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D.J. González, J.A. Alonso. Charge transfer in simple metallic alloys. Journal de Physique, 1983, 44 (2), pp.229-234. 10.1051/jphys:01983004402022900 . jpa-00209589

HAL Id: jpa-00209589
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Classification
Physics Abstracts
61.55H

Charge transfer in simple metallic alloys

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(*Reçu le 26 mars 1982, révisé le 6 septembre, accepté le 30 septembre 1982*)

Résumé. — Le concept de transfert de charge électronique est très adéquat pour l'étude de la contribution ionique des liaisons chimiques dans les alliages métalliques. Dans cet article nous analysons les différentes définitions possibles du transfert de charge. Cela nous amène à introduire quelques états de référence de façon que le transfert de charge soit défini comme la différence nette entre la charge d'une cellule atomique dans l'alliage de référence et la charge de la même cellule dans l'état fondamental de l'alliage. Les conditions requises pour qu'il y ait consistance interne et accord avec les résultats empiriques nous permettent de faire la discrimination entre les états de référence possibles ainsi que de sélectionner une définition du transfert de charge convenable.

Abstract. — The concept of electronic charge transfer is a convenient one to study the ionic contribution to the chemical binding in simple metallic alloys. In this paper we analyse several possible definitions of charge transfer. This leads us to introduce several reference alloy states, such that charge transfer is defined as the net difference between the charge of an atomic cell in the reference alloy and the charge of the same cell in the ground state of the alloy. The requirements of internal consistency and consistency with empirical expectations permit us to discriminate between the possible reference states and to select a convenient definition of charge transfer.

1. **Introduction.** — The concepts of electronegativity [1] and electronic charge transfer [2] have proved very useful for an understanding of chemical trends in molecules [1, 3-9], alloys and compounds [1, 2, 10-33]. The electric dipole moment of a molecule AB can be related to the difference $(X_A - X_B)$ between the electronegativities of atoms A and B [3]. The ionic character of the bond can be quantified by the charge transfer Q, which is a function of the electronegativity difference. The simplest proposal for this function (in the small charge transfer limit) is a linear function, that is,

$$Q = \gamma(X_A - X_B)\,, \qquad (1)$$

where γ is a constant. Then the dipole moment D can be calculated as $D = QR$, where R is the internuclear distance. More sophisticated functional relationships between Q, X_A and X_B have also been proposed [10]. Equation (1) (and more refined versions) have been used for estimating chemical shifts in photoemission spectroscopy [5, 6], quadrupole coupling constants and infrared vibrational intensities [7]. The effect of the charge transfer on dissociation energies [8], force constants and bond lengths has also been studied [9]. The relation between Q and $(X_A - X_B)$ has not been tested in a convincing way due to the difficulties in defining [2] and calculating the charge transfer. The density functional theory, initiated by Hohenberg and Kohn [34], has helped to put the concept of electronegativity on sound grounds. Parr *et al.* [35] have identified the electronegativity with the negative of the chemical potential of the density functional theory.

The concepts of electronegativity and charge transfer have also been used in the study of the chemical binding in alloys and compounds. As selected applications we mention that Miedema *et al.* [11-13] have developed a successful semiempirical theory of alloy formation which gives satisfactory semiquantitative estimates of the heat of formation ΔH of solid and liquid alloys. In this theory

$$\Delta H \propto c_1(X_A - X_B)^2 + c_2(n_A^{1/3} - n_B^{1/3})^2 \qquad (2)$$

where $(X_A - X_B)$ is the difference of electronegativity between the two metals and $(n_A^{1/3} - n_B^{1/3})$ is the difference of interstitial electron density (to the power one third). c_1 and c_2 are known constants. Miedema *et al.* have successfully extended this theory to other important problems like the heat of adsorption [14] and surface segregation [15, 16]. The concept of charge transfer is crucial in the interpretation of Mössbauer

Article published online by EDP Sciences and available at http://dx.doi.org/10.1051/jphys:01983004402022900

isomer shifts [17, 18]. Photoemission threshold data are also related to electronegativities [4, 10].

