

Solid solubilities in divalent alloys

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Solubility trends for a variety of solutes in seven prototypical simple divalent metal hosts are examined. In this paper, we present a macroscopic model for predicting solubility trends. This model should prove more successful than the classical approaches of Hume-Rothery or Darken and Gurry. The method is an extension of a cellular scheme developed by Miedema, and involves two chemical coordinates. These coordinates, which characterize charge transfer between neighboring cells and the charge-density mismatch at cellular boundaries, appear to be superior coordinates for determining solubilities trends, as contrasted with classical coordinates such as atomic size or electronegativity. Moreover, we note the Miedema's coordinates are shown to accurately describe recent experiments that involve site energy preferences of metastable implants in Be. This dramatic result suggests that Miedema's coordinates may describe metastable systems and as a consequence are more widely applicable than might be expected. Finally, we note that our results have consequences for a pseudopotential description of intermetallic alloys and compounds.

I. INTRODUCTION

The prediction of extensive solid solutions for a given solute and solvent in intermetallic alloys is a formidable problem, and it remains one of the major unsolved problems in metallurgy. No metal can be prepared in a state of absolute purity and, therefore, the nature of impurity solubility in a host lattice is of more than academic interest. We know that the impurities are commonly found in the form of solid solutions with the host lattice, and that the detailed properties of a metal such as tensile strength, malleability, ductility, etc., may depend crucially on impurity additions and impurity-based solid solutions. Unfortunately, however, very little theoretical progress in this area has been achieved over the last 40 years, and many fundamental questions persist. For example, a clear understanding as to the nature of interatomic forces between impurities and metal-host atoms has yet to be elucidated. Also, we still lack direct evidence, or predictive power, for the preferred geometric arrangement of arbitrary impurities in a host-metal lattice which would enable us to distinguish between substitutional and interstitial site preferences.

Two events have occurred in the last five years that lead us to believe that some of the formidable barriers to understanding solid solubility in intermetallic alloys may be removed. The first event has been the realization of an extraordinarily successful global scheme that predicts and systematizes heats of formation for regular intermetallic alloys. The scheme has been developed by Miedema and collaborators,¹ and is phenomenological in origin. It is an isotropic cellular theory based upon two elemental variables which characterize charge transfer between neighboring cells and a

charge-density (or surface-tension) mismatch at the cellular boundary. Since the direct quantum-mechanical calculation of alloy thermodynamic properties is almost prohibitive, the scheme of Miedema provides us with hope that a workable and general, albeit phenomenological, description of alloy properties may yet be achieved.

The second event consists of recent experimental work by Kaufmann and coworkers.² In their experiments, ion-implantation techniques have been coupled with ion-channelling measurements. The use of ion-implantation techniques provides a wide range of new and unique metastable alloy systems which cannot be obtained by the usual metallurgical procedures. Perhaps the most dramatic result of these experiments which so far have concentrated on Be as a solvent host, is that the *site* geometries of the solute atom have, for the first time, been directly and systematically determined. Since the nature of a solid solution may differ radically depending on whether the solute occurs substitutionally or interstitially, the latter advance may be described as "revolutionary".

Traditionally, the study of solid solutions has attempted to form criteria by which interstitial and substitutional solutions may be distinguished.³ For an interstitial solution to be formed in equilibrium with the melt, certain conditions must be met. We might expect, for example, that unless the impurity atom is quite small, so that solute atoms may enter the interstices or holes in the solvent lattice, interstitial solutions would be unlikely as contrasted with substitutional solutions.

At this point, we would like to illustrate, schematically, how such criteria might be defined. Consider the case of a self-interstitial. The maximum self-interstitial solubility will occur when considerable strains are present in the lattice. In

fact, we expect these strains to be sufficiently disruptive so that locally the host lattice resembles the liquid state. We may then attempt to estimate the enthalpy change associated with the long-range structural energy which is lost as we pass from the ideal crystal to this disrupted site. We write $\Delta H_{si} = nkT_f X_i$, where T_f is the melting point of the host, X_i is the molar fraction of self-interstitials, and k is the Boltzmann's constant. In order to estimate n we consider two limiting cases. If we ignore bonding effects of the self-interstitial, then classically by the equipartition theorem we expect $n=3$. However, this estimate for n is too small and a more realistic value for n is possible. Consider a typical liquid metal for which in the melt each atom has on the order of six nearest neighbors. If we assume pairwise interactions and include some second-neighbor energies, the value of n is more probably $n=4-5$. Given an ideal entropy of mixing, we may estimate X_i^i with a value of $n=4.5 (\pm 1)$. If the free-energy change vanishes, then the entropy term $T\Delta S$ equals ΔH_i . For the entropy of mixing we have $\Delta S \cong kX_i \ln X_i$ and, consequently, $X_i \cong \exp(-nT_f/T)$. Suppose as a typical room temperature we choose $T = \frac{1}{2}T_f$; then $X_i = e^{-2n} = e^{-9} = 10^{-4}$ [using our suggested limits $n \leq 4.5 (\pm 1)$ we have $10^{-5} \leq X_i \leq 10^{-3}$].

Of course, interstitial-impurity solubilities will be different from those of self-interstitials because of enthalpy site differences (i.e., bonding differences from interstitial and substitutional sites). Nevertheless, for simple host lattices, on the average we expect a room-temperature solubility limit of $X_i \geq 0.01$ at.% to be indicative of a *substitutional* solution rather than an *interstitial* solution.

This concept has been confirmed in Kaufmann's² work. His results demonstrate conclusively that for a close-packed beryllium host extensive solubility *always* implies a substitutional geometry for the solute atom, and restricted solubilities imply an interstitial geometry for the solute. Of course, a crucial question yet to be resolved is the critical value of solubility X_i which distinguishes interstitial from substitutional solid solutions. In the case of Be it turns out that a solubility $X_i \geq 0.01$ at.% implies a substitutional geometry; for solubilities $X_i \leq 0.01$ at.% an interstitial geometry is preferred. One of the goals of this paper is to account for trends in the critical solubility X_i from one close-packed host to another.

To accomplish this task we need a more thorough understanding of the nature of microscopic forces present between the solute and solvent atoms. For example, if the dominant forces are long range, then we expect the procedures used in previous theoretical investigations, which have concentrated

on Fermi-surface and band-structure effects in alloys, to be applicable to solid solubilities.^{3,4} Actually, this is *not* the case. It has been established by a number of workers that the predominant forces affecting alloy solubilities are short range and isotropic in nature. As noted by Heine and Weaire, among others,^{3,4} both theoretical and experimental evidence suggests that in an alloy each atom approximately retains its volume as if it were a small macroscopic piece of the bulk element. This idea, in conjunction with recent efforts by Miedema, has led to a cellular picture of alloys where directional or shear forces play a secondary role, as contrasted with volume-dominated or hydrostatic forces. We emphasize this point of view because band-structure effects, or Fermi-surface effects, which result from long-range forces, have been used successfully in analyzing anisotropic properties of simple hcp metals, e.g., c/a ratios.⁴

To rephrase the situation, we note that Pearson⁵ has pointed out that the main criterion for observing energy-band effects in a series of related alloys is that nearest-neighbor coordination should not change significantly from one structure to another, so that the major contribution to the enthalpy remains unchanged. In general, nearest-neighbor or short-range interaction energies are much greater than the small electron energies associated with band-structure effects. For the case of an arbitrary solute in a host, we expect the coordination to change from solute to solute, and we do not expect long-range forces to be consequential. So, while band-structure effects have been used by Hume-Rothery, Raynor, Heine, and Weaire^{3,4} among others to describe c/a ratios of hcp metals, these effects will be of only secondary interest to us.

