Review
The relation between the electron to atom ratio and some properties of metallic systems

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Hume-Rothery and his co-workers demonstrated the importance of the electron-to-atom (e/a) ratio in controlling the range of stability of solid solutions, intermetallic compound formation and liquidus temperatures in metals and alloys. Since then, this parameter has been shown to vary in a systematic manner with a number of other properties such as the axial ratio of hexagonal phases, formation of defect phases, stacking fault energy, electronic specific heat coefficient, flow stress, superconducting transition temperature, stress corrosion cracking, elastic constants, activation energy for diffusion etc. These relationships are reviewed here to show that the e/a ratio constitutes a useful parameter for rationalizing the effect of solute additions, in dilute concentration, on several properties of the solvent matrix. This approach can also be used in a limited way even in concentrated alloys. © *2001 Kluwer Academic Publishers*

1. Introduction
The modification of the physical properties of materials is one of the principal aims of research in material science. After any physical property is measured, the question arises regarding its rationalization with composition. From an energetic point of view, the change in energy of a metal upon alloying can be attributed to the change in electronic energy or the misfit or strain energy [1]. The relative importance of both factors in controlling the change in the energy due to alloy formation is discussed in detail by Oriani [2–6], who states that whenever the misfit energy arising from the different atomic sizes of the solute or solvent is made the basis of estimating heat of solution, contradictory results are achieved for different alloy systems. Oriani further states that all changes in the energy of alloy system owe their origin to the electronic considerations. Proceeding on a similar basis, this article is a survey of the variation of the properties with the e/a ratio. In many cases, a pattern emerges whenever the magnitude of a physical property is plotted against the e/a ratio. A breakdown in the regularity of this relationship is usually an indication of significant changes in electronic structure of the matrix.

Hume-Rothery listed four factors of importance in relation to the electronic structure of alloys: (a) the difference between the electronegativities of the two metals, (b) a tendency for elements near the end of short periods and B subgroups to complete their octet of electrons, and a similar tendency to fill the d shell in later transition elements, (c) orbital type restrictions in structures with certain types of hybrid bonding and

(d) the formation of definite crystal structures at characteristic e/a ratios (equal to 3/2, 21/13 and 7/4) [7]. Hume-Rothery pointed out the importance of e/a ratio in controlling the phase stability and phase boundaries in binary alloys [8, 9]. Bradley generalized this concept and suggested that there is a tendency for many alloy phases to occur when the ratio of number of free valence electrons agrees with the monotonic sequence $[2n-1]/n$ where $n = 1, 2, 3, 4, 5, 6, 7$ [10]. The characteristic e/a ratio for intermetallic phases in Cu based alloy systems were shown to follow this sequence.

High quality data on the effect of the e/a ratio on the physical properties is present in the literature in a dispersed manner. While the role of e/a ratio in phase stability is well catalogued, it is not often recognized that this ratio can affect the mechanical behavior. This paper is in the nature of a tour-de-horizon to show that a single parameter can control diverse physical properties of metallic systems. A survey of the relationship of the e/a ratio with the following physical properties is presented:

(1) the range of stability of solid solutions,
(2) intermetallic compound formation,
(3) liquidus temperature in metals,
(4) the axial ratio of hexagonal phases,
(5) formation of defect phases,
(6) stacking fault energy,
(7) electronic specific heat coefficient,
(8) flow stress,
(9) superconducting transition temperature,
(10) stress corrosion cracking,

(11) elastic constants and

(12) activation energy for diffusion

All these properties may vary in a systematic manner with the e/a ratio. The extent and diversity of the relationship of e/a ratio to physical properties suggests that it may be a useful parameter for optimization of physical properties.

In a recent paper Ogwu and Davies [11] have described other applications such as the relationship between electronic structure and (a) dislocation motion and ductility in metals, intermetallics, semiconductors and ceramics, (b) formation of martensite in shape memory alloys, (c) hardness of carbides and borides, (d) work of adhesion between metals and ceramics, (e) transformation kinetics in steel, (f) transition metal oxide sintering additives on the densification of ceramics and (g) propagation of cavities in superplastic ceramics. In the last two decades, there has generally been very little work done in the style of Hume Rothery to make predictions based on simple parameters. Earlier work [12] used the Engel-Brewer theory for the electronic distribution in pure metals to correlate the e/a ratio with the bulk elastic moduli, cohesive energy, bond energy, atomic volume, heat of fusion and melting temperature. All these plots reveal fairly linear relations, with the bulk modulus more sensitively related to the electron concentration than the other physical properties. Recent references do not use the terminology used by Hume Rothery to express their results, so it is difficult to compare the older results with recent calculations. While being fully aware of the limitations of such ideas, we believe that documentation of the relationship between a broad spectrum of physical properties that show a correlation with the e/a ratio should be brought to light and that there is an obvious utility in the use of simple parameters to understand complicated electronic processes. Some of the explanations provided below are well known, but are included for the sake of completeness. The present approach has practical utility as well, providing a method for fine tuning the compositions for practical applications such as development of superalloys, change in elastic moduli of alloys, formation of metallic glasses and similar applications which are based on the above properties.

2. Theoretical consideration

The attempt to discuss the compositional variation of the physical properties on the basis of the e/a ratio implies that the nearly free electron gas assumption adequately describes the state of extra-core electrons even in alloys [13–15]. Mott pointed out that valence differences among the constituents of dilute alloys must be neutralized by excess electrons within a distance of atomic dimensions in order for long range electrical fields to be eliminated. The excess alloy charge must also be screened from the bulk metal in equilibrium to ensure electronic conductivity. Individual cells of an alloy, thus, preserve an electronic distribution quite similar to that in the pure metals. The net effect of alloying is to change the wave vector for electrons at the Fermi level without modifying the band structure of the matrix in any essential manner. It was shown that the cohesive energy is proportional to the Fermi energy [13]. Thus, through the dependence of the Fermi energy on the e/a ratio, the importance of e/a ratio in controlling the cohesion has been shown for monovalent metals. Its extension to more complicated situations is also possible. In evaluating the cohesive energy of the crystal, variations in the important contributions such as exchange interactions between closed shells of ions and kinetic energy of the lowest electronic state are small if the atomic volume is unaltered. Thus as long as large volume changes are avoided (which is valid for dilute alloys and over a limited concentration range in concentrated alloys) the major change in the cohesive energy of the crystal is again accounted by the change in Fermi energy. Within these constraints, a variation in the cohesive energy of the crystal with e/a ratio is again proportional to the Fermi energy. Valvoda and Sprucil [16] have shown that so long as the functional dependence of cohesive energy on volume is unchanged, the cohesive energy bears a constant ratio to several properties of the crystal such as specific heat, heat of fusion, compressibility, Debye temperature and energy for vacancy formation. Thus, so long as changes in the Fermi energy of the outer electrons makes a predominant contribution to the relative changes in the cohesive energy of the crystal, an interrelationship between e/a ratio and some physical properties of metallic matrices can be expected within the constraints noted above.

3. Atomic size consideration

Before discussing in detail the variation of the e/a ratio with specific physical properties, a consideration of the atomic size factor seems relevant as it has been extensively employed to discuss the effect of solute additions on the properties. The size factor is structurally important in the formation of Laves phases and interstitial compounds. Since the atomic size depends upon the charge of the nucleus, if the two atoms have vastly differing atomic sizes, it can imply that the nuclear charge in the two cases are very different and so will be the energy levels and the nature of extra core electrons. This factor has been termed by Hume-Rothery as orbital-type restrictions on the formation of extensive substitutional solid solutions [17]. Under these conditions, if electronegativity and ionization potential are favorable, compound formation is likely.