Another important use of electronegativity in crystal binding theory is the construction of structural maps for solid compounds and solubility maps for alloys. By characterizing each binary solid compound by two coordinates, one of them being usually a measure of the difference of electronegativity between A and B, and plotting the points in a map where the two axes measure the two coordinates mentioned above, it is possible to delineate simple contours which locate different crystal phases in different regions of the map. This method, first used by Mooser and Pearson [19], has been applied recently by several authors with great success [20-25]. Similar maps have also been constructed to establish a systematics of solid solubility in metallic alloys [26-30] and to predict the type of sites adopted by ions implanted in metals [30-33].

Although the advances in computational solid state physics have been enormous during the past years, some of the problems mentioned above are still too difficult to be treated by *ab initio* computations and semiempirical methods are at present the only way of tackling those problems. Electronegativity and charge transfer are at the heart of those semiempirical methods. It is then interesting to inquire deeply into these two concepts. A self-consistent calculation of the electron density in the alloy can, in principle, give the charge transfer between the components. The main difficulty is to set up the reference state with respect to which the charge transfer is measured. One can imagine several useful references, for instance : *a*) the fictitious alloy formed by placing unrelaxed free atoms at the appropriate lattice sites. This construction of the reference alloy corresponds to the usual linear superposition of atomic densities often used in constructing the crystal potential in an energy band calculation [36], *b*) the pure metals, *c*) transformed metals with atomic volumes equal to the volume per atom in the alloy, etc. These different reference alloys often lead to a different magnitude of the charge transfer, and in some cases to a qualitative disagreement with the results expected from the empirical electronegativity scales. In spite of these undesirable features, the concepts of charge transfer and electronegativity are currently used because these concepts provide a convenient framework to study chemical trends in classes of compounds.

Two important requirements that a definition of charge transfer (that is, a definition of the reference alloy) should satisfy are : *a*) internal consistency, *b*) agreement with the expectations from the empirical electronegativity scales. Internal consistency means that the calculated charge transfer should agree with the expectations from the electronegativity differences in the reference alloy. This assumes that we have a theory that gives a way of calculating the difference of electronegativity in the reference alloy. The second requirement is self-explanatory.

In the rest of this paper we compare the results obtained for the charge transfer in simple metallic alloys, corresponding to three different definitions of the reference alloy. The more successful results are obtained for a reference alloy introduced by Alonso and Girifalco [37].

2. **Three possible definitions of the charge transfer in a simple alloy.** — Let us consider two pure metals A and B, with equilibrium volumes per atom Ω_A^0 and Ω_B^0 and with electron density distributions $n_A^0(\mathbf{r})$ and $n_B^0(\mathbf{r})$. The formation of an $A_{0.5}$ $B_{0.5}$ alloy can be separated in two steps. (In what follows we assume that the excess volume of formation is zero.)

Model 1. — In the first step the metals are cut up into atomic cells and these cells are then placed at the appropriate lattice sites in order to form the alloy. The electron density is assumed to be frozen during this process. The reference alloy built up in this way is composed of atomic cells with volumes Ω_A^0 and Ω_B^0, but the electron density (equal to $n_A^0(\mathbf{r})$ in the A cells and equal to $n_B^0(\mathbf{r})$ in the B cells) is different from the ground state electron density of the alloy. In a second step the electron density is allowed to relax, to reach its ground state distribution $n_{AB}(\mathbf{r})$. The charge transfer Q_1 is defined as the charge flowing between cells in the second step, that is

$$Q_1 = \int_{\Omega_A^0} [n_{AB}(\mathbf{r}) - n_A^0(\mathbf{r})]\, d\mathbf{r}$$

$$= - \int_{\Omega_B^0} [n_{AB}(\mathbf{r}) - n_B^0(\mathbf{r})]\, d\mathbf{r}. \qquad (3)$$

The situation is depicted in figure 1. The electron density of the reference alloy is discontinuous across the surface between unequal cells. Since the electron density is defined as a positive quantity, Q_1 is positive if the A cells, with volume Ω_A^0, end up with an excess of electrons after the relaxation step; and it is negative if the A cells end up with a deficit of electrons.