Since treatments that concentrate on Fermi-surface effects are not appropriate for solid solutions, we need to approach this problem from a fresh perspective. In doing so we wish to take advantage of all the empirical and experimental evidence available to us. It is, therefore, unfortunate that our knowledge of metals is less complete than that for simple insulators or semiconductors. For many metals, the electronic structure is characterized only for energies at or very near the Fermi surface. While the largest set of data for intermetallic-alloy formation is the thermochemical information contained in binary phase diagrams,⁶ the data here are often complex. Regrettably, no generally accepted procedure exists for extracting interatomic interactions from phase diagrams which could in turn be applied to the problem of solid solubility. Moreover, with respect to defects or impurities, there has been few quantitative

studies. One exception to this latter point is the case of fast interstitial diffusion.^{7,8} Here a number of systems have been examined and trends have been studied, but only for a half dozen or so hosts, e.g., Pb, Sn, In, Tl, etc.

An approach that we might attempt is the direct quantum-mechanical calculation of thermochemical parameters. However, because of the very small energy differences involved in such calculations, the prediction of alloy properties from *ab initio* calculations does not appear to be feasible. A practical approach to these problems has therefore concentrated on the use of elemental-configuration variables. Classical examples of configuration variables include atomic size and electronegativity. The goal of constructing such variables is to describe the essential features of interatomic interactions, e.g., charge transfer, within the framework of a simple scale or index. Using elemental coordinates or variables, we hope to systematize the chemical data on solubility trends.

In this paper we shall confine our attention to simple close-packed divalent metals (e.g., Be, Mg, Zn, etc.). As solvents these metals provide an excellent base for a theoretical study. For example, these are common metals, thus extensive experimental data exist for their properties. Since these metals are all close-packed, relaxation effects associated with any long-range strain fields should be similar for each host. Finally, other studies on these metals and their alloys have been performed: *c/a* ratios, structural trends, and ordered phases have been examined.^{3,4}

In this paper, we propose to apply a recent set of chemical coordinates to the problem of solid solubility. The coordinates are those derived by Miedema and his collaborators. While Miedema's coordinates serve as the basis for our discussion, we shall extend them and introduce other coordinates as well. The paper will be organized as follows: in Sec. II we will review some recently devised chemical coordinates and the scheme of Miedema, in Sec. III we will discuss the applicability of the Miedema coordinates to the problem of solid-solution formation, in Sec. IV we will explicitly apply the scheme to several systems and discuss the extension to the general problem; and in Sec. V we will review our conclusions and basic results.

II. MODERN ELEMENTAL CONFIGURATION VARIABLES

While the Hume-Rothery criterion^{3,9} along with the graphical scheme of Darken and Gurry¹⁰ provide a credible basis for predicting solubilities, an improved scheme is clearly desirable. For example,

the Hume-Rothery size criterion is quite accurate in providing a necessary, but not sufficient, condition for extensive solubility (e.g., a maximum solubility in excess of 5 at.%). It has been determined¹¹ that if the atomic sizes of the solute and solvent atoms are not within ~15% of each other, then Hume-Rothery's rule predicts, with an accuracy of ~95%, that extensive solid solutions will not be formed. On the other hand, if the solute and solvent sizes are nearly equal, then Hume-Rothery's rules are of little use. Approximately 50% of these solvent-solute combinations will not result in extensive solutions.¹¹

In this context we seek more precise coordinates, i.e., coordinates that will accurately describe the essential features of solid solutions. Several new coordinates have been introduced in the last twenty years,¹²⁻¹⁷ but the motivation of these coordinates was to systematize structural energies and not solubility data. While these coordinates are useful and much knowledge has been gained from their application to structural properties, they do not appear appropriate for the problem at hand.

The chemical coordinates that we seek should be widely applicable and, preferably, derived from quantum-mechanical variables. Unfortunately, such coordinates do not exist at present. Nevertheless, the coordinates of Miedema and his collaborators appear to most closely approximate our prescription. Miedema's coordinates are empirical, and this is their greatest deficiency. However, a quantum-mechanical justification of Miedema's work has, at least partially, been presented by Chelikowsky and Phillips.^{16,17}

The work of Miedema is based upon an analysis of well over 500 intermetallic-alloy systems. Within his scheme two elemental coordinates are introduced. As indicated earlier, the coordinates are ϕ^* and n_{WS} ; he relates these variables to the work function of the elemental metal and to the electron density of the elemental metal at the boundary of the Wigner-Seitz cell, respectively. In Miedema's cellular scheme for binary alloys, a difference in ϕ^* between constituents results in a charge transfer across boundaries between dissimilar cells. This transfer provides a negative "potential-energy-like" contribution to the heat of formation. A difference in n_{WS} , conversely, implies the need to expend energy in order to smooth the discontinuity in the electron density at the cellular boundary. This "kinetic energy" type of contribution provides a positive term to the heat of formation. The delicate interplay between the two opposing contributions decides the resultant sign for the heat of formation.

In practice, Miedema has determined his two co-

ordinates by making small empirical adjustments in an initial set of coordinates determined from bulk elemental data (e.g., work functions, compressibilities, and molar volumes). The adjustments were executed so that perfect agreement was nearly achieved for the signs of the heats of formation for several hundred alloy systems.

The form Miedema takes for ΔH_f is

$$\Delta H_f = -P(\Delta\phi^*)^2 + Q(\Delta n_{ws}^{1/3})^2 - R\theta_d\theta_s, \quad (1)$$

where P , Q , and R are positive constants. R is presumed to represent a constant p - d hybridization term which vanishes unless the alloy system combines simple s and transition d metals. Because there are 100+ empirical variables in Miedema's scheme (i.e., two elemental variables (ϕ^* , $n_{ws}^{1/3}$) for over 50 elements), and because of some ambiguities inherent in a phase-diagram analysis, doubts have been raised about the physical significance of Miedema's variables. However, a connection has been made between the Miedema coordinates and spectroscopically defined nonlocal^{16,17} pseudopotentials for simple metals and metalloids. This connection reduces Miedema's 50+ adjustable variables to eight coupling parameters which relate orbitally dependent radii to ϕ^* and n_{ws} .

One of the ambiguities in discussing binary phase diagrams is the relative importance of enthalpy and entropy dominated processes. Miedema overcomes this problem to a certain extent by examining only the *signs* of ΔH_f and presenting rules for the sign determination. If ordered phases exist in an alloy systems and persist to low temperatures, then ΔH_f is assumed to have a negative sign. If no ordered phases exist and the solubility is not extensive (i.e., less than 10 at.%), then ΔH_f is assumed to have a positive sign.

In this manner, Miedema reduces a vast, sometimes complex, phase-diagram compilation to a data formed by a binary set of signs. Miedema's scheme works exceptionally well in ascertaining the signs for ΔH_f ; however, it is more efficacious for transition-transition metal systems and non-transition-transition metal systems than for non-transition-nontransition metal systems. A significant observation is made by Miedema¹ in the latter case: namely, the scheme is more reliable for *liquid* nontransition-nontransition metal alloy systems than for the corresponding solid alloys. This situation suggests that Miedema's scheme fails to describe systems in which structural or covalent energies play a significant role. The isotropic nature of (1) precludes any structural description of ΔH_f , so that this limitation of Miedema's scheme is not surprising.