Hume-Rothery and his co-workers showed that the probability of the formation of extensive solid solution is extremely limited if atomic size differences exceed 15% [18, 19]. Darken and Gurry provided a simple explanation for this fact [20]. However, according to Oriani it is impossible to assert whether atomic size as such is important, or some other property of the atom which varies with atomic number, since discussion of the energies of solid solutions on the basis of elastic energy arising from atomic size misfit leads to inconsistencies [2, 6]. The calculation of the free energy or the enthalpy of the formation of a solid alloy arising from atomic misfit is based on the balancing of

a hydrostatic compression or expansion of the solute atom by a distributed shear stress in the surrounding lattice. Such a calculation always leads to a positive number so that when the enthalpy of formation is negative such as in Au-Cu system, it cannot be explained [4, 21]. Again, it is not obvious why size factor considerations based on elasticity theory should give good agreement for Au-Ni system and fail for Au-Cu system [5, 6].

A second related question is that since a liquid cannot support static shear, the elastic theory model based on atomic size effect cannot be applied in cases of liquid alloys. On the other hand, a survey of the formation enthalpies of liquid and solid solutions in liquid binary alloys of Cu, Ag and Au systems show that atomic size influences this parameter more or less identically in liquid as well as solid state [4]. If the size considerations are really significant in influencing the formation of solid solutions, the liquid solutions must be relatively insensitive to these differences in comparison to the solid solutions. In addition to the negative enthalpy of formation in Au-Cu alloy system, the identical manner in which the atomic size influences the formation enthalpies of binary solid as well as liquid alloys in Cu, Ag and Au systems presents another example of inconsistency in this regard [4–6, 21]. Hence atomic size consideration alone cannot be employed as a basis for a discussion of the composition variation of the physical properties and electronic factors arising from the differences in valency can be significant.

A more critical test of the role of atomic sizes in controlling the physical properties is provided by the experiments of W. R. Hibbard, Jr [22]. The presence of local stresses due to atomic misfit should affect most predominantly the plastic yielding behavior of the matrix. Such a misfit will lead to a change in lattice parameter also. Hibbard experimentally showed that at constant lattice parameter, the flow stress of copper alloys containing Al, Sn and Zn is found to be nearly invariant at constant e/a ratio. Therefore, solid solution strengthening models based on difference in atomic size are inconsistent with the result on copper based alloy systems and physicochemical factors are clearly more important.

4. Stability of phases

A quantum mechanical interpretation of the effect of e/a ratio on phase stability was given by Jones [14, 17]. The Jones theory [23, 24] explains the extent of solid solubility and the occurrence of certain crystal structures in copper based systems in a quantitative manner. This can in principle be extended to solid and liquid phase changes as well as the occurrence of the sigma and omega phases discussed later. The first requirement is that the change in internal energy makes a predominant contribution to the free energy. It is also assumed that changes in the ionic repulsive energy with composition are not significant in dilute alloys as well as over a limited range in concentrated alloys. These assumptions pave the way for the Fermi energy to have a controlling influence on the change in the internal energy.
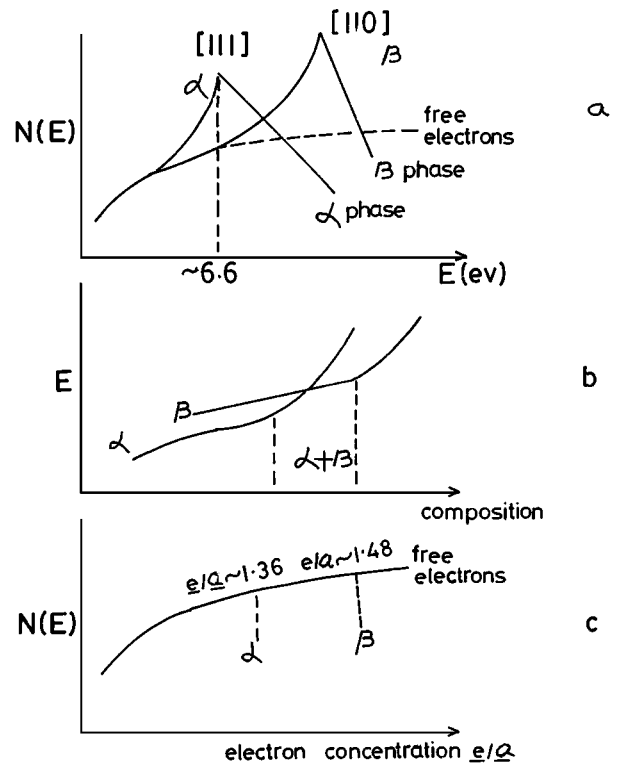

Figure 1 Schematic presentation (not to scale) of Jones model to account for primary solid solubility of copper alloys [a] Band gap across the [111] face of zone for fcc structure and [110] faces of zone for bcc structure. [b] Total electronic energy for and phases [c] Density of states for free electrons as a function of the e/a ratio [After Massalski].

The density of states is a function of the nuclear charge and the crystal structure of the matrix. The nature of the curve is parabolic except near the boundary of the Brillouin zones. In the rigid band scheme used by Jones, the nature of this curve is not significantly altered by alloying and hence the chief contribution to the internal energy of the matrix is made by the change in density of electrons or the e/a ratio. In case of Cu, Ag and Au, the number of valence electrons is unity and the first Brillouin zone is only half filled. With the addition of higher valence solutes, the zone starts getting filled up. For fcc and bcc phases this filling up is complete for the e/a ratio values of 1.4 and 1.5 respectively. There is a discontinuity in the density of states curve at the zone boundary which coincides with the peak of the curve (Fig. 1). The cross over to a new phase occurs when a falling density of states with an increase in electronic energy level raises the total energy of the crystal sharply, leading to the destabilization of the original structure of the matrix.

This cut off point in the electronic energy controlling the limit of primary solid solubility and the occurrence of f.c.c. and b.c.c. phases for Cu-based systems was calculated by Jones [23, 24] from the crystal structure, X-ray scattering factor and the density of state curve. Using the lowest value of energy for which discontinuity occurs on any plane, the limiting magnitude of the e/a ratio theoretically estimated for copper-based alloy systems was found to be in good agreement with e/a ratio values empirically established by Hume-Rothery for the boundary of fcc and bcc phases. A schematic representation of Jones' model is given in Fig. 1 [7]. In

this way, Jones demonstrated that e/a ratio can control the stability of phases when the Fermi levels of competing phases have a deciding influence on their internal energies. A recent interpretation of the Jones theory is now stated [25–27]:

The Jones theory was the first direct attempt at the application of quantum mechanics to the stability of alloy phases in metallic systems. The theory was, however, beset with two basic difficulties. Firstly, there was no basis for the assumption that a kink in the density of states versus wave vector plot constituted a valid driving force for the destabilization of a given phase. Jones also assumed that just before the kink in the density of states plot, a high density of states associated with falling values of dE/dk ensured structural stability. However, the prediction of molecular chemistry are just the opposite. In molecular chemistry, hybridized states are divided into bonding and antibonding states separated by a region of small or zero density of states and the structure is most stable when the density of states is small at the Fermi level. Jones himself tried to correct this lacunae in a later version of his theory. It was found that it is the total band structure energy rather than the absolute value of the electron energy at a point which will have a controlling influence on the relative thermodynamic stability of the competing phases. Towards this goal, it is imperative to calculate the energy of electrons in k-space in all the regions of the zone. The second difficulty with the Jones theory was the neglect of s-p-d hybridization in copper. The noble metals Cu, Ag and Au are intermediate between the transition and alkali metals. Although they have filled d-shells, the highest energy levels of d-band lie apart by only 2 eV above the Fermi level and they influence the sp levels through hybridization. Because of the high density of states in the d-band, hybridization, as in the case of transition metals, is strongly favored among degenerate sp and d states. Hence for a complete theory of electron phases, detailed band structure calculations as well as the hybridization between sp and d states should to be taken into account. When this is done, fcc phases are indeed found to be stable between e/a of 1 to 1.4 and the bcc structure has been found to have maximum stability at $e/a = 1.55$.

