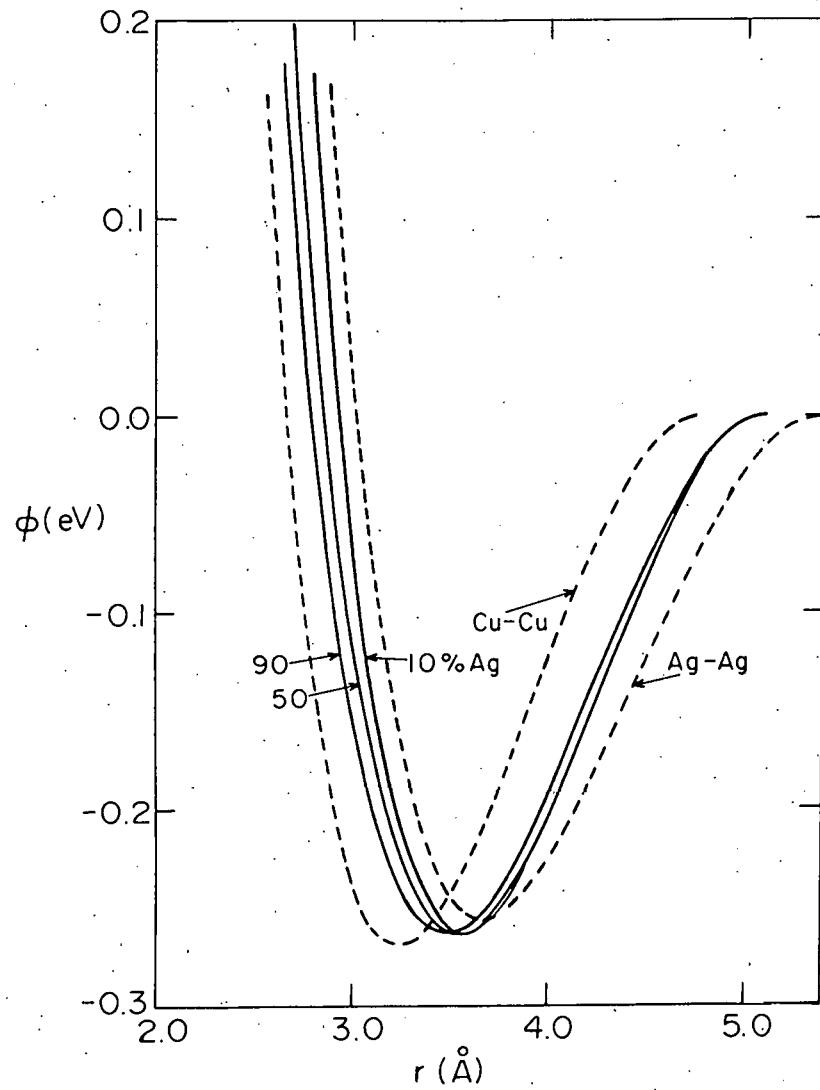


Fig. 1a Full lines: Cu-Cu and Ag-Ag potentials in pure metals.
Dotted lines: Cu-Ag potentials for three different concentrations of Ag in Cu.