III. APPLICABILITY OF CELLULAR COORDINATES

An ideal binary solution, e.g., the mixing of two ideal gases, occurs with no net change in enthalpy and an increase in entropy. For a solid intermetallic solution, the ideal situation is never achieved. The enthalpy term may be nonzero because of charge transfer between the immersed solute atom and the host or because of lattice strains introduced by size and valence mismatches between the solute and solvent atoms. Moreover, the entropy term is never as large as that obtained from ideal solution expressions because of short-range order or clustering effects about the impurity. Nevertheless, provided the enthalpy change is not too positive the entropy term will prevail and the free energy will be reduced by the formation of solid solutions. A large negative change in enthalpy, however, may not favor solid solutions, even though the free energy is reduced. For this case often an ordered phase is obtained and the formation of solid solutions is inhibited.³

The requirement of a "small" enthalpy change relative to the entropy term for the formation of extensive solid solutions is implicit in the rules of Hume-Rothery³ and the scheme of Darken and Gurry.¹⁰ Qualitatively, if the sizes of solute and solvent atoms are radically different the elastic strain energies will be too severe to form extensive solutions; this effect should be reflected in a large and positive ΔH_f . For large electronegativity differences, we expect the electrochemical factor to make enthalpy changes large and negative through charge-transfer effects. When electrochemical factors dominate, ordered phases become strongly favored by electrostatic considerations.^{1,3} For these systems, structural energies become important and we anticipate problems in any scheme that does not include directional or structurally dependent forces.

If enthalpy trends are important for the systematization of solubility data, then the coordinates of Miedema's scheme should be an appropriate choice for systematizing solubility trends. However, the Miedema scheme was not developed primarily to treat solubility problems, and several aspects of Miedema's work prevent its direct application to solubility problems. The scheme is restricted in that it predicts only *signs* for heats of formation with a high degree of accuracy. The quantitative predictive powers of the scheme work best for systems in which binary-compound formation exists with the concentration of one component exceeding ~20%.¹ In this regime, enthalpy processes dominate and entropy considerations are not of much concern. When entropy considerations become significant, we expect correlations with Miedema's

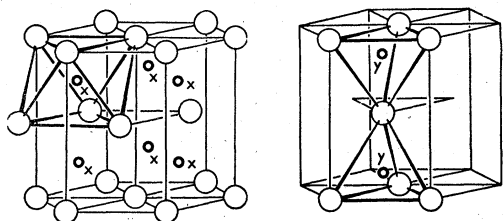


FIG. 1. Interstitial holes in close-packed hexagonal structures. The octahedral holes are labeled by x , the tetrahedral holes by y . (After Hume-Rothery, Ref. 3.)

coordinates, but not necessarily in the form of Eq. (1). More importantly, for low concentrations of the solute and large electrochemical differences between the host and the solute, structural energies will dominate entropy changes. In these cases, we expect significant errors to be produced by the isotropic force model of Miedema.

To illustrate both the appropriateness and the accuracy of Miedema's coordinates to the problem of impurity atoms in a metal host, we consider the recent ion implantation work of Kaufman *et al.*² In this work implanted impurities in Be were formed for approximately 25 elements. The implanted elements were found to occupy one of three sites: a substitutional site (s), an interstitial octahedral hole site (o), or an interstitial tetrahedral hole site (t). The site positions are indicated in Fig. 1. At this point we should stress the essential differences between an implanted impurity and an impurity that is introduced from the melt. Implanted alloys involve the direct injection of the solute. During the implant process the injected element at the end of range simulates a system at a very high temperature. The substitutional implants may easily be formed in this case by the creation of Be self-interstitials.

While we can understand the creation of substitutional implants, it is very surprising that interstitial sites are occupied at all. If touching spheres were inserted in the interstitial sites, they would be quite small. If r_i is the radius of such a sphere and r_h corresponds to the host radius, then for a close-packed lattice we have $r_i(t) = 0.225r_h$ and $r_i(o) = 0.41r_h$. Employing Hume-Rothery's³ criteria for the formation of extensive interstitial solutions prepared from the melt, we see that only hydrogen would be small enough to form an interstitial solution with Be. Since Kaufmann *et al.*² find several large interstitial implants, e.g., Cs, Ge, I, Xe, etc., it follows that these systems are probably metastable and are accompanied by large long-range strain fields.

At first, it might appear hopeless to apply any of the coordinates discussed so far to this problem. After all, the impurity configurations in most

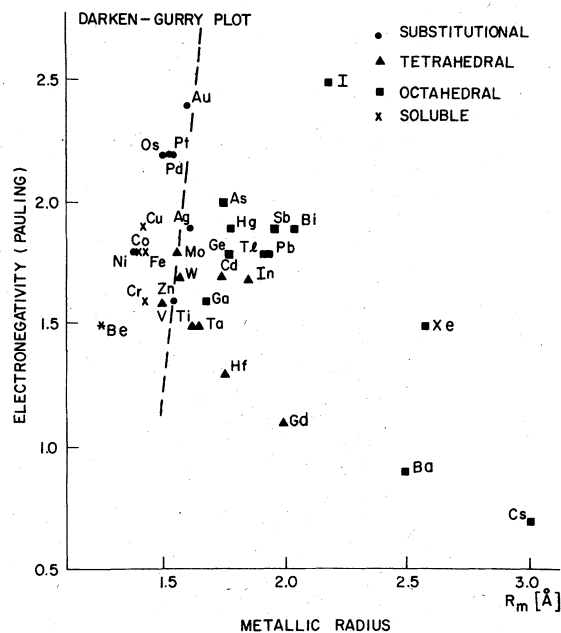


FIG. 2. Darken-Gurry map for metastable Be microalloys. The ordinate is the Pauling electronegativity (Ref. 23) of the element and the abscissa is the metallic radius defined from the molar volume (Ref. 1). Symbols are identified in the figure. The dashed line shows an approximate division of substitutional and interstitial impurities.

cases correspond to metastable "microalloys" and coordinates such as Miedema's are derived from systems in stable thermal equilibrium. In fact, the usual approaches do not appear to work. A few cases will illustrate the situation. One approach is to consider the electron charge density as a single coordinate. We define the density coordinate in terms of the r_s parameter: $r_s = (3Z/4\pi\Omega_c)^{1/3}$, where Z is the number of valence electrons in a bulk-unit-cell volume Ω_c . This index has often been used to describe trends in simple metals (i.e., a nearly-free-electron treatment).¹⁸ However, for the problem at hand, no statistically significant correlation is achieved using r_s . The majority of octahedral site implants have larger r_s values than do the substitutional site implants, but the implants residing in octahedral and tetrahedral sites are not separated. We know that r_s as a chemical index works better for simple metals than for transition metals, so its failure to produce an accurate separation is not surprising.

A more metallurgical approach to this implant problem is displayed in Fig. 2. Darken and Gurry coordinates,¹⁰ i.e., atomic size and electronegativity, are used in an attempt to systematize the data. The attempt is only partially successful. Simple domains which separate "size-electronegativity" space into simple s , t , or o domains cannot be

interesting analogy. In Miedema's scheme $n_{WS}^{1/3}$ correlates roughly in an inverse fashion with atomic size. We note the Miedema coordinates of Be place it near the boundary between substitutional and tetrahedral site domains, i.e., Be self-interstitials should occupy tetrahedral sites. This placement results in a value of $n_{WS}^{1/3}$ (Be) which is larger than many of the substitutional implants and *all* of the octahedral site implants. Thus, as with the Darken and Gurry map, it appears that large atom implants (e.g., Cs and Ba) chemically prefer to reside in the very small octahedral hole sites—a surprising result.

One additional comment is in order concerning the site expansion via Miedema's coordinates [Eq. (2)]. The reader will note that we have not included any terms of the form $\Delta R = \Delta R(o, t) - \Delta R(s)$. According to Miedema, R corresponds to a p - d hybridization term. By setting $\Delta R = 0$ we assume the p - d hybridization term is independent of the site of the implanted element. This approximation may be justified in part by an examination of the energy distribution of p -like states in the Be conduction band. If an energetically broad distribution of p states exists in Be, as suggested by band calculations, then it is reasonable for us to assume that the local density of p states is constant, so that the hybridization term will not change radically from one implant site to another. This would allow the omission of a ΔR term in Eq. (2) without serious loss of accuracy.