Application of psuedopotential theory to the stability of Hume Rothery electron phases showed that instead of trying to estimate the band structure energy on the basis of Brillouin zone arguments, one can analyze the many electron screening effects and evaluate the changes in the electronic band structure energy due to screened periodic lattice potentials. In this formalism, the structural contribution to the total energy depends upon the screened pseudopotential of the matrix element and the density response function. The screening is small at small wave numbers and rises rapidly as the reciprocal lattice vector passes through $2k_F$. It was shown that at $e/a = 1.36$, where the Fermi surface touches the Brillouin zone boundary, screening rapidly increases and raises the band-structure energy to its free electron value. The corresponding effect in the bcc structure occurs at $e/a = 1.48$. More significantly, a common tangent drawn to those two energy e/a curves touches them

at about $e/a = 1.36$ and 1.48 respectively. This theory has also been applied to a number of noble metal alloys and self consistent total energy calculations in the coherent potential approximation have also confirmed the pseudopotential interpretation. It is interesting to note that the detailed band structure calculations as well as the psuedopotential method uphold, although for different reasons, the validity of Jones original idea that the interaction of the Fermi surface and the Brillouin zone acts to alter the stability of the structure.

It is of course well known that rapid strides have been made in first principles calculations of many of the properties mentioned above. Predictions of the formation of intermetallic compounds, the occurrence of specific crystal structures as a function of composition, calculation of the density of states for electrons, Fermi energy and cohesive energy calculations have made enormous advances [28, 29]. Calculation of defect energies and prediction of elastic constants have also been successful. For example, Gyorffy et al studied order and disorder in metallic alloys using a self consistent KKR-coherent potential approximation method [28]. Their first principles mean field theory, while subject to limitations due to the neglect of certain correlations, treats all the classic Hume Rothery factors on an equal footing and without any adjustable parameters. Similarly Turchi *et al.* performed first principles study of phase stability in a Cu-Zn substitutional alloy. The Cu-Zn system is a classic example of the Hume Rothery phases, since phase stability is governed by the e/a ratio [29]. A combination of quantum mechanics and statistical thermodynamics was used to describe the equilibrium properties of Cu-Zn alloys. This approach pointed to the importance of configuration dependent properties which evolve as a function of the e/a ratio, thereby confirming Hume-Rothery's concept.

4.1. Extent of primary solid solubility

The factors which limit the solid solubility of solutes were enumerated by Hume Rothery and his co-workers, namely, the electrochemical nature and the difference in the atomic size and the valence number. They also demonstrated that when plotted against the e/a ratio, the solid solubility lines in metals like copper, silver and gold superimpose (Fig. 2). The Jones calculation based on the rigid band model described above predicts correctly the terminal solid solubility in copper alloys in terms of the e/a ratio. These observations serve to show that when atomic sizes and electrochemical differences are small, e/a ratio exerts a limiting influence on the extent of solid solubility.

A critical evaluation of various factors affecting solid solubility was also made by Hume-Rothery. As stated above, liquidus as well as solidus lines tend to superimpose when plotted against e/a ratio. This observation clearly establishes the importance of electron-to-atom ratio in controlling the limit of solid solubility. The departure from exact superposition is related to lattice distortion, in the sense that increasing lattice distortion lowers the solidus lines. The lattice distortion at constant electron concentration is important, not that
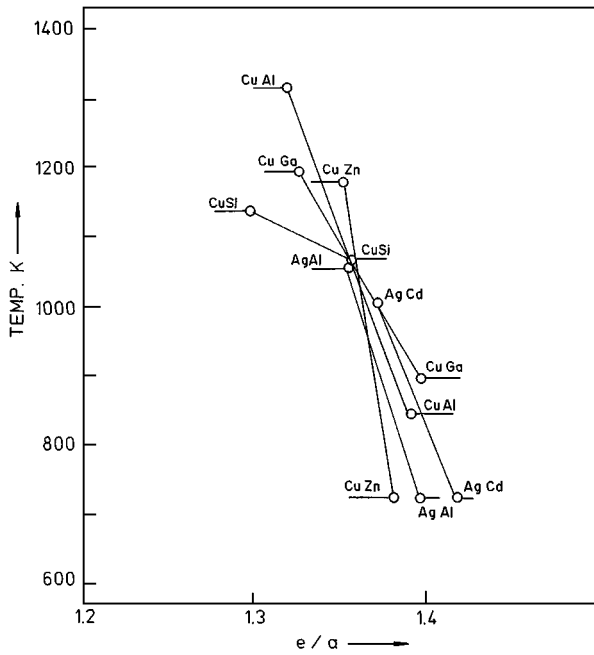
Figure 2 Solid solubilities of various alloying elements in copper and silver alloys as a function of the e/a ratio [After Hume-Rothery *et al.*].
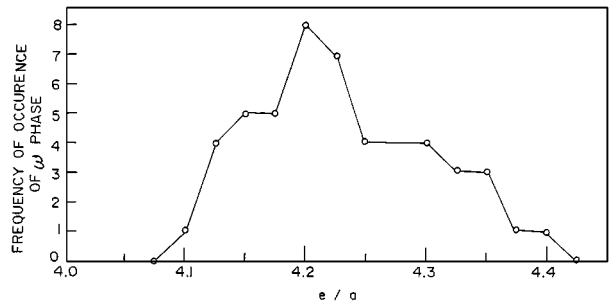

Figure 4 Composition range of the omega phase plotted against e/a ratio [After Collins].

shows this effect in alloys in which omega phase formation has been studied [33]. The dependence on e/a ratio is evident in Figs 3 and 4.

5. Electron phases with hexagonal symmetry

Hexagonal close packed electron phases fall into three groups and are denoted by Greek letters ε, η and ζ [34]. Excluding the range of 1.89–1.93, these phases occur between the e/a ratio values of 1.32–2.00 [7]. A detailed investigation of the physical properties of these systems has provided data on the influence of the e/a ratio on the crystal structure of these phases. Fig. 5 shows the electronic specific heat, superconducting transition temperature, Debye-temperature etc. plotted as a function of the e/a ratio. These graphs, particularly electronic specific heat, axial ratio and Debye temperature show a fairly simple linear relationship with the e/a ratio.
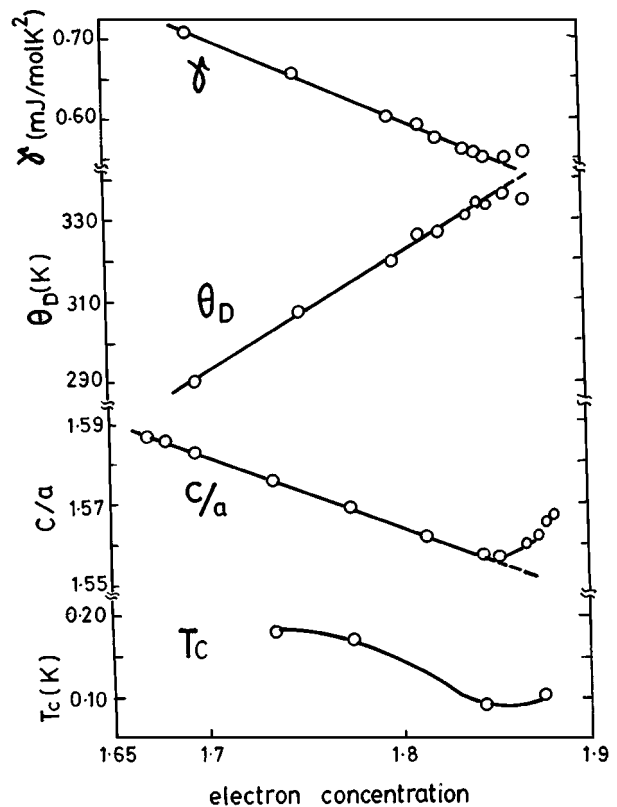
at constant atomic percentage of the solute. The factors responsible for lattice distortion at constant electron concentration are: differences in electronegativity, size-factor and orbital type of restrictions, which give rise to differences in energy levels of the electrons of the solvent and solute atoms.