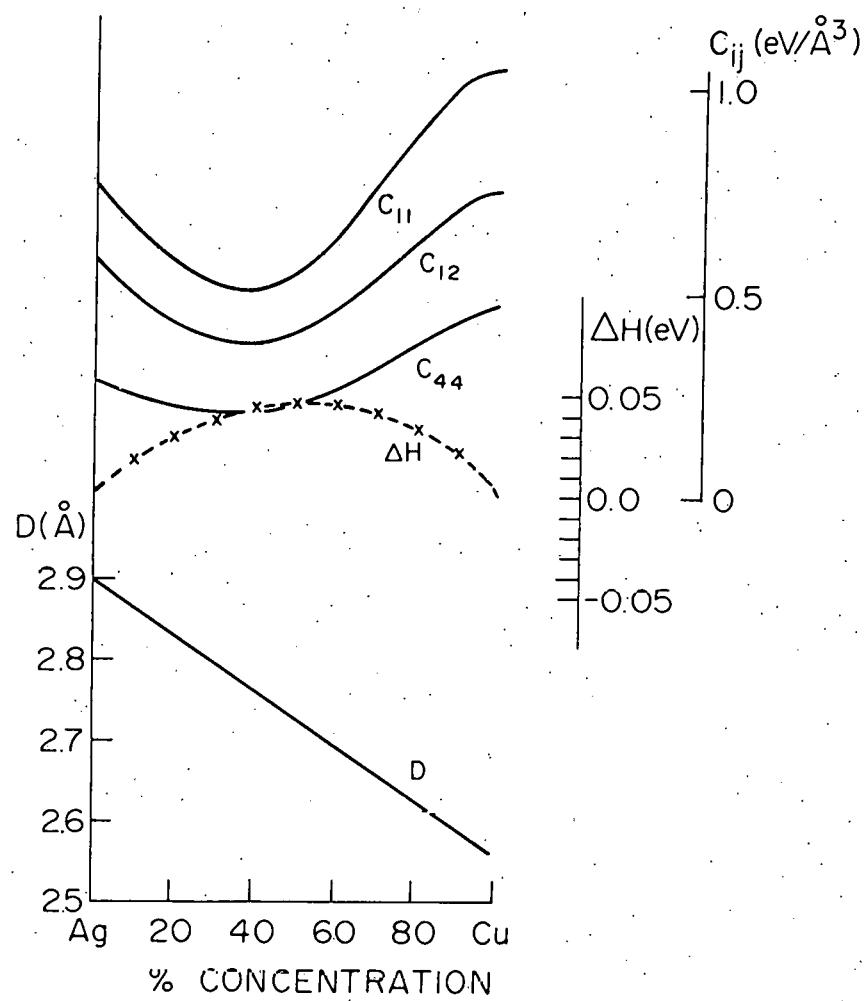


Fig. 1b Calculated dependence of elastic constants (C_{11} , C_{12} , C_{44}), nearest neighbors spacing (D) and enthalpy of mixing ΔH on concentration in Cu-Ag alloy. x experimental values.

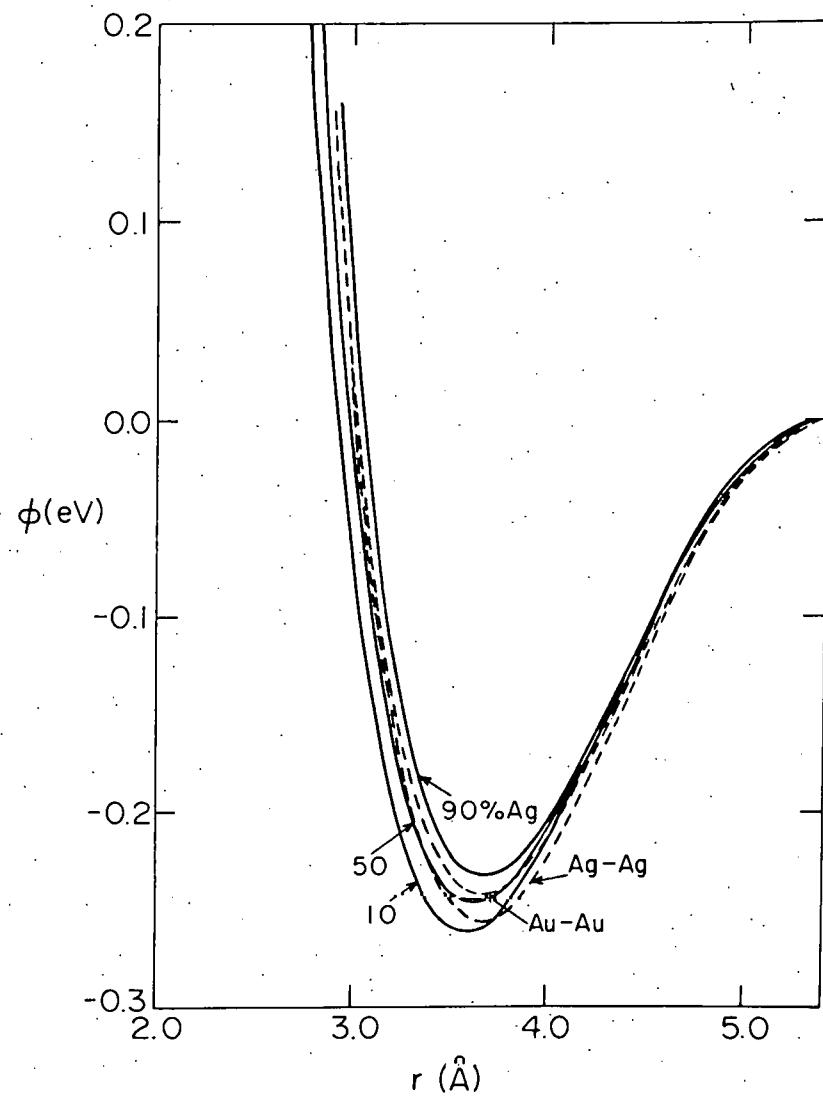


Fig. 2a Full lines: Au-Au and Ag-Ag potentials in pure metals.
Dotted lines: Au-Ag potentials for three different concentrations of Ag in Au.