IV. EXTENSION AND APPLICATION OF CELLULAR COORDINATES TO SOLID SOLUBILITY

The striking success of Miedema's coordinates, especially as contrasted to the limited usefulness of the Darken and Gurry map for the Be implants, leads us to believe that his coordinates will be well suited for describing the general situation of foreign metal atoms in a metal host. However, before presenting a detailed discussion of solid solubility trends in terms of Miedema (ϕ^* , n_{WS}) plot, we will illustrate and comment on the Darken-Gurry procedures.¹⁰ We will concentrate on two prototypical simple close-packed metal hosts, Mg and Pb. Darken and Gurry solubility maps for these hosts are displayed in Figs. 4 and 5.

In our solubility maps, we do not categorize the solubilities as previous workers have.^{10,11} Earlier studies have used the following binary classification scheme: if the maximum solid solubility for a specific solute exceeded 5 at.% the solubility was characterized as "extensive", otherwise, the solubility was characterized as "limited". Obviously, such a classification scheme does not allow fine distinctions. Moreover, the 5-at.% dividing line figure refers to the maximum solubility achieved at any temperature. This value may be quite different from the largest solubility achieved at room temperature. As a consequence, the previous classification schemes were difficult to use in making any cross comparisons.

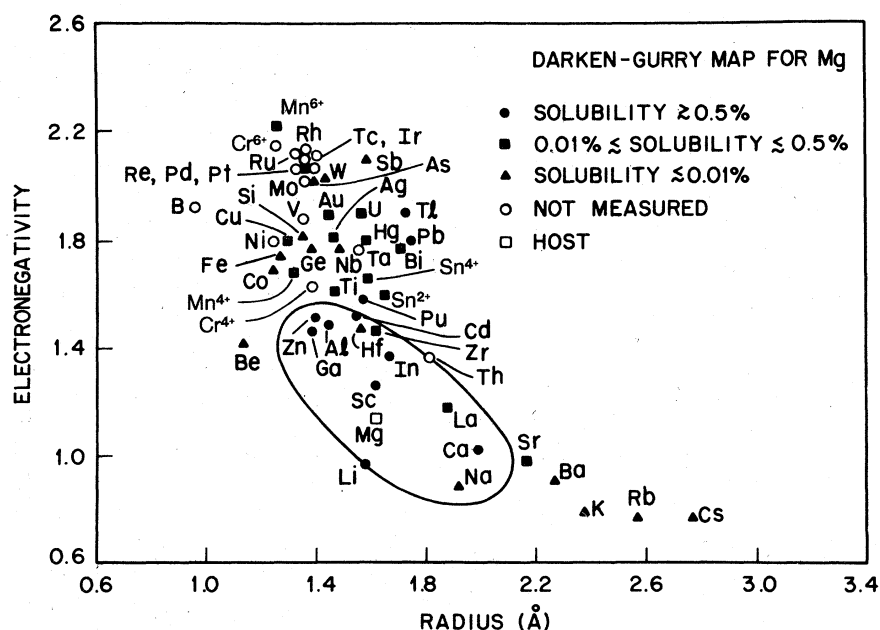


FIG. 4. Darken-Gurry map for Mg. The solubility divisions are discussed in the text. The enclosed region around Mg is to indicate a high-solubility domain. The electronegativities are from Gordy and Thomas (Ref. 24); the atomic radii are from Pauling (Ref. 23).

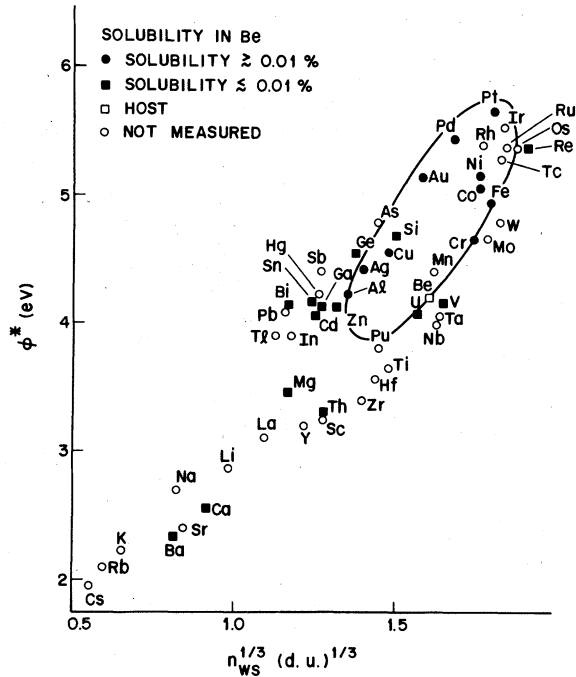


FIG. 6. Miedema plot for intermetallic solid solubility in a Be host. Note the close analogy with Fig. 3. This suggests that extensive solubility implies a substitutional solution. d. u.: density units.

configuration has often been speculative and often the evidence for a substitutional or interstitial site preference has been obtained from quite indirect evidence. Here (Figs. 3 and 6) we have direct evidence of the site choice for foreign species in Be. Moreover, that we are able to systematic the data in a simple fashion using the Miedema coordinates is a spectacular result.

With reference of Fig. 6 we note that there exist only two possible exceptions to our rule that extensive solubilities imply substitutional solutions and restricted solubilities imply interstitial solutions. The two exceptions are Zn and Si. Si has most recently been characterized as having "negligible" solubility in Be,⁶ however, the Miedema coordinates for Si place it in a region where we would expect the solubility of Si in Be to be in excess of 0.01 at.%. This current placement may be the consequence of poorly defined Miedema coordinates for Si. In general, Si strongly prefers tetrahedral coordination with respect to interatomic bonding in solids. This low coordination implies that structural or directional forces are important in determining enthalpy trends for silicides. However, Miedema's scheme does not consider directional forces. The solubility data indicate that Zn is insoluble in Be; however, Kaufmann's² experiments suggest that Zn implants are substitutional in Be

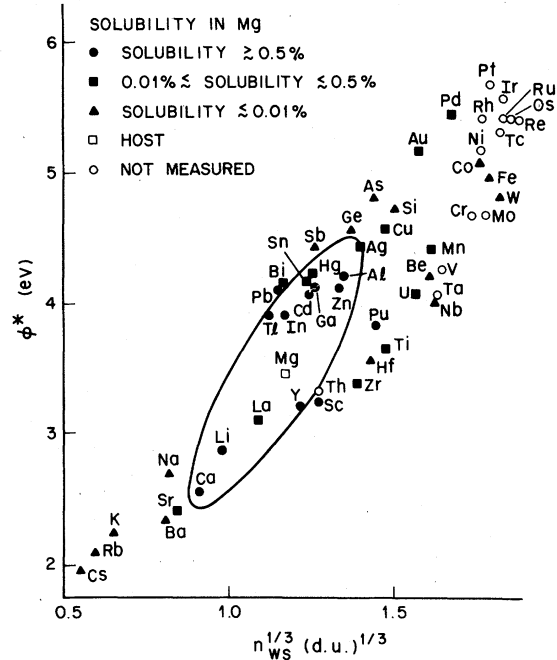


FIG. 7. Miedema plot for intermetallic solid solubility in a Mg host. Note the improved separation as contrasted with the Darken-Gurry plot in Fig. 4.

and not interstitial as we might expect from Figs. 3 and 6. Since the solubility data for the Zn-Be system is somewhat dated,⁶ a reexamination of this system might prove interesting.