4.2. Transition metal alloy phases

Transition metal alloys form a number of intermediate phases with complex layered structures. These phases are normally hard and brittle and their presence is undesirable in commercial alloys. The sigma phase in chromium bearing steels and omega phase in zirconium and titanium alloys have special technological significance. Hume-Rothery showed that the occurrence of sigma phases in transition metal alloys is related to the electron to atom ratio Fig. 3 [30]. The effect of the e/a ratio on the formation of omega phase has been investigated by Ezaki *et al.* and Luke *et al.* [31, 32]. Fig. 4

Figure 3 Composition range of sigma phase in transition metal alloy system as a function of e/a ratio [after Hume-Rothery].

Figure 5 Variation of electronic specific heat axial coefficient (γ), Debye temperature (θ) axial ratio [c/a] and the superconducting transition temperature [Tc] for hexagonal electron phases tc as a function of the e/a ratio [after Massalski].

6. Defect phases

An interesting series of compounds between transition elements (Fe, Co, and Ni) and non-transition elements (Al, Al, Sn, Sb, Se, S etc.) have been observed to form at constant e/a ratio of 1.5. Transition elements are assigned zero valency in this scheme. With the change in number of solute atoms, a change occurs in the number of atoms per unit cell in such a way that the e/a ratio is maintained unchanged through the creation of either vacancies or interstitials. Such defects (vacancy or interstitial), to differentiate them from those thermally generated, are designated as constitutional defects, since these are produced-- independent of the temperature-- to stabilize the structure. It is believed that they occur to maintain an optimum electronic energy; equiatomic Ni-Al alloy is a typical example of a defect phase. At 50% it possesses B2 crystal structure. If nickel content is increased beyond 50%, it goes to interstitial sites and there is a fall in lattice parameter and rise in the density, Fig. 6. However, with an increase of Al content also, lattice parameter and density decrease and detailed investigations have shown that this is caused by the formation of constitutional vacancies [35]. Below 49 at. % of nickel, the lattice spacing falls rapidly with increasing Al ratio. At the same point, the observed density curve breaks away from the calculated curved (shown dotted) and drops well below it. Similar behavior is observed in a series of phases, where composition gradually changes from AB to A_2B type. A point to be noted is that in the case of defect phases it is the number of valency electrons per unit cell (e/uc), rather than valency electrons per atom (e/a ratio) which is important. The e/uc is in fact a more fundamental quantity than the e/a ratio and in the case of defect phases, the structure adjusts so that e/uc is constant while e/a ratio may change.
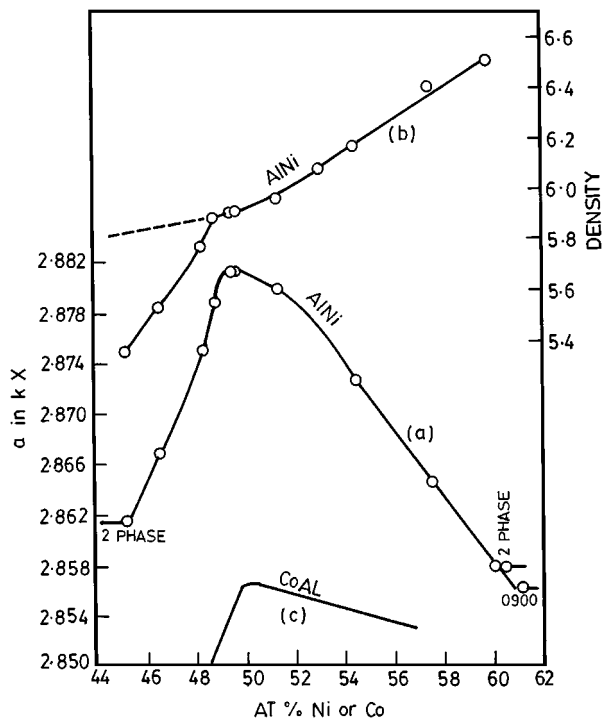

Figure 6 Lattice spacing and density of AlNi and AlCo systems as a function of composition [after Massalski].
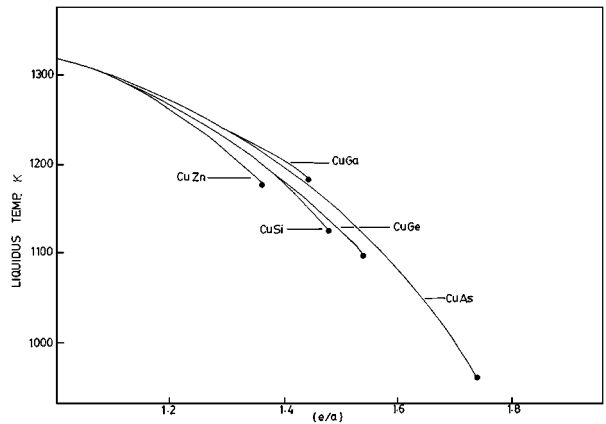

Figure 7 Liquidus temperatures of Copper alloys plotted against e/a ratio [After Hume-Rothery *et al.*].

7. Liquidus curves of primary metallic solid solutions

The liquidus curves of alloys of copper and silver when plotted against equal e/a ratio value nearly superimpose [19, 30]. Liquidus curves for various copper alloys are given in Fig. 7. The rationalization of the liquidus data on the basis of the e/a ratio indicates that the Jones concept may be valid for solid to liquid phase change also. Theoretically, it is difficult to establish this fact because it is not possible to estimate Fermi energy for liquid state with the desired degree of accuracy.

8. Stacking fault energy

Stacking fault energy [SFE] of metals and alloys affects their stress-strain relationships, recovery/recrystallization behavior as well as the deformation texture. In close packed lattices, stacking faults are formed by the dissociation of dislocations into two partials. However, in transition metals like iron, cobalt, nickel, ruthenium etc., formation of stacking faults depends upon the relative competition between energetically comparable structures. An estimation of the contribution of the d and s electrons to the cohesive energy shows that since d electrons make a major contribution to the cohesive energy, the favorable structures are determined by the number of d electrons per atom. The stacking fault energies as well as the allotropic behavior of transition metals conforms to this behavior [1].