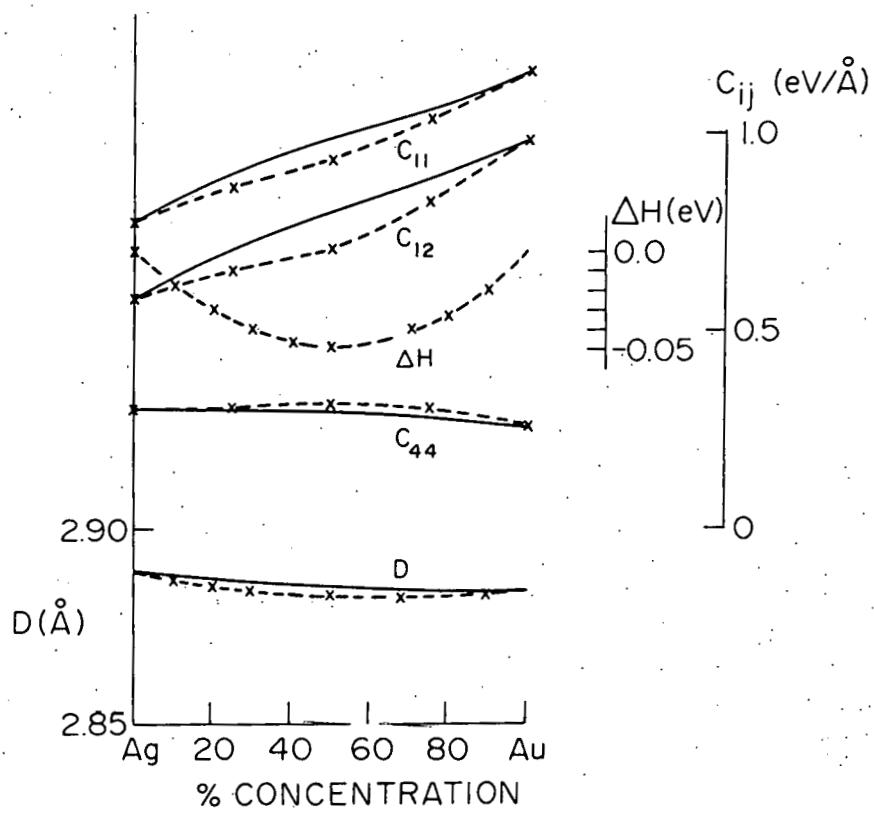


Fig. 2b Calculated dependence of elastic constants (C_{11} , C_{12} , C_{44}), nearest neighbor spacing (D) and enthalpy of mixing ΔH on concentration in Au-Ag. x experimental values.