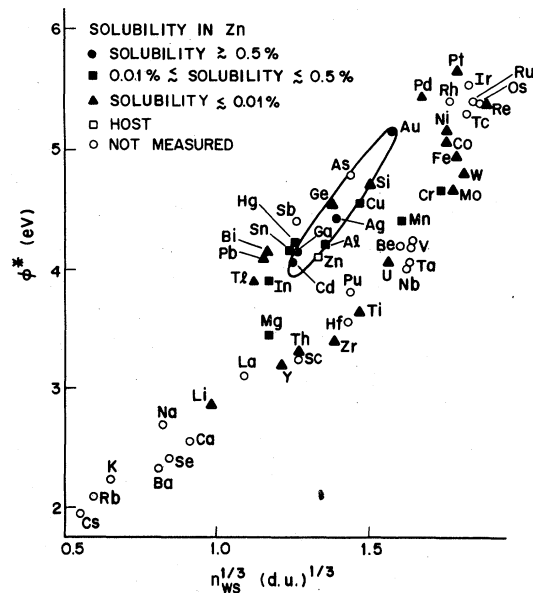


FIG. 8. Miedema plot for intermetallic solid solubility in a Zn host. Note the impotency of Zn as a solvent. Only four metals will dissolve extensively in Zn: Cd, Ga, Ag, and Au.

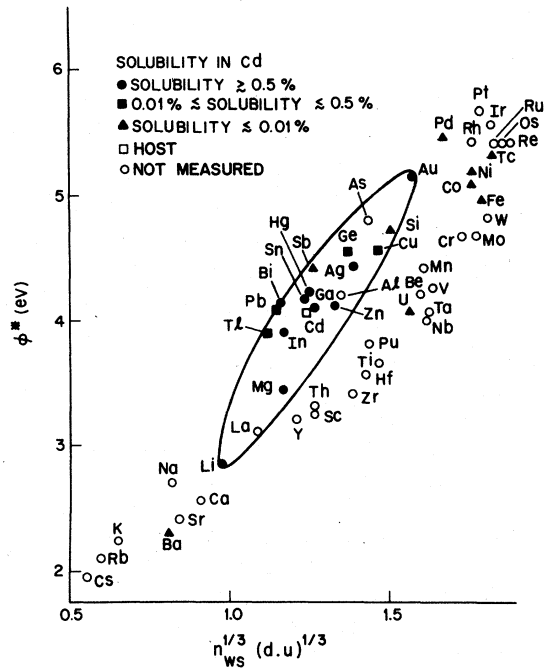


FIG. 9. Miedema plot for intermetallic solid solubility Cd. Note the site of the high-solubility region as compared to Zn.

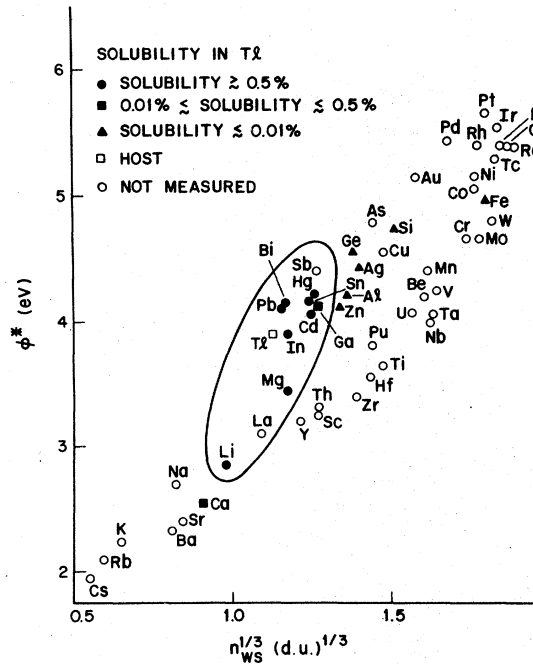


FIG. 11. Miedema plot for intermetallic solid solubility in a Tl host lattice.

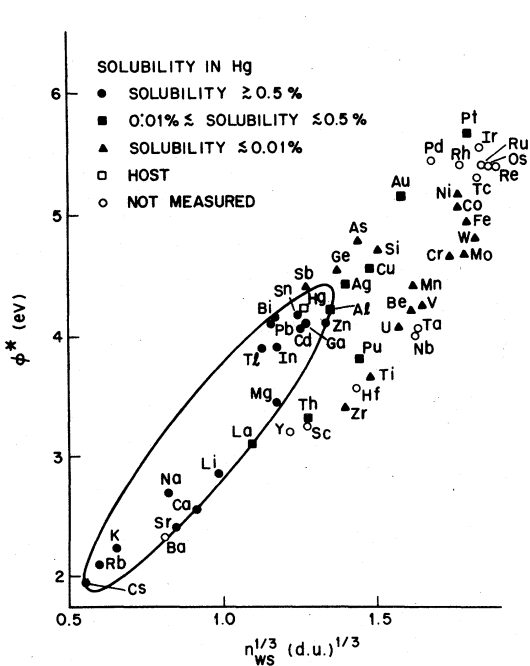


FIG. 10. Miedema plot for intermetallic liquid solubility in Hg. Note the analogous behavior of liquid solubilities to the solid solubility situation as typified in Fig. 9.

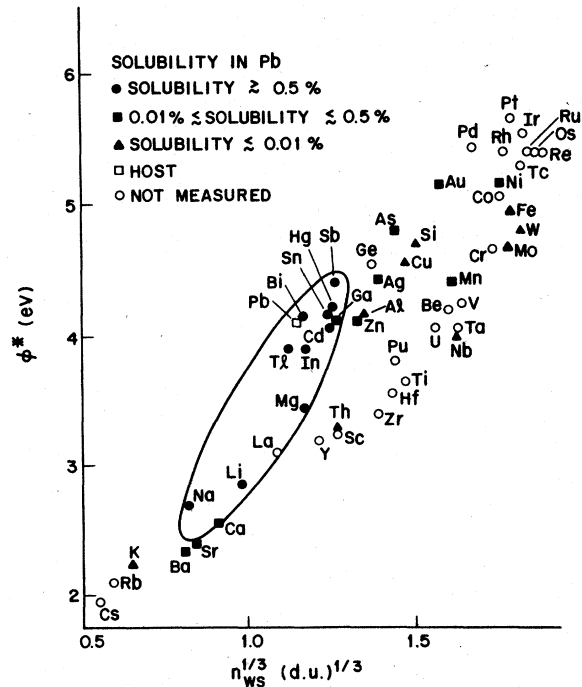


FIG. 12. Miedema plot for intermetallic solid solubility in a Pb host. Note the improved separation for the highly soluble elements as contrasted with Fig. 5.

In Figs. 7–12 we present solubility data in terms of Miedema (ϕ^* , n_{ws}) plots for several simple close-packed metals. We include Hg in our discussion although, properly speaking, the crystal structure of Hg is not close packed. In our study we hope to outline general trends rather than concentrate on specific successes or failures. For each plot we have sketched simple domains that contain solutes of fairly high solubility on the host. These domains are for illustrative reference and are not meant to be definitive boundaries. In sharp contrast to Darken and Gurry maps we find, in the majority of cases, that simple domains that contain very high percentages of extensively soluble elements can be constructed.

However, the construction of domains is only the first step in a comprehensive analysis. Once we have established a schematic scheme which results in a complete or nearly complete separation, the next step is to provide rules for defining boundaries of the domains. The second step is a very difficult one that may require analysis beyond the Miedema scheme. Nevertheless, we shall provide a procedure for describing trends in the domain constructions.