In noble metals and alloys, the perturbation of conduction electrons by the presence of faults in the stacking sequence is important. The change of direction produced by stacking faults results in an increase in the energy of the crystal; this increase in energy constitutes the stacking fault energy. Measurement of stacking fault energies in copper and its alloys are shown in Figs 8 and 9. While Thornton *et al.* [36] studied Ag-Al and Ag-Zn, Smallman and Westmacott [37] studied alloys of copper with Al, Zn, Sn etc. Both these investigations indicate that the stacking fault probability and hence the SFE is a function of the e/a ratio rather than the nature and content of the solute element.
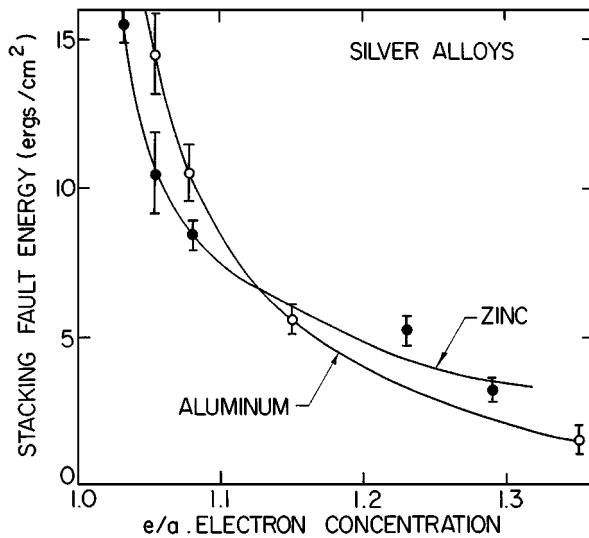
Figure 8 Variation of stacking fault energy with e/a ratio of silver alloys [After Thornton *et al.*].
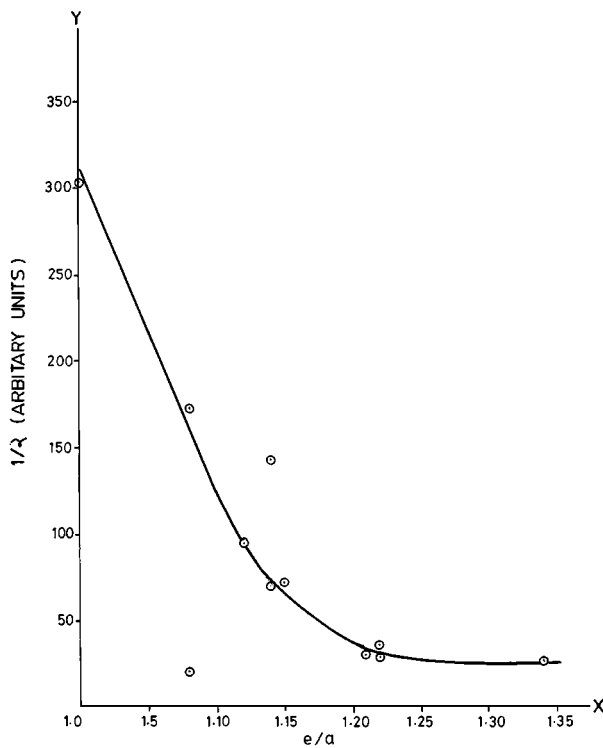

Figure 9 Variation of the stacking fault probability with e/a ratio in copper alloys.

9. Electronic specific heat coefficient

The electronic specific heat coefficient (ESHC) is governed by the density of states at the Fermi level. Considering only the interaction of electrons with the static lattice, the specific heat depends linearly on the absolute temperature:

$$C_v = \gamma T + \beta T^3 + (\text{OT})T^5$$

where the linear term is the electronic contribution to the heat capacity, β is the low temperature heat capacity contribution and OT signifies high temperature contributions. A simple and direct relationship between e/a and the ESHC is not expected. Experimentally however, it has been demonstrated that for lead as well as noble metal alloys, ESHC increases with e/a. The vari-
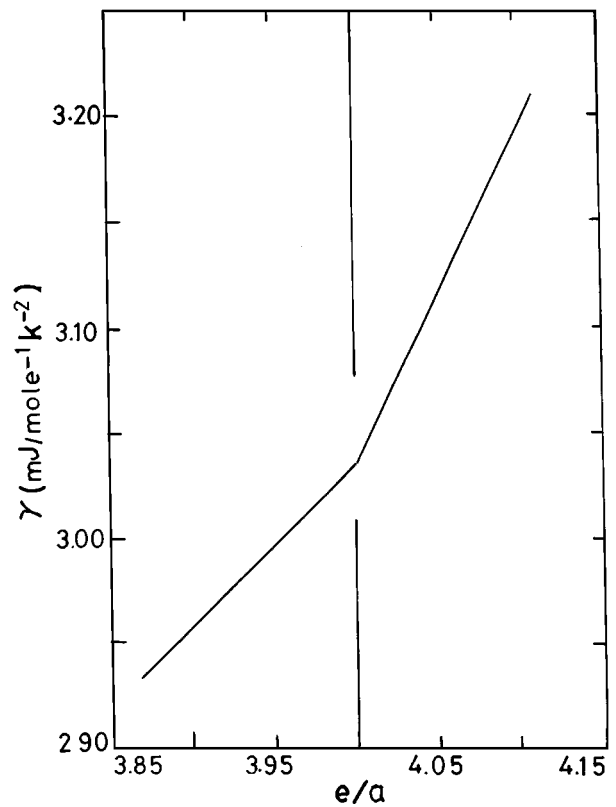

Figure 10 Electronic specific heat coefficient of Lead alloys as a function of the e/a ratio [After Clune and Green].
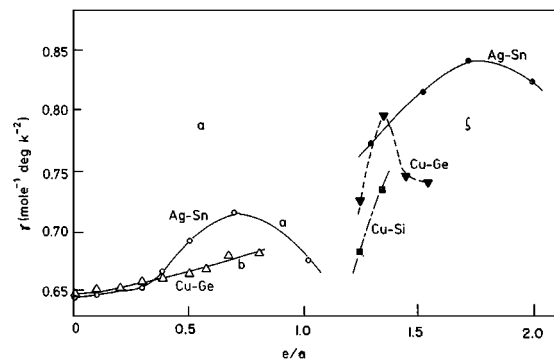

Figure 11 Electronic specific heat coefficient of copper and silver alloys as a function of the e/a ratio [after Massalski *et al.*].

ation of ESHC with e/a ratio for lead alloys is shown in Fig. 10.

The example where ESHC depends upon the shape of E vs $N(E)$ curve is shown in Fig. 11 [34]. An increasing trend is visible in the lower e/a range, followed by a broad maximum at intermediate value and a decreasing trend at higher e/a ratio.

10. Activation energy for diffusion

Fumi [38] has shown that the vacancy formation energy in metals [E_v] is related to the Fermi energy E_f by the equation:

$$E_v = K_1 Z E_f$$

where Z is the valence of the metal and in case of alloys it can be taken equal to the e/a ratio, K_1 is a numerical constant. Using the standard relation between Fermi
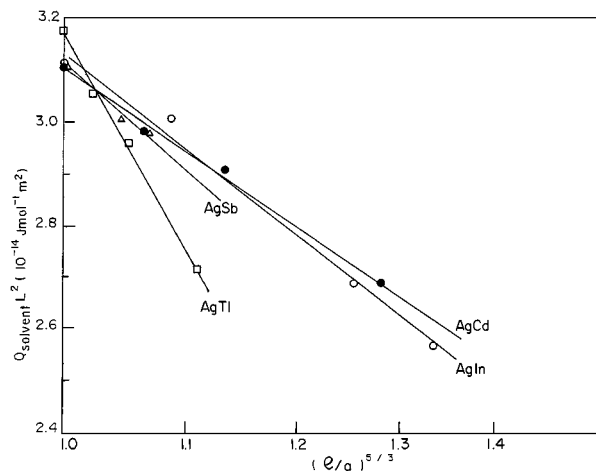
Figure 12 Activation energy for self diffusion of solvent, versus the e/a ratio for silver alloy system [After Tiwari *et al.*].

energy and the e/a ratio, Tiwari *et al.* [39] showed that Ev can be expressed in terms of the e/a ratio as

$$E_v = K_2[e/a]^{5/3}L^{-2}$$

where L is the lattice parameter and K_2 is another constant. This relationship can be extended to activation energy for diffusion (Q) because for a group of solids having identical physical and chemical properties, the ratio between Ev and Q is a constant. Fig. 12 shows that the linearity for individual alloy systems is maintained. However, if the e/a ratio is the only factor influencing Q in an alloy, then all the curve should superimpose. This does not happen due to factors like the differences in electronegativity.