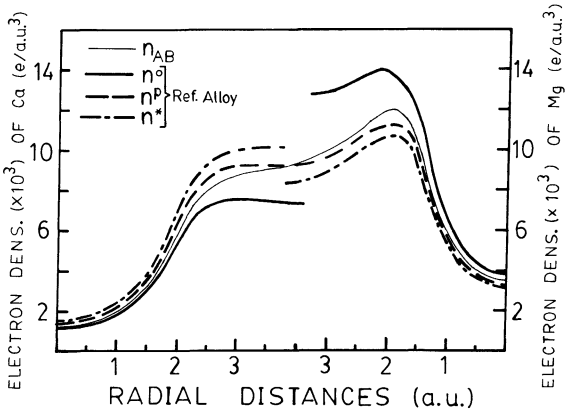

Fig. 1. — Electron density of $Mg_{0.5}Ca_{0.5}$ in the ground state ($n_{AB}(\mathbf{r})$), and in the reference alloy states of model 1 ($n^0(\mathbf{r})$), model 2 ($n^*(\mathbf{r})$) and model 3 ($n^P(\mathbf{r})$).

Model 2. — The pure metals are first transformed (one of them is compressed and the other is expanded) until they have equal atomic volumes, $\Omega_A^* = \Omega_B^*$, given by

$$\Omega_A^* = \Omega_B^* = (\Omega_A^0 + \Omega_B^0)/2 . \quad (4)$$

The transformed metals are now cut up into atomic cells and the reference alloy is built up by placing these cells at the appropriate lattice sites. The electron density is $n_A^*(\mathbf{r})$ in the A cells and $n_B^*(\mathbf{r})$ in the B cells. In a second step, the electron density is allowed to relax. After relaxation, the electron density becomes $n_{AB}(\mathbf{r})$ and the charge transfer, Q_2, is defined

$$Q_2 = \int_{\Omega_A^*} [n_{AB}(\mathbf{r}) - n_A^*(\mathbf{r})]\, d\mathbf{r} = -\int_{\Omega_B^*} [n_{AB}(\mathbf{r}) - n_B^*(\mathbf{r})]\, d\mathbf{r} . \quad (5)$$

The situation is depicted in figure 1. The electron density of the reference alloy is discontinuous across the surface between dissimilar cells, but the discontinuity is smaller than in model 1. Model 2 has been used by Hodges and Stott [38] in their theory of the heat of formation of simple alloys.

Model 3. — The pure metals are first transformed (one of them is compressed and the other is expanded) until they have new atomic volumes Ω_A^P and Ω_B^P, such that the electron densities at the surface of the atomic cells are equal, that is

$$n_A^P(R_A^P) = n_B^P(R_B^P) , \quad (6)$$

where R_A^P and R_B^P are the atomic cell radii of the transformed metals ($\Omega_i^P = \frac{4}{3}\pi(R_i^P)^3$; i = A, B). Ω_A^P and Ω_B^P are fixed by equation (6) plus the condition that the excess volume of formation is zero, that is,

$$\Omega_A^0 + \Omega_B^0 = \Omega_A^P + \Omega_B^P . \quad (7)$$

The transformed metals, with atomic volumes Ω_i^P and electron densities $n_i^P(\mathbf{r})$ (i = A, B) are now cut up into cells and these are placed at the appropriate alloy lattice sites. This procedure sets up the reference alloy. Finally, after relaxation of the electron density to reach its ground state $n_{AB}(\mathbf{r})$, the charge transfer Q_3 becomes

$$Q_3 = \int_{\Omega_A^P} [n_{AB}(\mathbf{r}) - n_A^P(\mathbf{r})]\, d\mathbf{r} = -\int_{\Omega_B^P} [n_{AB}(\mathbf{r}) - n_B^P(\mathbf{r})]\, d\mathbf{r} . \quad (8)$$

The situation is illustrated in figure 1. This reference alloy was introduced by Alonso and Girifalco [37] in a study of the heat of formation of alloys.

From the density functional theory of alloy formation formulated by Hodges and Stott [38], as well as from chemical intuition [1], one expects that, for small charge transfer, Q is linearly proportional to the difference $\Delta\mu$ between the internal electronic chemical potentials of the atomic cells in the reference alloy

$$Q_1 \propto (\mu_B^0 - \mu_A^0) , \quad (9a)$$

$$Q_2 \propto (\mu_B^* - \mu_A^*) , \quad (9b)$$

$$Q_3 \propto (\mu_B^P - \mu_A^P) . \quad (9c)$$

This expectation is also built up in semiempirical theories [1, 12, 13], although the semiempirical chemical potential (semiempirical electronegativity) can not be easily related to a reference alloy. μ_i^0 (i = A, B) is the internal chemical potential of the pure metal at the equilibrium volume Ω_i^0. μ_i^* and μ_i^P are the internal chemical potentials of the pure metal at the transformed volumes Ω_i^* or Ω_i^P.