A survey of the data presented in Figs. 6–12 reveals some interesting solubility trends. For example, the extensively soluble elements tend to cluster in elliptical domains about the host. This is the case with a Mg host, elements which are extensively soluble, e.g., Pb, Tl, In, Y, and Cd, cluster about Mg as opposed to elements that show restricted solubility, e.g., Cs, Hf, Nb, W, and Co. In all cases, the ellipses tend to be elongated along an axis defined by $\phi^* \sim 3n_{ws}^{1/3}$. In many cases the solvent host coordinates are displaced from the origin of the ellipse. Examples of this situation are found in the hosts: Be, Zn, Hg, and Pb. However, it should be stated that with the possible exception of Pb the other hosts are somewhat atypical. Be, for example, is a first-row element and as such has a different core structure than the other hosts. Moreover, the data base for Be-based alloys is not extensive, and as a consequence the coordinates of Be may not be well defined. Like Be, Zn is atypical in that only a few elements are extensively soluble in it. In such situations the boundary of the elliptical domain is very difficult to define. For Hg the data presented are for alloys; we present the data mainly for completeness. Parenthetically we note that since the liquid data are amenable to an almost complete separation between soluble and insoluble elements, our scheme may work well for both solid and liquid alloys.

For many solid solutions the maximum solute concentration as a function of temperature is given

by³

$$\ln X_m = \Delta H_f^0 / RT + \ln X_0, \quad (3)$$

where X_m is the molar fraction of solute and ΔH_f^0 is the energy change per solute atom. We would like to use Miedema's scheme to estimate ΔH_f^0 , e.g., as in (1). In this fashion we would have a formula for estimating the domain size and shapes. If we assume the form of (1) for an approximate ΔH_f^0 , the results do *not* agree with Figs. 6–12. Equation (1) would imply hyperbolic patterns; instead, we observe elliptical patterns for our domains. This result is surprising and a bit distressing. However, we should realize that since the Miedema scheme was constructed for binaries where $X_m \approx 0.2$ – 0.8 , there is no reason to believe ΔH_f^0 as from (1) will adequately describe $X_m \ll 0.1$. Moreover, (3) is based on the assumption of an *ideal* solution, which is certainly not justified when compound formation is favored. In fact, Miedema has demonstrated that as electrochemical differences become large, compound formation becomes favored.^{1,3} Since compound formation involves directional interatomic forces, the Miedema scheme fails in such situations. Nevertheless, we still expect the Miedema coordinates to be superior to the classical Darken-Gurry coordinates. The only difficulty is that (1) will no longer be appropriate for estimating ΔH_f .

We may improve Miedema's scheme by considering anisotropic forces. To illustrate this, consider the size of solubility domains in Figs. 6–12. In some of these domains only a few elements are present (e.g., Zn); in others (e.g., Pb), almost a dozen elements are present. In order to obtain an index for the solubility potency of a host lattice, we extend Miedema's isotropic approach and include anisotropic shear forces. We propose to examine the potency of the solvent in terms of a dimensionless index by which we characterize shear deformability. To define this index we examine the ratios C/B and C'/B where B is the bulk modulus, and $C = C_{44}$ and $C' = C_{66} = \frac{1}{2}(C_{11} - C_{12})$ are elastic constants in the customary notation.¹⁹⁻²¹

We display the behavior of these two indices for seven close-packed simple metals (Fig. 13). Before discussing any trends in Fig. 13, we note the following expectations. First, we note that a soft or deformable lattice should have a small value for C/B or C'/B (a liquid would have a vanishing ratio); conversely, a hard lattice should possess relatively large values for these coordinates. Second, we expect a monotonic decline in both C/B and C'/B as we descend a column in the Periodic Table. This trend would be consistent with the ideas of Mooser and Pearson¹³: directional bonding forces are stronger for low principal quantum num-

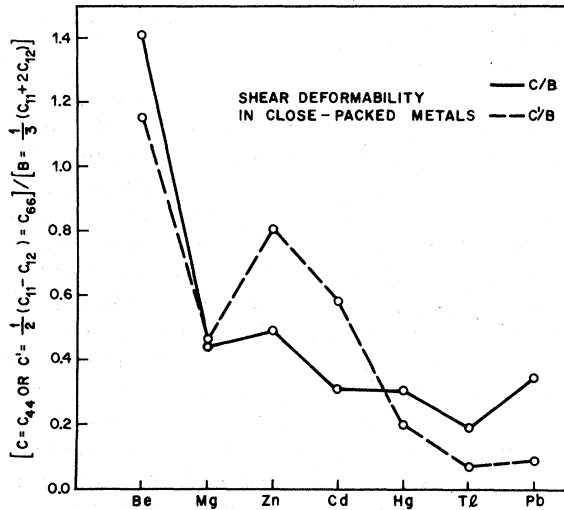


FIG. 13. Shear deformability for simple-close-packed metals (including Hg). For definitions of C_{11} , C_{12} , C_{44} , and C_{66} see Ref. 19. The experimental values are from Refs. 19–21.

ber elements than for high principal quantum number elements. We see that these two ideas are, in part, upheld by the experimental values shown in Fig. 13. For example, we observe small values of $(C/B, C'/B)$ for Pb and Tl, which we know have lattices that may be easily deformed. Conversely, Be and Zn have "hard" lattices and larger values of $(C/B, C'/B)$. However, we do not observe a monotonic decrease in C/B or C'/B . Note the behavior of Zn in the series Be-Mg-Zn-Cd-Hg. This anomaly is traceable to the d -core electrons which occur first in the case of Zn.

From Fig. 13 we expect C'/B to be a better coordinate than C/B . C'/B experiences more variation describing the column than does C/B , and as a consequence appears to be more sensitive to changes in the lattice properties. We can justify this speculation more precisely by examining the C and C' shear modes. In Fig. 14 we display the interstitial hole sites for a face-centered cubic lattice (our arguments will also be valid for a hexagonal close-packed lattice). A shear wave along the $\langle 110 \rangle$ axis separates the C and C' modes as shown. The motions of the atoms are displayed with the cube center serving as a fixed origin. We see motions associated with a pure C mode move the corner atoms toward interstitial holes.

In terms of our deformability index C'/B , we hope to characterize the capacity of a host to dissolve other elements. A problem arises, however, in how to define precisely a measure of the potency of the solvent (especially considering the quality of the solubility data). We have chosen to define an index as follows. We arbitrarily specify a critical

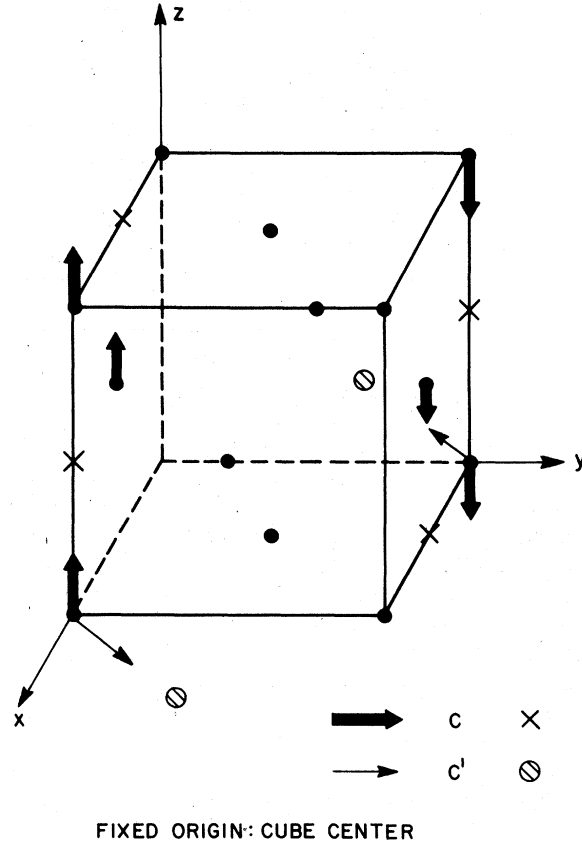


FIG. 14. Atomic displacements for a shear wave along the $\langle 110 \rangle$ direction in a cubic-close-packed lattice. C and C' modes separate for this wave. Note that the C' mode displaces the corner atoms toward their nearest neighbor, while the C mode displaces the atoms toward interstitial holes. An analogous displacement occurs for hexagonal-close-packed lattices.

solubility and determine the number of elements for a given host which equal or exceed the critical value. (The more elements soluble beyond the specified solubility, the more potent the host will be.) This index is a bit arbitrary, but, nevertheless, it provides a simple and widely applicable measure. It is preferable to an index which, for example, measures the area of a domain as we have, at present, no quantitative *ab initio* means of constructing the boundary.