11. Flow stress in solid solutions

The effect of alloying is to increase the yield stress of the alloy and the strengthening produced by the solute additions is designated as solid solution hardening. Allen *et al.* [40] examined the tensile properties of copper based zinc, gallium, germanium and arsenic solid solutions to evaluate the effect of solute additions. The tensile behavior of the alloys was studied in the annealed condition at approximately identical grain size so that the resistance to plastic deformation in different alloys can be compared effectively and the effect of alloying can be discerned clearly. In Fig. 13, true stress strain curves of four alloys having approximate e/a ratio of 1.087 are shown. The weight percentages of zinc, gallium, germanium and arsenic is 9, 4.05, 3.34 and 2.48 respectively. The true stress strain curves for all of them nearly superimpose on each other. 0.5 percent proof stress of the these alloy was also found to exhibit similar behavior with respect to the e/a ratio.

More direct experimental evidence for the e/a ratio as controlling parameter in plastic deformation of dilute alloys was provided by W. R. Hibbard. Jr. [22], who carried out his experiments in copper-based alloys having nearly identical grain size as well as lattice parameter (to eliminate any possible influence of these factors in the comparison of plastic yielding behavior). At constant e/a, the stress-strain curves superimpose [40]. A plot of yield strength versus the e/a ratio at constant
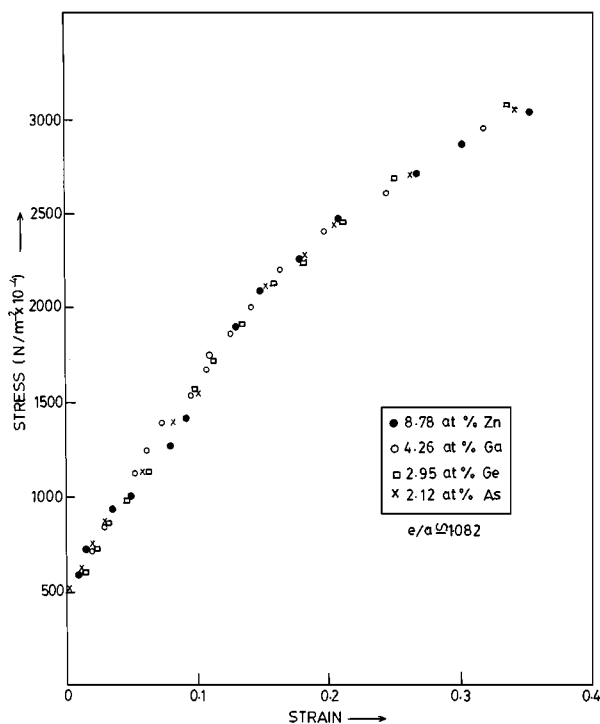

Figure 13 Stress-strain curves of copper base solid solution with same the e/a ratio [After Allen *et al.*].
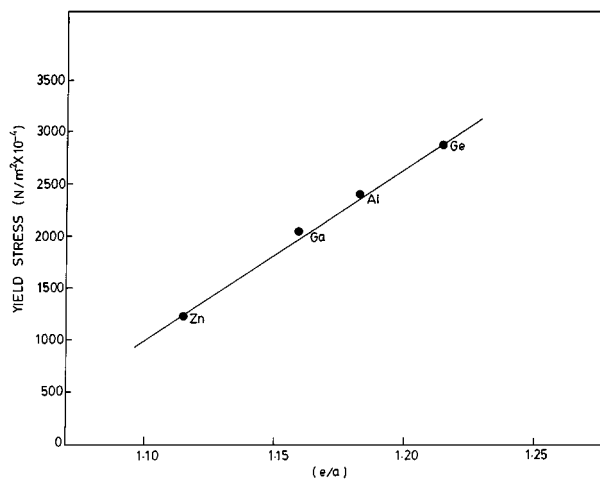

Figure 14 Yield stress values for copper based alloys of equal lattice parameters [After Hibbard Jr.].

values of lattice parameter and the grain size is shown in Fig. 14. The data shows a linear increase in yield strength with the e/a ratio. Hibbard also showed in conformity with Suzuki's predictions [41], that the flow stress depends only slightly on the temperature. If size factors effects are significant in influencing the plastic deformation, temperature should cause a dramatic decrease in the yield strength with temperature. Thus the e/a ratio appears to play a more significant role in influencing the plastic yielding behavior of alloys as compared to the atomic size factor.

12. Elastic constants

A fair amount of data are available on the dependence of elastic constants on e/a. Neighbours and Smith [42] extended Fuchs [43] treatment of elastic constants of

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copper to present an elegant demonstration of the dependence of these parameters on e/a. The expression, with a being the lattice parameter, for electrostatic stiffness for C_{44E} and $0.5(C_{11} - C_{12}) = C'_E$ were as follows:

$$C_{44E} = 0.9478(2e^2/a^4)$$
$$C'_E = 0.1058(2e^2/a^4)$$

Ionic stiffness contribution were also calculated in a similar fashion. Outside the filled closed ion shell, copper has got one electron. After alloying, the contribution of electrons for each atom to the respective charge distribution is $e/a = Z$. Then equations for C_{44E} and C'_E are modified for the alloys as follows:

$$C_{44E} = 0.97478(e^2 Z^2/a^4)$$
$$C'_E = 0.1058(2Z^n e^2/a^4)$$

Changes in ionic stiffness parameter are small in comparison to the changes in the electrostatic stiffness and can be accounted by introducing a proportionality factor α. Proceeding on this basis, the following expressions were derived for the changes in the elastic constants due to alloying [42]

$$\Delta C_{44} = C_{44}(Z^2 - 1) + C'\alpha x$$
$$\Delta C' = C'(Z^7 - 1) + C'\alpha x$$

In order to arrive at the change in the elastic constants that can be ascribed to alloying, the values of ΔC_{44} and $\Delta C'$ obtained from the above equations have to be adjusted for the changes in lattice parameter upon alloying. The magnitude of the adjustment can be obtained from the differentiation of the above two equations. Neighbors and Smith measured the C_{44} and C' of a number of copper alloys and the experimental values of ΔC_{44} and $\Delta C'$, after adjustment for a volume change, were substituted in the above two equations to evaluate Z and α. The value of Z so obtained was compared with the actual values of e/a calculated on the basis of alloy composition (Table I). The close correspondence between Z and actual e/a shows the importance of e/a in determining the elastic constants. Near constant value of α for each alloy system provides further support for their method.

The most important assumption in the above analysis is the uniform distribution of negative charge. It is well established that in substitutional alloy the valence charge must pile up in the vicinity of more highly charged solute. This should make Z less than q. However, in the rigid band approximation, so long as the electronic band structure does not change or exhibits any singularity, the assumption of uniform charge distribution is not too restrictive. The anisotropy factor also shows that a smooth linear dependence upon e/a is present [42].