3. **Results.** — The electron density of the reference alloy (that is, $n_i^0(\mathbf{r})$, $n_i^*(\mathbf{r})$ and $n_i^P(\mathbf{r})$; i = A, B) has been

Table I. — *Difference of chemical potential between the* B *and* A *cells of the reference alloy and electronic charge transfer.* $\Delta\mu$ *is given in atomic units and* Q *in electron units.*

	Model 1		Model 2		Model 3	
Alloy (A-B)	Q_1	$\mu_B^0 - \mu_A^0$	Q_2	$\mu_B^* - \mu_A^*$	Q_3	$\mu_B^P - \mu_A^P$
Mg-Ca	− 0.39	− 0.016 6	0.25	0.064 1	0.08	0.044 3
Mg-Sr	− 0.53	− 0.020 1	0.35	0.085 8	0.11	0.058 4
Mg-Ba	− 0.58	− 0.021 3	0.40	0.094 5	0.13	0.064 2
Ca-Sr	− 0.16	− 0.003 6	0.11	0.024 1	0.04	0.016 7
Ca-Ba	− 0.24	− 0.004 7	0.17	0.034 7	0.05	0.023 6
Sr-Ba	− 0.08	− 0.001 2	0.05	0.010 5	0.02	0.007 2
Na-K	− 0.22	− 0.000 0	0.11	0.031 4	0.04	0.027 5
Na-Rb	− 0.28	− 0.000 7	0.14	0.042 0	0.05	0.033 8
Na-Cs	− 0.37	− 0.002 7	0.20	0.053 0	0.08	0.042 6
K-Rb	− 0.07	− 0.000 8	0.03	0.009 1	0.01	0.007 4
K-Cs	− 0.17	0.002 7	0.10	0.022 9	0.04	0.018 5
Rb-Cs	− 0.11	0.001 9	0.06	0.014 1	0.02	0.011 4
Mg-Li	− 0.33	− 0.017 4	− 0.38	− 0.028 2	0.05	0.044 8
Al-Li	− 0.83	− 0.060 1	− 0.58	− 0.014 9	0.11	0.116 3

computed by using a self-consistent density functional pseudopotential method [39], applied previously by the authors to study the elastic properties of pure metals [40-42]. The pseudopotential used is Ashcroft's model potential [43]. The only parameter in this pseudopotential is the ionic empty core radius. This radius has been chosen by requiring that the theoretical equilibrium atomic volume equals the experimental value. The ground state electron density $n_{AB}(\mathbf{r})$ of the alloy has been obtained by an extension of the same method to alloys. The method has been recently used to calculate the heat of formation of disordered alloys of simple metals [44]. In the computation of $n_{AB}(\mathbf{r})$, the alloy is separated in two types of atomic cells (A cells and B cells) and appropriate matching conditions are imposed at the cell boundaries. In the alloy, each element is characterized by the same pseudopotential used for the pure metal. Calculations have been performed for twelve homovalent alloys (six alkaline alloys and six alkaline-earth alloys) and two heterovalent alloys (Li-Mg and Li-Al). The results are given in table I. Three sets of results are given in this table.

The first set gives the charge transfer Q_1, according to model 1, and the difference $[\mu_B^0 - \mu_A^0]$ between the electrochemical potentials of the pure metals. The second set gives the charge transfer Q_2, according to model 2, and the difference $[\mu_B^* - \mu_A^*]$ between the internal chemical potentials of the (transformed) metals with equal atomic volume. The third set gives the charge transfer Q_3, according to model 3, and the difference $[\mu_B^P - \mu_A^P]$ between the internal chemical potentials of the (transformed) metals with equal cell boundary electron density. Table I shows that the sign of $[\mu_B - \mu_A]$ depends on the election of the reference alloy. It is positive for all alloys in model 3. The same happens in model 2 except for the two heterovalent alloys. The situation is very different in model 1, where $[\mu_B^0 - \mu_A^0]$ is negative except for K-Cs and Rb-Cs. Also the sign of the charge transfer Q, depends on the model. If the model is internally consistent, the electronic charge will flow from the cells with the higher chemical potential to the cells with the smaller chemical potential. Since Q has been defined as the excess number of electrons in the A cells, Q and $[\mu_B - \mu_A]$ should be of equal sign if the model is internally consistent. Table I shows that this condition is violated by two alloys, K-Cs and Rb-Cs, in model 1. Equations (9) form a more precise statement of the internal consistency requirement. The analysis is provided in figure 2, where the charge transfer is plotted against the difference of chemical potential. In this figure $\Delta\mu$ is defined positive, that is