We expect a soft lattice (small C'/B) to be a more potent solvent than a hard lattice (large C'/B). To make this idea quantitative in Fig. 15 we plot B/C' and the number of elements that are soluble to greater than 0.5 at.% for the simple close-packed metals; Be-Mg-Zn-Cd-Hg. The results are quite dramatic. The nonmonotonic behavior of B/C' (or C'/B in Fig. 13) is reflected in the number of extensively soluble elements. Only three or four elements are extensively soluble in the harder lat-

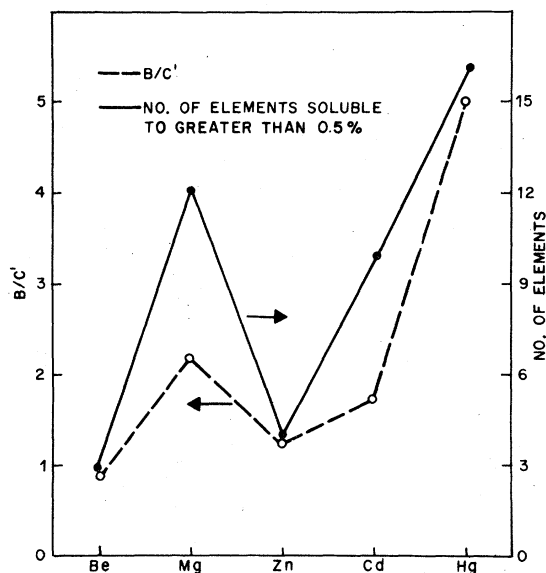


FIG. 15. This plot demonstrates the usefulness of B/C' as an index of solvent potency for close-packed metals. A soft lattice, e.g., Mg, has a large value of B/C' and is capable of dissolving numerous metallic solutes. Conversely, a hard lattice, e.g., Be, has a small value of B/C' and will only dissolve a few elements extensively.

tices of Be and Zn, while ten or more elements are soluble in the softer lattices of Mg, Cd, and Hg. This confirms our comments and expectations with respect to the importance of the specific shear deformability of the host lattice with respect to solubility properties.

V. CONCLUSIONS

In this paper we have attempted to review and update the problem of solid solubilities in intermetallic alloys. Our efforts have been stimulated by two important developments. The first is a series of dramatic experiments by Kaufmann *et al.*² In their measurements they have determined in a direct fashion the preferred site locations of impurities in a metal host. Heretofore, there existed no direct evidence for impurity site locations (although in a few cases, e.g., fast-diffusion data, indirect evidence is available). Kaufmann's experiments have also provided us with new and unique alloy systems which could not be prepared by chemical means.

Through an analysis of his results we were able to suggest a relationship between the extent of solubility and whether interstitial or substitutional solution formation is favored. In essence, if a solute is soluble to more than a critical solubility limit, then substitutional solutions will be formed instead of interstitial solutions. Conceptually and historically this is an important result. It appears not to

have been generally recognized in previous investigations that such a criterion was possible.

The second development which has made a review of solubility problems possible is the dramatic success of a recently devised scheme to predict heats of formation of intermetallic alloys. The scheme was invented by Miedema *et al.*,¹ and involves two elemental configurational variables that are of a semi-empirical origin. As indicated in the text *ab initio* calculations appear to be a fruitless approach, and we have tried to invoke chemical scaling arguments in which Miedema's variables play a predominant rule.

We have also presented arguments that in Miedema's scheme¹ short-range isotropic forces are implicitly assumed. Further, we noted that this assumption is responsible for the phenomenal success of Miedema's work, as short-range isotropic forces predominate in most intermetallic alloys. We, therefore, excluded from our discussion approaches that have been based on long-range force descriptions such as these involving Fermi-surface contacts with the Brillouin zone. The long-range force arguments are applicable only for isostructural alloy systems, and are not appropriate for solubility trends.

While Miedema's scheme can successfully account for solubility trends in metals, as contrasted with Darken and Gurry's¹⁰ scheme, it does not appear to be completely adequate for forming a description of solubility trends. Miedema plots are quite useful for defining domains of extensive solubilities; however, the size of the domains is not explicable solely in terms of Miedema's coordinates. To define trends in domain sizes, or in essence the potency of the solvent, we must include directional forces or anisotropic coordinates. We, therefore, introduced an index C'/B , where C' is an elastic constant and B is a bulk modulus for the host. We found that this coordinate was capable of accurately describing the nearest-neighbor interatomic forces. Further, it correctly accounted for the nonmonotonic trends in the potency of the solvent in the Be-Mg-Zn-Cd series. This nonmonotonic behavior is completely inexplicable in terms of Fermi-surface variations as those proposed to account for several properties of hcp metals including c/a ratios.

In addition to a description of intermetallic alloys, our studies have consequence to pseudopotential theory. While pseudopotential calculations, in general, have been most useful in accounting for the electronic structure of solids, they have exhibited a notable lack of success for impurities or defects in metals. For example, a recent pseudopotential calculation for the heat of formation of vacancies in Al yielded a negative (unphysical) val-

ue.²² This calculation, and most such calculations, have employed a "soft"-core pseudopotential. Our studies of nonlocal hard-core pseudopotentials devised by Bloch and Simons,¹⁵⁻¹⁷ along with the present investigation, suggest that these potentials may provide a superior approach. As we have noted, short-range forces play a significant role in determining the properties of defects in alloys. This suggests the core regions of the potential are more significant for the problem at hand. In this context, the hard-core potential seems more physical (especially since we have found these potentials capable of structural separations). This idea is reinforced by the fact that trends in Miedema's ϕ^* coordinate may be accurately defined in terms of the Bloch-Simons potential.¹⁵⁻¹⁷

Finally we note that the results of Kaufmann's experiments and our studies may have important ramifications with respect to other studies of defects in metals, e.g., the phenomena of fast interstitial diffusion.^{7,8} A classic example of a fast diffuser is Au in a Pb host. In this system Au diffuses several orders of magnitude faster than the self diffusion of Pb. A crucial question in the fast interstitial diffusion system is the nature of the diffusion mechanism. There is extensive indirect evidence that suggests fast diffusers are not substitutional. Experiments such as Kaufmann's may illuminate the preferred impurity geometry and conform the interstitial nature of fast diffusers. In addition, the coordinates that we have used to distinguish site differences (Fig. 3) may be useful to systematize the activation energies of fast interstitials.

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APPENDIX

As the reader has no doubt noted, we must have accurate coordinates to achieve the separation obtained in Fig. 3 between the *s*, *t*, and *o* domains. In particular, the region of *p* metals (e.g., In, Cd, Zn, Al, Ga, Sn, etc.) requires a very delicate determination of the coordinates. Indeed, our original analysis using Eq. (2) failed to obtain an exact separation, and we found it necessary to alter (very slightly) the Miedema coordinates for a few elements: Al, Cd, Ca, In, and Ga to obtain an exact separation. With the possible exception of In, the shifting of Miedema's original coordinates did not damage the quality of his fits with respect to the phase diagrams. The modified coordinates are listed in Table II, and the phase-diagram data are

summarized in Table III.