The influence of e/a on the elastic constants in transition metal alloy system has been reviewed [44]. The alloy systems Zr-Nb-Mo-Re have been examined in detail (Figs 15 and 16). In these alloy systems, the measurement of elastic constants has been carried out as a

TABLE I A comparison of Z and electron to atom ratio for some copper based alloys

Alloy	Atom composition (percent)	α	Z	q, electron/atom ratio
CuZn	4.50	−1.0	1.08	1.05
CuAl	4.81	−0.9	1.11	1.10
	9.98	−0.8	1.25	0.20
CuGa	1.58	−1.4	1.03	1.03
	4.15	−1.0	1.09	1.08
CuSi	4.17	−2.5	1.13	1.13
	5.16	−3.0	1.18	1.16
	7.69	−3.0	1.25	1.23
CuGe	1.03	−3.6	1.06	1.03
	1.71	−3.3	1.09	1.05

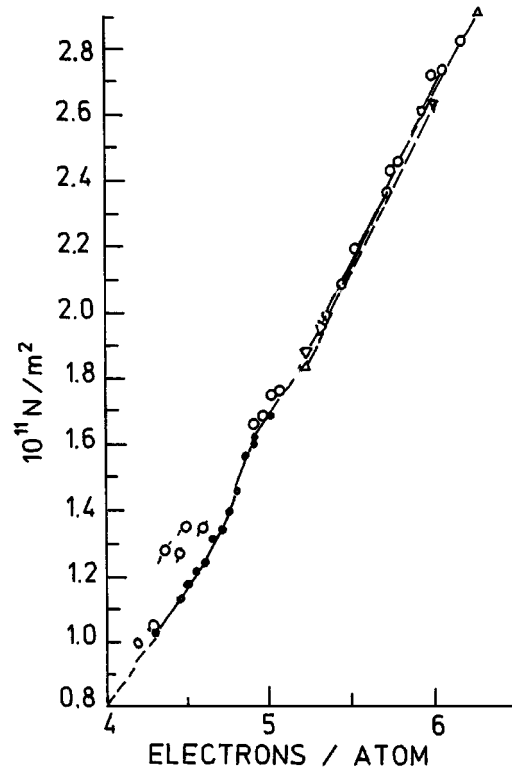*Figure 15* Composition dependence of K for Zr-Nb-Mo-Re and Nb-Ti, Nb-Hf, Nb-W alloys. $K = 0.5(C_{11} + 2C_{12})$, Δ = Mo-Re, 0, ∇ = Nb-Mo, °, $\square$ = Zr-Nb, . . . = Nb-W, Nb-Hf, Ti 40 Nb, O = Ti-Nb polycrystal, Solid line = 100 K, dashed line = 300 K.

function of temperature and pressure. The latter data can provide information on the effect of volume on elastic constants. This information can be used to correct for the measured changes in elastic constants attributable to alloying. As discussed above such a separation of the volume effect from the net change is essential to establish the intrinsic dependence of elastic constants on e/a. Two different scenarios are considered while discussing the effect of e/a on elastic constants in transition metal alloy systems:

12.1. Rigid band behavior
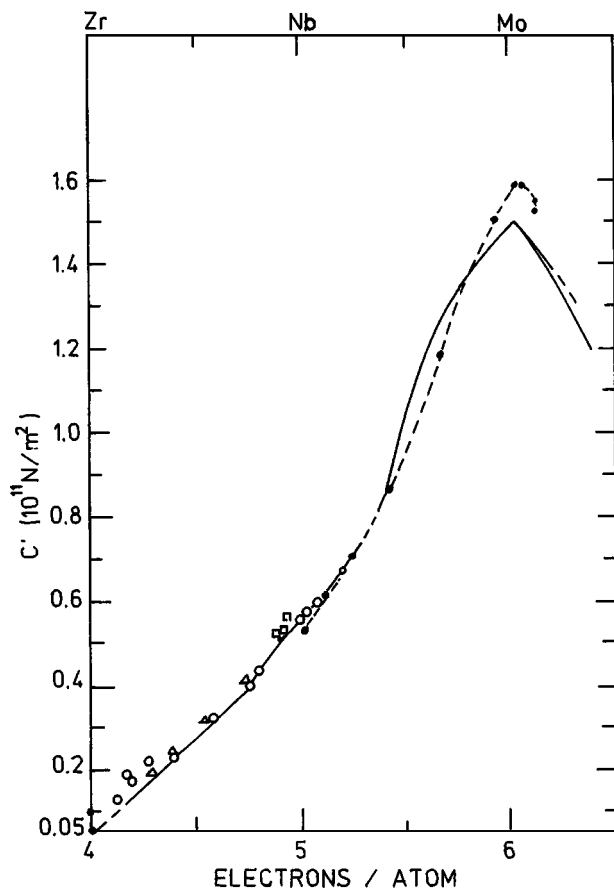The rigid band model correctly reproduces the magnitude as well as the temperature dependence of elastic

Figure 16 Composition dependence of c' in 3d, 4d and 5d bcc solid solutions at 300 K. Base: Zr-Nb, Nb-Mo, Mo-Re, 4d △: Ti, Ti-V, V-Cr, Cr, 3d O: Ti-Cr, 3d o...: Ta, Ta-W, W-Re, 5d ▽: Ti 40 Nb, Nb-Hf, Nb-W, □.

Figure 17 Transition metal T_c as a functioof e/a ratio [after Gladstone *et al.*].
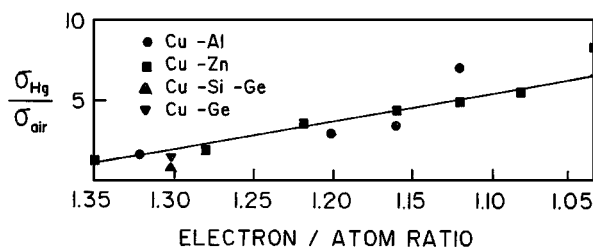
Figure 18 Tendency for stress corrosion cracking as a function of e/a ratio [after Westwood].

constants. Here the effect of alloying is merely to change the density of the negative charge and not the shape of band. In this case, when the elastic constants are plotted against e/a, there are no singularities and relationship is properly represented by a straight line.

12.2. Anomalous behavior

In several alloys systems the linear relationship between the elastic constants and e/a is absent [44]. There is a regular variation which is punctuated with singularities at some fixed values of e/a which is governed by the topology of the Fermi surface. The singularity in the e/a versus elastic constant plot is an indication of a significant alteration in the electronic structure. This interpretation is supported by the fact that anomalous change in the elastic constants with the composition corresponds almost exactly to the changes in magnetic susceptibility [45].

13. Superconducting transition temperature [Tc]

The correlation between e/a ratio and the superconducting transition temperature (Tc) comes in importance next only to the phase stability [46–48]. The work of Mathias and his workers established systematics of the relationship between e/a and the superconducting temperature [49, 50]. As one moves along with the vari-
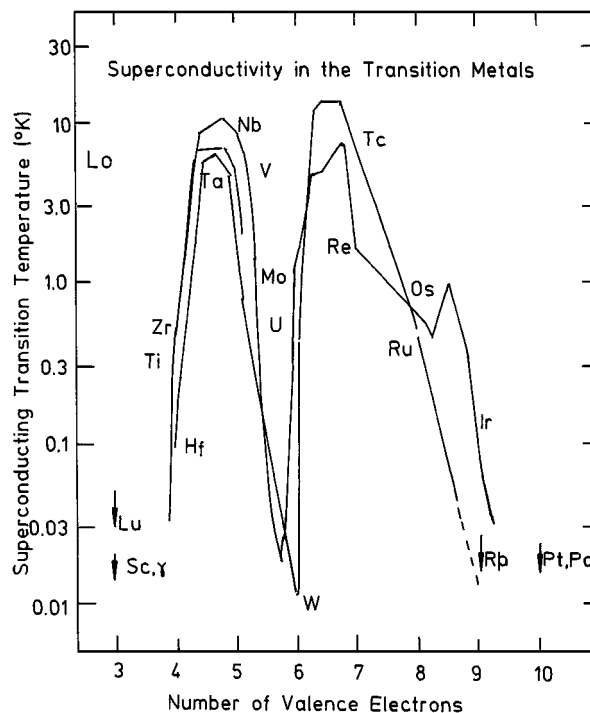
ous rows of the periodic table, the variation of Tc is surprisingly systematic. In transition metals and alloys superconducting transition temperature (which provides among other things some measure of Fermi surface density of states) can be qualitatively predicted using only e/a ratio as shown in Fig. 17. Among transition metals and alloys, Tc peaks at around 4.5 and 7.0 electrons per atom. The applicability of this relationship is indeed extensive. In fact a large number of superconductors can be discovered provided one follows the curve shown in Fig. 17. A demonstration of the validity of the correlation depicted in Fig. 17 is provided by a 50–50 alloy of molybdenum (which is non-superconducting) and ruthenium (Tc = 0.6 K). This alloy has the same number of valence electrons per atom as technetium and a Tc of 10.6 K which compares well with the Tc for technetium which is 11 K. A plot similar to that shown in Fig. 17 has been prepared for niobium alloys by Wernick [51]. The above observations make it reasonable to think in terms of a universal model for conduction band of transition metals in which the array of metallic ions can be visualized as a "rigid band" structure into which electrons are incorporated and the properties of the matrix are determined by the number of conduction electrons per atom. An explanation of the

variation of Tc with composition for transition metals may be given on the basis of the BCS theory of superconductivity, which shows that the variation of Tc with e/a follows a systematic behavior.