$$\Delta\mu = \mu_+ - \mu_- , \qquad (10)$$

where μ_+ is the higher of (μ_A, μ_B) and μ_- is the lower of (μ_A, μ_B). The charge transfer Q is defined positive if the flow of electrons is in the right direction, that is, from the cells of high chemical potential (μ_+) to the cells with low chemical potential (μ_-). As we have already mentioned, model 1 is found unsuccessful because : *a*) Q_1 is negative in two cases, *b*) many alloys with a similar (and small) $\Delta\mu$ have widely differing values of Q_1. The interpretation of this failure is the following one : figure 1 shows that the electron density is discontinuous at the boundaries between A and B cells. This discontinuity can be smoothed out by a transfer of electrons from the cells with the higher electron density to the cells with the smaller electron density. The charge transfer induced by the density mismatch can, in some cases, oppose the charge transfer induced by $\Delta\mu^0$. The two exceptions in figure 2 (K-Cs and Rb-Cs) correspond to a situation in which the effect of $\Delta n^0(R^0)$ dominates. In conclusion, the driving force for charge transfer in model 1 is not $\Delta\mu^0$, but the combined effect of $\Delta\mu^0$ and $\Delta n^0(R^0)$. This combined function can not be easily defined, and this model 1 is not a convenient one to study charge transfer effects.

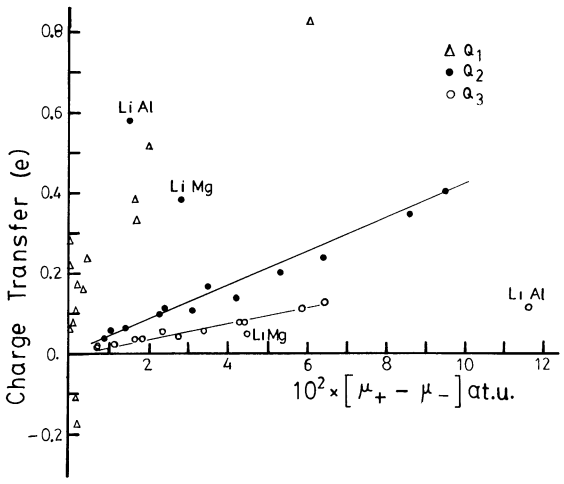

Fig. 2. — Electronic charge transfer *versus* the difference of internal chemical potential $\Delta\mu$ in the reference alloy for the alloys presented in table I. $\Delta\mu$ is defined as positive.

Models 2 and 3 are more successful. The sign of the charge transfer agrees with the expectations from the chemical potential difference in the reference alloy. Both models give rise to a linear relation between Q and $\Delta\mu$ for the alloys with $\Delta Z = 0$. ΔZ is the difference of valence between the two components of the alloy. The two alloys with $\Delta Z \neq 0$ do not fit into this particular linear relation, but the results for $\Delta Z = 0$ suggest that other linear relations will also be obtained for alloys with $\Delta Z = 1$, $\Delta Z = 2$, etc. In conclusion, figure 2 disfavours model 1. In this context, models 2 and 3 are both internally consistent. In model 2 the density is also discontinuous across the boundaries between unequal cells of the reference alloy. But since this discontinuity is much reduced, compared to model 1, the problems of model 1 are not present in model 2.