To review the motivation for obtaining the new coordinates we shall briefly discuss each case. With respect to Al, Miedema used values of $\phi^* = 4.20$ and $n_{WS}^{1/3} = 1.39$. These values placed Al fairly deep within the substitutional domain. However, Al is known not to be substitutional, but rather interstitial. Whether Al is an octahedral or tetrahedral interstitial is unknown.²⁵ If we wish our plot in Fig. 3 to reflect this fact we should move Al toward the domain boundary (between *s* and *t*). If we alter $n_{WS}^{1/3}$ to 1.34 we accomplish this, but we do not seriously affect Miedema's fit for Al alloys. Miedema's original coordinates make four errors: Al-Tl, Al-Si, Al-Ge, and Al-Sb. (In all these cases we expect structural energy terms to invalidate Miedema's isotropic approach). Only two possible errors are introduced with $n_{WS}^{1/3} = 1.34$: Al-Ga and Al-Zn. In either case, the phase-diagram data do not yield an unequivocal sign for the heat of formation.

In the case of Ga, Miedema uses nearly identical coordinates for both Ga and Zn. This seems unphysical; furthermore, it places Ga in the *t* region while it is observed to be *o*. If we move Ga as Al, which would seem to follow by analogy, we place Ga in the octahedral region and actually improve the phase-diagram data. Miedema's original coordinates make six errors (Table III); however, our modified coordinates make five errors.

Similar arguments may be made for Cd and In. In these cases, they were originally located in the *o* domain, but experimentally they should be placed in the *t* region. Thus we attempted a larger value for $n_{WS}^{1/3}$ on both cases. For Ce, Miedema's fit was unhurt. In both the original and modified coordinates, six errors were made (Table III). Unfortunately, in the case of In we do not improve Miedema's fit; however, the modified coordinates are only slightly worse. Originally, Miedema's coordinates for In make two errors (In-Ge and In-Bi). Our modified coordinates make four errors. Inter-

TABLE II. Modified Miedema coordinates as suggested from the Be implant data. These coordinates, with the possible exception of In, will not affect the quality of Miedema's fits, and are compatible with the domains in Fig. 3.

Element	Original		Modified	
	ϕ^*	$n^{1/3}$	ϕ^*	$n^{1/3}$
Al	4.20	1.39	4.20	1.34
Ga	4.10	1.31	4.10	1.24
Cd	4.05	1.24	4.05	1.26
In	3.90	1.17	3.86	1.22
Ca	2.55	0.91	2.55	0.90

TABLE III. Signs for the heats of formation for binary intermetallic-alloy systems involving Al, Cd, In, and Ga. The signs given are from experiment (*E*), and as calculated from Eq. (1) using Miedema's original coordinates (*O*) and our modified coordinates (*M*) from Table II. If the heat of formation is positive we denote it by a (+) sign. If it is negative, then we use a (-) sign. In a few cases the value is unknown, but thought to be small but positive (O^+) or small but negative (O^-). Undetermined heats of formation are medicated by an (*X*). For rules in determining the signs from phase diagrams see Ref. 1 and the text.

Element	Al			Ga			In			Cd		
	(<i>E</i>)	(<i>O</i>)	(<i>M</i>)	(<i>E</i>)	(<i>O</i>)	(<i>M</i>)	(<i>E</i>)	(<i>O</i>)	(<i>M</i>)	(<i>E</i>)	(<i>O</i>)	(<i>M</i>)
Sc	-	-	-	-	-	-	-	-	-	-	-	-
Ti	-	-	-	-	-	-	-	-	-	-	-	-
V	-	-	-	-	-	-	+	+	-	-	+	-
Cr	-	-	-	-	-	-	+	+	+	+	+	+
Mn	-	-	-	-	-	-	-	-	-	+	-	-
Fe	-	-	-	-	-	-	+	+	+	+	+	+
Co	-	-	-	-	-	-	-	-	-	-	-	-
Ni	-	-	-	-	-	-	-	-	-	-	-	-
Y	-	-	-	-	-	-	-	-	-	-	-	-
Zr	-	-	-	-	-	-	-	-	-	-	-	-
Nb	-	-	-	-	-	-	-	-	-	-	-	-
Mo	-	-	-	-	-	+	+	+	+	X	-	-
Te	-	-	-	-	-	-	X	+	-	+	+	-
Ru	-	-	-	-	-	-	-	-	-	X	+	-
Rh	-	-	-	-	-	-	-	-	-	X	-	-
Pd	-	-	-	-	-	-	-	-	-	-	-	-
La	-	-	-	-	-	-	-	-	-	-	-	-
Hf	-	-	-	-	-	-	-	-	-	-	-	-
Ta	-	-	-	-	-	-	X	+	-	X	+	-
W	-	-	-	+	-	+	X	+	+	X	+	+
Re	-	-	-	X	-	-	X	+	-	X	+	+
Os	-	-	-	-	-	-	X	+	-	X	+	+
Ir	-	-	-	-	-	-	-	-	-	X	-	-
Pt	-	-	-	-	-	-	-	-	-	-	-	-
Th	-	-	-	-	-	-	-	-	-	-	-	-
U	-	-	-	-	-	-	-	-	-	-	-	-
Pu	-	-	-	-	-	-	-	-	-	-	-	-
Cu	-	-	-	-	-	-	-	-	-	-	-	-
Ag	-	-	-	-	-	-	-	-	-	-	-	-
Au	-	-	-	-	-	-	-	-	-	-	-	-
Li	-	-	-	-	-	-	-	-	-	-	-	-
Na	+	+	+	-	+	-	-	-	-	-	-	+
K	+	+	+	-	+	+	-	-	+	-	-	+
Rb	+	+	+	-	+	+	-	-	+	-	+	+
Cs	+	+	+	-	+	+	-	-	+	-	+	+
Be	+	+	+	+	+	+	+	+	+	+	+	+
Mg	-	-	-	-	-	-	-	-	-	-	-	-
Ca	-	-	-	-	-	-	-	-	-	-	-	-
Sr	-	-	-	-	-	-	-	-	-	-	-	-
Ba	-	-	-	-	-	-	-	-	-	-	-	-
Zn	0^+	+	-	+	+	+	+	+	+	+	+	+
Cd	+	+	+	+	+	+	0^+	+	-	-	-	-
Hg	+	+	+	+	+	+	-	-	-	-	-	-
Al	-	-	-	0^+	+	+	+	+	+	+	+	+
Ga	0^+	+	-	-	-	-	0^-	+	+	+	+	+
In	+	+	+	0^-	+	+	-	-	-	0^+	+	+
Tl	+	-	-	+	+	+	0^+	+	+	+	+	+
Si	+	-	-	+	-	+	+	+	+	+	+	+
Ge	+	-	-	+	-	-	+	-	-	+	-	-
Sn	+	+	+	+	+	+	0^-	-	-	0^+	-	-
Pb	+	+	+	+	+	+	0^-	-	-	+	+	+
As	-	-	-	-	-	-	-	-	-	-	-	-
Sb	-	+	+	-	-	-	-	-	-	-	-	-
Bi	+	+	+	+	+	+	+	-	-	+	+	+

estingly enough, the additional errors arise from In-Rb and In-Cs; Miedema's Cd coordinates also fail for these alloys.

Finally, with respect to Ca we suggest a slightly smaller value of $n_{WS}^{1/3}$ (Table II). We do not tabulate the new signs in Table III, because only one sign change arises from the original to modified case.

The sign of Ca-Ru changes from (-) to (+). No experimental determination has been made for this alloy system. We propose the smaller value of $n_{WS}^{1/3}$ to place Ca with the other alkali earths that are found to be in the *o* domain. In general, the reader should note that the small shifts shown in Table II are similar for Al and Ga, and for Cd and In.

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