In high temperature oxide superconductors, there is a mixture of covalent and ionic bonds. As such, a simple correlation between e/a ratio and Tc is unlikely to exist in oxide superconductors. Two correlations have been proposed [52, 53]. Villars *et al.* discussed an empirical relationship based on an averaged valence-electron number, differences in orbital and electronegativity difference encompassing metallic as well as oxide superconductors. Li-Yuan examined 70 oxide superconductors and noted that all of them lie between averaged electronegativity value between 2.5 and 2.7. The averaged valence [which is same as the e/a ratio] for superconductors having these electronegativity values varied between 2 and 2.45. From the above discussion, it is fair to conclude that other than electronegativity and size factors, a critical value of the e/a ratio may be an important factor controlling Tc in oxide superconductors.

14. Stress corrosion cracking

In a study of adsorption sensitive fracture properties, it was shown that the severity of embrittlement changes with a variation in the stacking fault energy and the elastic constants [54]. Since e/a ratio affects both stacking fault energy and elastic constants, it is expected that the fracture stress in mercury of copper base alloys could be correlated with the e/a ratio (Fig. 18) and a good linear fit was indeed obtained between the fracture stress and the e/a ratio of these alloys.

15. Aperiodic structures

The important trend in the structure of crystals are also reflected in the formation of liquid alloys, metallic glasses as well as quasicrystalline compounds. This trend has been discussed in detail [25–27] and the salient points are noted below. In weakly interacting systems such as Mg-Zn, the geometrical requirements of sphere packing leads to random polyhedral structure. In systems with pronounced difference in electronegativities and electron densities, mutual interactions predominate as a result of reduced screening effects. In this situation, as in the case Ca-Zn, formation of strong Zn-Zn bonds dominate the structure which consists in trigonal arrangement of larger Ca atoms around Zn-Zn bonds. In the intermediate case represented by systems formed by the mixing of noble metal with elements of higher valency (which form Hume-Rothery electron compounds), electronic influence appears to control the formation of metallic glasses and quasicrystals. The starting point for the consideration of electronic influence on the formation of a periodic structure is the conclusion reached from the application of the pseudopotential method to the Hume-Rothery electron compounds. It states that the structural energy rises rapidly as the reciprocal lattice vector (Q) passes through $2k_F$. In real space, it implies that the lattice spacing is same as the wave length of electrons of the Fermi level. For close packed structures, this situation will arise at smaller lattice spacings and low values of e/a ratio. As the e/a ratio increases, the wavelength of electron at the Fermi level becomes larger leading to the formation of more open structure at larger e/a values. This statement agrees with the fact that the maximum stability of fcc, bcc and γ - brass structure occur at e/a values of 1.36, 1.48 and 1.8 respectively. Continuing this line of argument, it is logical to infer that the more open aperiodic structure will be formed at still higher values of e/a. Simple metallic glasses like Mg-Zn or Ca-Mg and the glasses formed by noble metals and polyvalent elements do in fact satisfy the $Q = 2k_F$ criterion. For crystalline matrics, the condition $Q = 2k_F$ is associated with constructive interference between the pair correlation function $g_{ir}(R)$ and pair potential $\varphi_{ir}(R)$, such that the maximum $g_{ir}(R)$ coincides with minimum in $\varphi_{ir}(R)$. Another consequence of this feature is the occurrence of a minimum in the density of states at the Fermi level. The preceding discussion helps us to arrive at a criterion for the occurrence of periodic as well as aperiodic structures. For a given value of e/a, the most stable structure will be the one for which both the criteria of (i) $Q = 2k_F$ and (ii) the minimum in the density of states at the Fermi level are satisfied. This conclusion finds support from electronic band structure calculations as well as from photo-electron spectroscopy data.

Alloys of the noble metals with the polyvalent elements that fall to the right of the noble metals in the periodic table have been used to test theories of the Hume Rothery phases. This is because the d-band of these alloys is filled and the e/a ratio can be easily changed. Studies by Mizutani [55] have shown that glass formation in several alloys such as Au-Si, Ag-Si, Cu-Ag-Ge and Au-Si-Ge is clearly a function of the e/a ratio (Fig. 19). The formation of the amorphous phase can be clearly correlated with specific range of values of e/a ratio.

Quasicrystalline phases of many alloys fall in the range of $e/a = 2.1$–2.4. This suggests that a similar mechanism may be important in stabilization of quasicrystalline phases. Three dimensional structure maps defining the stability range of many crystalline
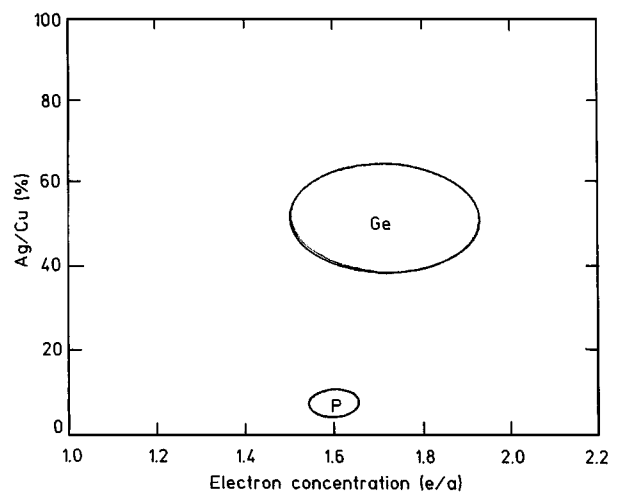
Figure 19 Electron concentration dependence of amorphous regions in Cu-Ag-Ge and Cu-Ag-P alloy systems [after Mizutani].

and hypothetical mono-atomic quasicrystalline structure have been constructed and it was found that the quasicrystals are stable in a narrow region separating close packed and open crystalline structure. Although no element lies in this region, virtual crystal parameters of known quasicrystalline alloy fall into the proper parameter range. It was concluded that the quasicrystalline state is stabilized by a mechanism similar to that mentioned earlier for metallic glasses. Al-based quasicrsytals are also thought to be stabilized by a similar mechanism [56]. Experimental (electrical transport measurements, soft x-ray spectroscopy) and theoretical studies suggest that the quasicrystal is stabilized when a pseudogap develops in the density of states, arising when the Fermi surface touches the quasizone boundary, thus increasing the cohesive energy. The quasizone boundary is analogous to Brillouin zones in ordinary crystals.

16. Summary

A wide variety of physical properties may exhibit a systematic variation when plotted against the electron to atom ratio. Empirical correlation of these properties with the electron to atom ratio has been documented: the range of stability of solid solutions, intermetallic compound formation, liquidus temperature in metals, the axial ratio of hexagonal phases, formation of defect phases, stacking fault energy, electronic specific heat coefficient, flow stress, superconducting transition temperature, stress corrosion cracking, elastic constants and activation energy for diffusion. These correlations may serve as a base for first principles calculations of these properties. The correlations discussed can also be used to fine tune the composition in order to optimize the desired properties.

Acknowledgements

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