These three models can be further compared in a plot of Q *versus* the empirical electronegativity

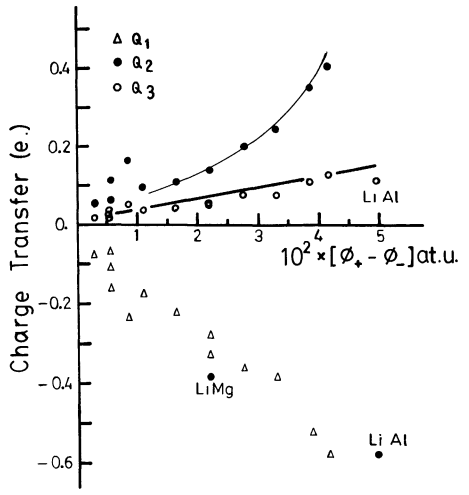

Fig. 3. — Electronic charge transfer *versus* the difference of empirical electronegativity. $\Delta\phi$ is defined positive.

difference, $\Delta\phi$. The scale of Miedema *et al.* [12, 13] has been used for this purpose. The results are given in figure 3. $\Delta\phi$ has been defined positive, that is

$$\Delta\phi = \phi_+ - \phi_- , \qquad (11)$$

where ϕ_+ is the largest and ϕ_- is the smallest of (ϕ_A, ϕ_B), ϕ_A and ϕ_B being the empirical electronegativities of metals A and B. Q is defined positive if the flow of electrons is in the direction predicted by $\Delta\phi$, that is, from the metal of electronegativity ϕ_- to the metal of electronegativity ϕ_+. To make contact with equation (10) and figure 2 we must notice that chemical potential and electronegativity have opposite signs. In fact, Parr *et al.* [35] have defined the electronegativity of an atom as the negative of the electronic chemical potential obtained from the density functional theory. Figure 3 shows that model 1 fails again because Q_1 has, for all these alloys, the wrong sign. Model 2 fails for alloys with $\Delta Z \neq 0$. Finally, model 3 is in agreement with empirical expectations, since the sign of Q_3 agrees in all cases with the sign of $\Delta\phi$. The figure shows that the function $Q_3 = Q_3(\Delta\phi)$ is approximately linear for small $\Delta\phi$.

4. **Discussion and conclusions.** — The three reference alloy states analysed in this paper have been used by several workers in connection with the transfer of electronic charge in metallic alloys. The reference alloy corresponding to model 1 has been used by Tamaki *et al.* [45]. They found that, in liquid Mg-Sn alloys, electrons are transferred from Sn cells to Mg cells. This direction of the charge flow disagrees with the expectations from the empirical electronegativity scales [13]. This is a common defect of the definition of charge transfer in model 1, as we have shown in figure 3. In consequence, we conclude that the pure metal atomic volumes are not useful reference volumes in the alloy. A separation of the alloy in equal-volume atomic cells has also been used by several authors [38, 46-52] and it corresponds to model 2 of this paper. The definition of charge transfer given by this model is more successful, but it also presents some difficulties, as figure 3 shows. This means that the Wigner-Seitz cells of a binary alloy do not have much physical significance in connection with charge transfer. Finally, the definition of charge transfer induced by model 3 does not present the problems of the other two models. First, it is internally consistent, that is, the charge transfer Q_3 is proportional to the difference of chemical potential between the atomic cells of the reference alloy, and second, it is consistent, in all the cases studied, with the expectations from the empirical electronegativity scales. This fact makes model 3 a convenient framework to study the electronic charge transfer. The reference alloy with neutral cells of volumes Ω_A^P, Ω_B^P and electron densities $n_A^P(\mathbf{r})$ and $n_B^P(\mathbf{r})$ is similar, in spirit, to the valence state introduced by Parr *et al.* [35] for molecules.

We therefore conclude that the volumes Ω_A^P and Ω_B^P are a convenient measure of the effective volume of atoms A and B in a binary alloy, and that Q_3 is a convenient measure of the effective charge. The energy effect associated to the charge transfer is considered in other papers [37, 38, 44]. Due to the transfer of electronic charge, a lowering in the energy of the alloy is obtained, which, in the small charge transfer regime, can be written (for the $A_{0.5}$ $B_{0.5}$ alloy)

$$\Delta H_{\text{ionic}} = -\tfrac{1}{4} Q_3(\mu_B^P - \mu_A^P) . \qquad (12)$$

Nevertheless, two comments are necessary. First, we stress that the discussion of charge transfer given in this paper is restricted to simple alloys formed by nontransition metals. In the case of transition metal alloys, changes in the electronic configuration at a site which conserve the total number of electrons at the site (that is, an interchange of d and s-p electrons conserving the number of s-p plus d electrons at the site) occur in addition to charge transfer between atoms at neighbour sites. These configurational changes at a site are very important for the cohesion of transition metal alloys and the intersite charge transfer may not be the optimum characterization of the charge transfer.