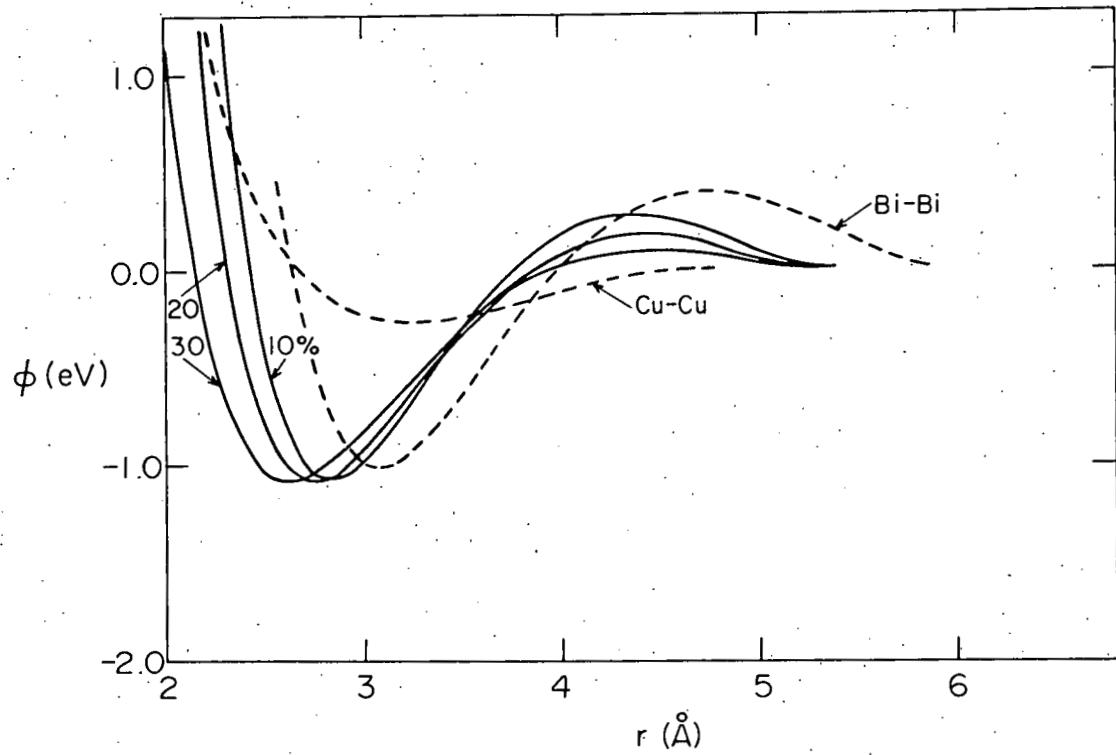


Fig. 3a Full lines Cu-Cu and Bi-Bi potentials in pure metals.
Dotted lines: Cu-Bi potentials for three different concentrations of Bi in Cu.

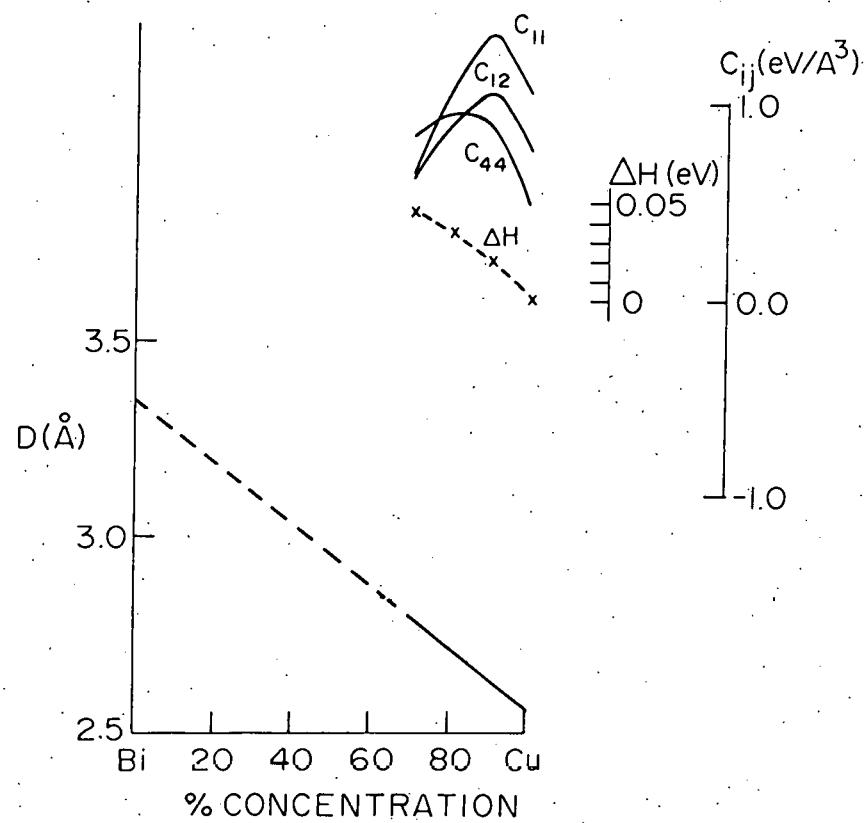


Fig 3b Calculated dependence of elastic constants (C_{11} , C_{12} , C_{44}), nearest neighbor spacing (D) and enthalpy of mixing ΔH on concentration in Cu-Bi alloy. x experimental values.