Second, our discussion does not imply that the energetic effect associated to the charge transfer is responsible for the energy of cohesion of the alloy (with respect to the pure metals). In other words, we are not advocating an ionic picture of alloy formation. What we have treated here is the ionic contribution to the heat of formation. But other contributions exist. For instance, electron density mismatch contributions [11-13, 37]. These contributions are taken into account in model 3. Covalent contributions also exist which are crucially important in transition metal alloys [53-55]. A convincing theory of cohesion in transition metal alloys has been given by several authors [53-56].

The picture of alloy formation provided by model 3 is correct in particularly simple classes of alloys, like alloys formed by two alkali metals or two alkaline-earth metals. This has been recently shown by the authors [44] by comparing the heat of formation calculated from the two steps of model 3 with the heat of formation obtained by direct subtraction of energies calculated using the density functional formalism.

Acknowledgments. — The authors thank the support from Comisión Asesora de Investigación.

References

[1] PAULING, L., *The Nature of the Chemical Bond.* (Cornell University Press, Ithaca) 1960.

[2] Bennett, L. H. and Willens, R. H., Editors, *Charge Transfer and Electronic Structure of Alloys.* The Metallurgical Soc. of AIME (Warrendale, Pa) 1974.

[3] NETHERCOT, A. H., *Chem. Phys. Lett.* **59** (1978) 346.

[4] NETHERCOT, A. H., *Chem. Phys.* **59** (1981) 297.

[5] SIEGBAHN, K., NORDLING, C. N., JOHANSSON, G., HEDMAN, J., HEDÉN, P. F., HAMRIN, K., GELIUS, U., BERGMARK, T., WERME, L. O., MANNE, R. and BAER, Y., *ESCA applied to free molecules.* (North Holland, Amsterdam) 1969.

[6] SHIRLEY, D. A., *Adv. Chem. Phys.* **23** (1973) 85.

[7] NEWTON, J. H. and PERSON, W. B., *J. Chem. Phys.* **64** (1976) 3036.

[8] PASTERNAK, A., *Chem. Phys.* **26** (1977) 101.

[9] RAY, N. K., SAMUELS, L. and PARR, R. G., *J. Chem. Phys.* **70** (1979) 3680.

[10] NETHERCOT, A. H., *Phys. Rev. Lett.* **33** (1974) 1088.

[11] MIEDEMA, A. R., DE BOER, F. R. and DE CHÂTEL, P. F., *J. Phys. F : Metal Phys.* **3** (1973) 1558.

[12] MIEDEMA, A. R., DE BOER, F. R. and BOOM, R., *CALPHAD* **1** (1977) 341.

[13] MIEDEMA, A. R. and DE CHÂTEL, P. F., *Theory of Alloy Phase Formation.* Ed. L. H. Bennet. The Metallurgical Soc. of AIME (Warrendale, Pa) 1980, p. 344.

[14] MIEDEMA, A. R., *Z. Metallkde* **69** (1978) 455.

[15] MIEDEMA, A. R. and DORLEIJN, J. W. F., *Surf. Sci.* **95** (1980) 447.

[16] MIEDEMA, A. R. and NIEUWENHUYS, B. E., *Surf. Sci.* **104** (1981) 491.

[17] MIEDEMA, A. R. and VAN DER WOUDE, F., *Physica B* **100** (1980) 145.

[18] SHAM, T. K., WATSON, R. E. and PERLMAN, M. L., *Mössbauer spectroscopy and its chemical applications.* Ed. J. G. Stevens and G. K. Shenoy. Advances in Chemistry Series No 194 (Amer. Chem. Soc.) 1981, p. 39.

[19] MOOSER, E. and PEARSON, W. B., *Acta Crystallogr.* **12** (1959) 1015.

[20] PHILLIPS, J. C., *Rev. Mod. Phys.* **42** (1970) 317.

[21] ST JOHN, J. and BLOCH, A. N., *Phys. Rev. Lett.* **33** (1974) 1095.

[22] MACHLIN, E. S., CHOW, T. P. and PHILLIPS, J. C., *Phys. Rev. Lett.* **38** (1977) 1292.

[23] ZUNGER, A., *Phys. Rev. Lett.* **44** (1980) 582.

[24] ZUNGER, A., *Structure and Bonding in Crystals.* Vol. 1. Ed. M. O'Keeffe and A. Navrotsky. (Academic Press. New York) 1981, p. 73.

[25] WATSON, R. E. and BENNETT, L. H., *J. Phys. Chem. Solids* **39** (1978) 1235.

[26] DARKEN, L. S. and GURRY, R. W., *Physical Chemistry of Metals* (Mc Graw Hill, New York) 1953.

[27] CHELIKOWSKY, J. R., *Phys. Rev. B* **19** (1979) 686.

[28] ALONSO, J. A. and SIMOZAR, S., *Phys. Rev. B* **22** (1980) 5583.

[29] LÓPEZ, J. M. and ALONSO, J. A., *Physica B* **113** (1982) 103.

[30] SINGH, V. A. and ZUNGER, A., *Phys. Rev. B* **25** (1982) 907.

[31] KAUFMAN, E. N., VIANDEN, R., CHELIKOWSKY, J. R. and PHILLIPS, J. C., *Phys. Rev. Lett.* **39** (1977) 167.

[32] SOOD, D. K., *Phys. Lett. A* **68** (1978) 469.

[33] ALONSO, J. A. and LÓPEZ, J. M., *Philos. Mag. A* **45** (1982) 713.

[34] HOHENBERG, P. and KOHN, W., *Phys. Rev. B* **136** (1964) 864.

[35] PARR, R. G., DONNELLY, R. A., LEVY, M. and PALKE, W. E., *J. Chem. Phys.* **68** (1978) 3801.

[36] KOELLING, D. D., *Rept. Progr. Phys.* **44** (1981) 139.

[37] ALONSO, J. A. and GIRIFALCO, L. A., *J. Phys. F* **12** (1978) 2455.

[38] HODGES, C. H. and STOTT, M. J., *Philos. Mag.* **26** (1972) 375.

[39] MEYER, A., UMAR, I. H. and YOUNG, W. H., *Phys. Rev. B* **4** (1971) 3287.

[40] LÓPEZ, J. M., IÑIGUEZ, M. P. and ALONSO, J. A., *Phys. Status Solidi B* **100** (1980) 701.

[41] LÓPEZ, J. M. and ALONSO, J. A., *Phys. Status Solidi B* **104** (1981) 307.

[42] GONZÁLEZ, D. J. and ALONSO, J. A., *Physica B* **112** (1982) 67.

[43] ASHCROFT, N. W., *Phys. Lett.* **23** (1966) 48.

[44] IÑIGUEZ, M. P., ALONSO, J. A., GONZALEZ, D. J. and ZORITA, M. L., *J. Phys. F* **12** (1982) 1907.

[45] TAMAKI, S., TSUCHIYA, Y. and WASEDA, Y., *J. Phys. F* **11** (1981) 1865.

[46] RATTI, V. K. and ZIMAN, J. M., *J. Phys. F* **4** (1974) 1684.

[47] CRAGG, D. M. and FLETCHER, G. C., *J. Phys. F* **7** (1977) 87.

[48] ALONSO, J. A. and GIRIFALCO, L. A., *J. Phys. Chem. Solids* **38** (1977) 869 ; **39** (1978) 79.

[49] INGLESFIELD, J., *Acta Metall.* **17** (1969) 1395.

[50] MORUZZI, V. L., WILLIAMS, A. R. and MARCUS, P., *Charge Transfer and Electronic Structure of Alloys,* Ed. L. H. Bennett and R. H. Willens, The Metallurgical Soc. of AIME (Warrendale, Pa) 1974, p. 149.

[51] MORUZZI, V. L., WILLIAMS, A. R. and JANAK, J., *Phys. Rev. B* **10** (1974) 4856.

[52] YAMASHITA, J., WAKOH, S. and ASANO, S., *J. Phys. Soc. Jpn.* **21** (1966) 53.

[53] WILLIAMS, A. R., GELATT, C. D. and MORUZZI, V. L., *Phys. Rev. Lett.* **44** (1980) 429.

[54] PETTIFOR, D. G., *Phys. Rev. Lett.* **42** (1979) 846.

[55] VARMA, C. M., *Solid State Commun.* **31** (1979) 295.

[56] WILLIAMS, A. R., KÜBLER, J. and GELATT, C. D., *Phys. Rev. B* **19** (1979) 6094.